**53Cr Solid-State Nuclear Magnetic Resonance: New Observations and Comprehensive Correlations as a Probe of Valence and Magnetic States**

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**Abstract**

New 53Cr solid-state NMR measurements are presented for Cr2N, CrB2, CrO2, Cr2O3, (NH4)2CrO4, and BaCrO4. Measurements of the 53Cr nuclear quadrupole coupling constants, asymmetry parameters, and chemical (Knight) shifts of chromium compounds provide important experimental data for the validation of quantum chemistry calculations. In this work, natural abundance 53Cr magnetic resonance, at 9.4 T, is used to examine the metals Cr2N and CrB2 as well as the diamagnetic insulating chromates (NH4)2CrO4 and BaCrO4 at room temperature. 14N and 11B NMR spectra are also obtained at room temperature for Cr2N and CrB2, respectively. The shift observed from CrB2 is believed to be the largest Cr(0) Knight shift (−9982 ppm) for any chromium-containing metallic material. 53Cr measurements in zero applied magnetic field as a function of temperature are reported for ferromagnetic CrO2 and antiferromagnetic Cr2O3. Within experimental accuracy the magnetization behaviour in CrO2 is modelled using Bloch spin wave theory where the magnetization decreases as T3/2 over temperatures from 4.2 to 295 K, which also appears to adequately model the sublattice magnetization of Cr2O3. These new experimental results are put into context of previous magnetic resonance results found in the literature by providing the first comprehensive tabulation of such 53Cr magnetic resonance data from solids for over 50 years. The low temperature zero applied magnetic field central frequencies are correlated with valence state, and spin stiffness has been calculated for sixteen chromium compounds. A knowledge of these parameters will enable further progress in using 53Cr magnetic resonance as a probe of electronic and magnetic structures thereby contributing to the more systematic development of novel materials.

**Keywords**: chromium, NMR, zero applied field, magnetic hyperfine interactions, quadrupolar, shifts, spin waves

**1. Introduction**

53Cr NMR studies of solid chromium-containing compounds were first reported in the 1960s as research teams sought to unravel the nature of the bonding in antiferromagnetic and ferromagnetic materials and to test theoretical schemes for approximating the nature of magnetic ordering [1-5]. With the current level of interest in quantum materials, for applications in spintronics and as topological insulators, the challenge of understanding, predicting, and controlling magnetic properties and quantum states in Cr compounds has reinvigorated 53Cr NMR studies [6-8]. The literature of relevance to the compounds observed here for the first time is introduced, followed by a report of new measurements of 53Cr NMR at 9.4 T and in zero applied field with 53Cr in natural abundance. These new results are compared with the literature where the ability to understand the valence and magnetic environment are highlighted. A key aim here is to provide a comprehensive overview of the literature on 53Cr magnetic resonance from 1961 to date. The implications for the trends in these data and the ability to probe bonding and spin properties for correlation with other materials properties (e.g. magnetization, spin density) are examined. Suggestions for future work are highlighted throughout the results and discussion.

**2. State-of-the-art of magnetic resonance observation of chromium in solids**

The first report of solid-state 53Cr (I=3/2, natural abundance 9.5%) NMR was in ferromagnetic CrBr3 by Gossard *et al*. [1]. The NMR lineshape could be obtained in zero applied field because of the existence of a strong internal magnetic hyperfine field at the Cr nucleus at temperatures below the ferromagnetic Curie point temperature TC = 37 K. Using the internal field in materials with spontaneous magnetization to observe the magnetic resonance signal is termed zero field NMR or ferromagnetic nuclear resonance (FNR). The temperature dependence of the 53Cr resonance was measured from 1.34 to 4.2 K, and the data were fitted with spin wave theory [9-11]. These 53Cr NMR results were the first experimental test of spin wave theory for a ferromagnetic compound using NMR. Three months after the Gossard *et al.* report [1], Narath [2] reported the first zero field 53Cr NMR in an antiferromagnetic compound, CrCl3 (Néel temperature, TN = 16.8 K) measured from 1.23 to 4.02 K, providing data for a further test of spin wave theory. The ferromagnet CrI3 (TC = 68 K) was subsequently characterized using 53Cr zero field NMR as a low temperature test of spin wave theory [3]. Anisotropic Cr orbital states form a current topic of materials research interest for spintronic devices, and as such the chromium trihalides are still under investigation experimentally and theoretically as 2D materials with intrinsic ferromagnetic and antiferromagnetic properties [12,13].

Rubinstein *et al.* [14] studied 53Cr in antiferromagnetic Cr2O3 in zero applied field using powder samples with 53Cr in natural abundance and enriched. For measurements at 1.6 K, the central line was detected at 70.43 MHz with the satellite transitions lying 262±10 kHz to either side, yielding a quadrupolar frequency nQ of 0.525 MHz and a quadrupole coupling constant CQ of 1.05 MHz for Cr2O3 (nQ and CQ defined in Section 4.1). The central line resonance frequency was reported as constant within the accuracy of the measurement over the temperature range studied from 1.6 to 16 K. To date no one has reported 53Cr NMR measurements of Cr2O3 at temperatures much above liquid helium temperature. Internal field magnetic resonance data are reported in the present work significantly extending the temperature range.

The first report of 53Cr NMR in ferromagnetic CrO2 was in 1963 by Yasuoka *et al.* [15] who detected a single peak at 36.14 MHz in zero field at 77 K with the weak signal disappearing above 240 K. A later study [16] at 4.2 K and zero applied field reported two 53Cr peaks at 26.3 and 36.7 MHz, even though a single chromium site is expected in the rutile structure of stoichiometric highly crystalline CrO2; the authors tentatively attributed the high frequency line to the expected single Cr site and the low frequency line to Cr atoms affected by vacancies. The origin of these two 53Cr sites has continued to be the subject of study. In 2007 Shim *et al.* [17] showed that the sites could not be due to vacancies, nor could they be due to Cr sites in domains and domain walls. Much recent work has been reported on 53Cr in CrO2 due to renewed interest in anomalous electronic states of half metallic chromium oxides [18-21], with the most robust recent attribution of the two sites to an electronic state caused by local orbital order [18-20].

53Cr NMR measurements in numerous diamagnetic chromates have been reported with nuclear quadrupolar coupling constants, CQ, ranging from 1.17 to 5.01 MHz for eleven chromates and 7.25 to 8.28 MHz for two dichromates [22-24]. The 53Cr chemical shift range reported in diamagnetic alkali earth chromate and dichromate compounds is −117 ppm to 188 ppm attributed to the small shielding anisotropies expected for d0 Cr(VI) complexes [22,25]. Nowak and co-authors [26,27] have reported 53Cr NMR in hexagonal and cubic chromium hydrides establishing these compounds as metals (Pauli paramagnets) and reporting the temperature independent Knight shift for each phase. Barnes and Graham determined the Knight shift in pure Cr metal in the paramagnetic state above TN = 313 K and at 300 K in Cr1−xVx alloys with up to 3 at% V [6]. Kontani [28] reported 53Cr NMR for the Cr1−-xMox system with x varying from 0.25 to 26.3 at%. Although there are several important Cr-containing stoichiometric compounds that are metals, e.g. the chromium boride refractory metals and the chromium nitrides, to date there has been very little 53Cr NMR reported in metals and alloys [29-31]. 53Cr has a nuclear gyromagnetic ratio, g, of −2.406 MHz/T which is low [29], and 53Cr is not the most favoured of the low-g nuclides for solid-state NMR, sometimes being referred to as exotic, miscellaneous, unreceptive, and difficult. However, it has been shown in recent years that a combination of relatively large samples and, for wide lines, techniques such as frequency stepping can aid in the observation of low-g nuclei [24,29,30,32], helping to overcome the challenges of low sensitivity, low natural abundance, and broad resonance lines. This study encompasses a wide range of samples some of which will have high internal magnetic fields or large Knight shifts which can produce a large fluctuating spin density/magnetic field at the 53Cr site resulting in short T1 relaxation times. In other samples, (e.g. non-magnetic insulating samples) the relaxation can be significant slower. Typically the recycle delays were set to produce relaxed or partially relaxed spectra tailored to the sample. In most samples fast relaxation occurs so a repetition time of 20-100 ms was used. The ability to recycle quickly for most samples means spectra can be rapidly collected helping the observation, especially when frequency-stepping strategies are adopted to locate the resonances by looking over a large frequency range. In addition, for ferro- and ferrimagnetic samples the way the electronic magnetization responds to applied rf field can lead to very significant additional boost to the magnitude of the signal through the enhancement mechanisms operating [33,34].

**3. Experimental details**

CrO2 and CrB2 powders (99% purity), Cr2O3 and BaCrO4 powders (purity ≥ 98%), and (NH4)2CrO4 powder (98% purity) were obtained from Sigma Aldrich. Industrial grade Cr2N powder (92% purity) was obtained from Japan. Powder X-ray diffraction (XRD) scans were measured using a Bruker D8 Advance spectrometer using Cu Ka radiation to confirm crystallinity and purity. Analysis of the data was performed using the Bruker XRD search match program EVA™4.2. Differential scanning calorimetry (DSC) was performed on 10 mg of the Cr2O3 powder using a Mettler Toledo DSC 2 at a heating rate of 10 K/min from 133 to 373 K in flowing nitrogen (40 ml/min). Analysis of the data was performed using the STARe software. A Zeiss Merlin field emission scanning electron microscope (SEM) was used to acquire images of the CrO2 powder at an accelerating voltage of 3 kV and 100,000x magnification.

High field (9.4 T) and zero applied field NMR spectroscopy were performed using a Bruker Avance 400 spectrometer to generate the pulses and detect the signal via a phase-cycled two pulse echo sequence using a pulse duration of ~4 to 10 ms, pulse separation of ~50 ms, and pulse repetition time of 20 to 500 ms depending on nuclear relaxation rate. The Larmor resonance frequencies for the investigated nuclei 11B, 14N, and 53Cr at B0 = 9.4 T are 128.40, 28.91, and 22.66 MHz, respectively. The reference 11B NMR zero line shift was set using NaBH4 in dilute aqueous solution; the reference for 14N was solid NH4Cl; the reference for 53Cr was (NH4)2CrO4 in saturated aqueous (D2O) solution. For CrO2, small low power 1 ms pulses were used since the signal strength is boosted by the inter- and intra-domain signal enhancement mechanism in ferromagnets described elsewhere [33,34]. There was not a systematic determination here of the enhancement factor, although for 53Cr the core domains (as opposed to the domain walls) where it is reported in the papers summarised here it is usually in the range 10-100 and typically around 30. The probe bandwidth was approximately 800 kHz (full width at half maximum (fwhm) of the tuning curve). The 53Cr zero field NMR lines were recorded at 77, 195, and 295 K at an operating frequency adjusted to put the line maximum at the centre of the frequency range. Frequency-stepped spectra [32] for 53Cr were obtained at 295 K for CrB2 and Cr2N at 9.4 T and at 77 and 195 K in zero field for Cr2O3. For the lines defined by frequency stepping, the width of the pulses was varied to achieve the pulse bandwidth for the chosen frequency slice: typically, 5 ms for a 200 kHz slice using 300 W transmitter power. For Cr2O3 the higher power 5 ms pulses were necessary since the signal enhancement mechanism that operates for ferromagnets is not applicable to antiferromagnets. The probe head was an 8 cm long cylindrical copper pot with an enamelled wire wound coil attached to a home-built matching circuit by a short, low thermal conductivity, transmission line [35].

**4. Results and discussion**

*4.1 Hyperfine interactions*

Hyperfine interactions experienced by a nucleus act as fingerprints of the different atomic sites in materials. In the case of the compounds examined here, the parameters determined by magnetic resonance measurements provide a sensitive probe of the local and magnetic structure around the 53Cr atomic sites. The interactions experienced by a 53Cr nucleus include quadrupolar via electric field gradients (efgs), shielding (either chemical shift from conventional localised electronic bonding or Knight shift from delocalised conduction electrons) and for electronic magnetism the local internal field [29,30,33,34]. An atomic nucleus with spin I > 1/2 has an electrical quadrupole moment which interacts with any efg, whose largest component Vzz (J/Cm2)is defined as

Vzz = ∂2V/∂z2 (Eq. 1)

Simulation of the lineshape features can give the nuclear quadrupole coupling constant, CQ, in units of frequency and asymmetry parameter η, defined as

CQ = eQVzz /h and η = (Vxx-Vyy)/Vzz (Eq. 2)

where Q is the quadrupole moment of the nucleus in units m2, e is the electron charge in units of Coulomb (C), h is Planck’s constant and Vii are the respective efg tensor components. In highly crystalline, well-ordered samples the resulting powder lineshapes of all transitions will be structured with clear peaks and singularities from which the quadrupolar interaction parameters can be extracted [29,30]. Often such structure cannot be observed, then the second-order perturbed central line width Δ (fwhm) can be used to estimate CQ via [29,30]:

Δ = (25(νQ2)/144 νL) (I(I +1)−3/4), where νQ = 3CQ [√(1+(h2/3))]/(2I(2I−1)) (Eq. 3)

The value of CQ from experiment can be compared with the Vzz calculated from density functional theory (DFT). This combination of spectroscopic measurement and quantum chemistry calculations of quadrupole parameters provides a powerful means to study the solid state (see for example Bastow *et al.* [36]).

Recently, DFT methods have also been used to calculate the magnetic shielding or hyperfine induced shift of the nuclear resonance (Knight shift, KS) in elemental metals [37] using the Wien2k program [38] where both orbital and spin contributions are needed for the transition metals. For 53Cr in pure Cr metal, the theoretical KS of 6818 ppm is in excellent agreement with the experimental KS of 6870 ± 100 ppm [4,37]. Where possible in this study, measured values for CQ and chemical (Knight) shift are compared to DFT predictions for these values. For Cr compounds with spontaneous magnetization, the Knight shift (in %) is related to the Pauli spin susceptibility χP per Cr atom (in cm3/mol) by

KS = [A][ χP /(NAμB)] (Eq. 4)

where A is the hyperfine coupling constant in T/μB, NA is Avogadro’s number 6.022 x 1023 mol−1 and μB = 9.27x10−24 J/T.

When there are unpaired electrons then an internal magnetic field is generated and usually no magnetic field needs be applied. The zero field applied NMR (zf) center-line resonance, νzf, (in units of MHz) is a measure of the hyperfine field at the 53Cr nucleus, Bhf (in units of T) through the relationship

Bhf = νzf /53γ (Eq. 5)

where 53γ is the gyromagnetic ratio of the 53Cr nucleus (in units of MHz/T). At 0 K, νzf(0), is related to the local magnetic moment at 0 K, M(0). The high field approximation is made here because the local field is the dominant determinant of the observed frequency. Other interactions can make small perturbations to the zero field frequency position [39]. The ground state magnetic moment M can be estimated from the spin-only contribution from the number, *n*, of unpaired electrons, M = √*n*(*n*+2) or estimated as the average magnetic moment through the Landé g-factor for the ion ground state with

M = gμBS (Eq. 6)

where S = *n*/2 is the spin, and μB is the Bohr magneton per Cr ion (μB/Cr), and M can be directly measured using neutron diffraction or magnetometry. The 53Cr Landé g-factor for ground state ions can be estimated from EPR measurements within ~ 4 % as 2 [40]. NMR measurements as the temperature approaches 0 K (liquid helium temperatures) in zero field are necessary to minimize thermal effects on the value of the hyperfine constants derived from the data and for comparison with quantum chemical calculations of hyperfine interactions. The sublattice magnetization and νzf will decrease as the temperature rises due to thermally excited spin waves. The relationship between the 53Cr νzf near 0 K and the magnetic moment M near 0 K in μB per Cr ion can be described by

νzf(0) = 53γ |A| M(0) (Eq. 7)

where |A| is the absolute value of the hyperfine coupling constant in T/μB. The gyromagnetic ratio of the 53Cr nucleus, 53γ = 2.406 MHz/T, is a constant. The absolute value of the hyperfine coupling constant, |A|, depends on the configuration and valence of the Cr ion in the compound, which is discussed in Section 4.7.1.

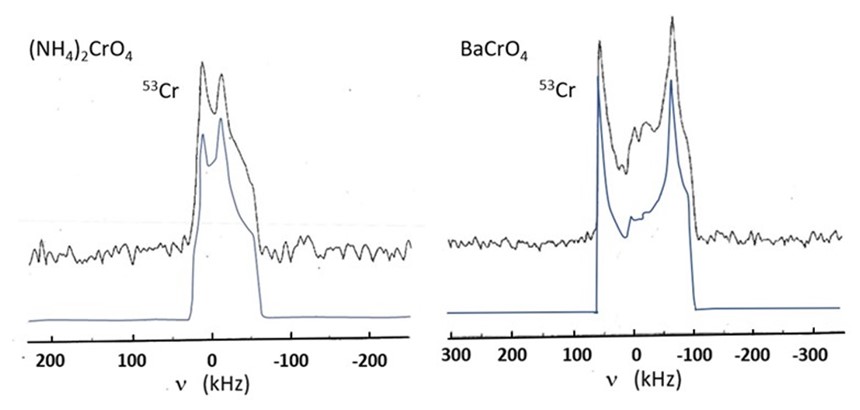
*4.2 (NH4)2CrO4 and BaCrO4*

Alkali metal chromates and alkaline-earth metal chromates have four Cr-O bonds of nearly equal length giving slightly distorted tetrahedral coordination of the Cr in the oxochromate (VI) anions, CrO42−. This configuration restricts the magnitude of the efg at the Cr site, such that the coupling constant for the electric hyperfine interaction, CQ, at the Cr site is typically less than 10 MHz [22]. In this circumstance the electric hyperfine interaction can be conveniently measured by conventional high applied field 53Cr NMR via a simulation of a second-order perturbed lineshape [39] which yields CQ and h (Eq. 2) where h measures the departure from axial symmetry of the efg tensor [29]. Ammonium chromate (NH4)2CrO4 is monoclinic with space group *C2/m*, [41] whilst barium chromate BaCrO4 is orthorhombic with space group *Pnma* [42]; both compounds have no electronic magnetic moment and no magnetic ordering.

Sharply defined 53Cr NMR spectra are presented for (NH4)2CrO4 and BaCrO4 obtained at 9.4 T, along with DMFIT [43] simulations of the central transition based on second-order quadrupole perturbation theory, in **Figure 1**. The 53Cr spectrum for (NH4)2CrO4 has not been previously reported although a preliminary value for CQ of ~2.5 MHz was mentioned in earlier work [44]. The values obtained here for CQ and h in BaCrO4 are in excellent agreement with parameters reported at higher fields as shown in **Table 1**. In these crystalline diamagnetic compounds, the central (1/2, −1/2) 53Cr NMR transition displays relatively sharp singularities enabling accurate measurement of CQ, h, and isotropic chemical shift δiso from the second-order quadrupolar features. The resulting isotropic chemical shift δiso = 0 ppm for both chromates, with the reference zero shift obtained from (NH4)2CrO4 in aqueous solution, is in good agreement with the previously reported value of δiso = 1750±20 ppm for BaCrO4 powder determined under MAS and referenced to Cr(CO)6 in chloroform solution known to be shifted −1797 ppm relative to the CrO42− used here [44,45]. Buhl [45] has calculated the chemical shift for CrO42− using two density functionals and has reported values of 21 ppm and 81ppm as compared to the experimental value of 0 ppm.

**Table 1** 53Cr quadrupolar coupling constant CQ and asymmetry parameter h for (NH4)2CrO4 and BaCrO4 measured at 9.4 T compared with values previously reported.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Compound** | **CQ (MHz)** | **h** | **Field Strength (T)** | **Reference** |
| (NH4)2CrO4 | 3.1±0.1 | 0.58±0.05 | 9.4 | present work |
| (NH4)2CrO4 | ~2.5 | not reported | 7.05 or 9.4 | [44] |
| BaCrO4 | 4.9±0.1 | 0.16±0.05 | 9.4 | present work |
| BaCrO4 | 5.0 ± 0.05 | 0.14 ± 0.03 | 11.75 and 18.8 | [22] |

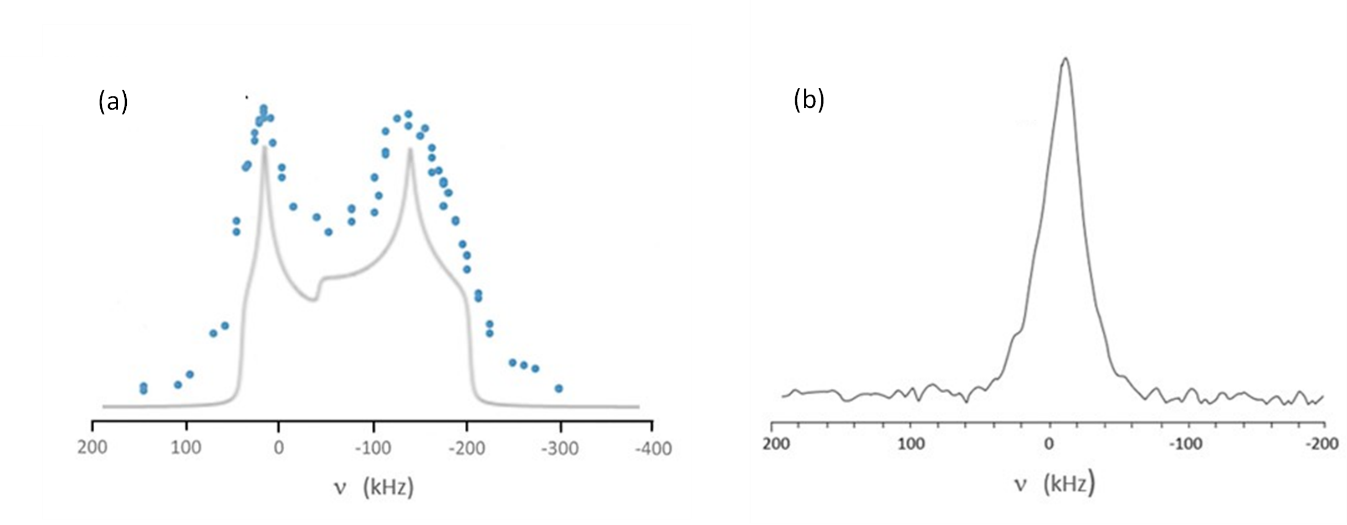


**Figure 1**. Experimental (top) and simulated (bottom) central (1/2, −1/2) transition static 53Cr NMR lineshape for static powder samples of (NH4)2CrO4 (left) and BaCrO4 (right) at 9.4 T. Intensity values are shifted on the y axis for clarity.

*4.3 Cr2N*

Cr2N is an interstitial compound showing metallic behaviour and no magnetic transitions; its principal use is as a tempering agent in steel making. The crystal structure is trigonal [46] with a single Cr site (fully occupied) with no axis of symmetry. The powder XRD spectrum [35] indicates a well crystallized specimen with minor impurity phases of CrN0.98 (6±1%) and Cr (1.6±0.9%). It may be noted in passing that mono-chromium nitride, CrN, is an insulator at room temperature and an antiferromagnetic metal below the Néel temperature of 286 K [47]. *Ab initio* DFT calculations for two dimensional Cr2N MXene have predicted an antiferromagnetic metal [48].

The 53Cr and 14N NMR spectra for Cr2N are reported here for the first time. There exists a relatively substantial electric quadrupole interaction at the Cr site. The 53Cr NMR spectrum (**Figure 2(a)**) at a magnetic field of 9.4 T has a width of approximately 300 kHz and a Knight shift of −1900 ppm. It was found not possible to capture the spectrum using standard (echo) pulsed NMR at a single operating frequency. The strategy employed here, and subsequently for the Cr2O3, was to record the amplitude using a frequency-stepped echo approach [32]. Simulation of the spectrum using DMFIT [43] gives CQ = 6.3±0.2 MHz and h = 0.15±0.10.



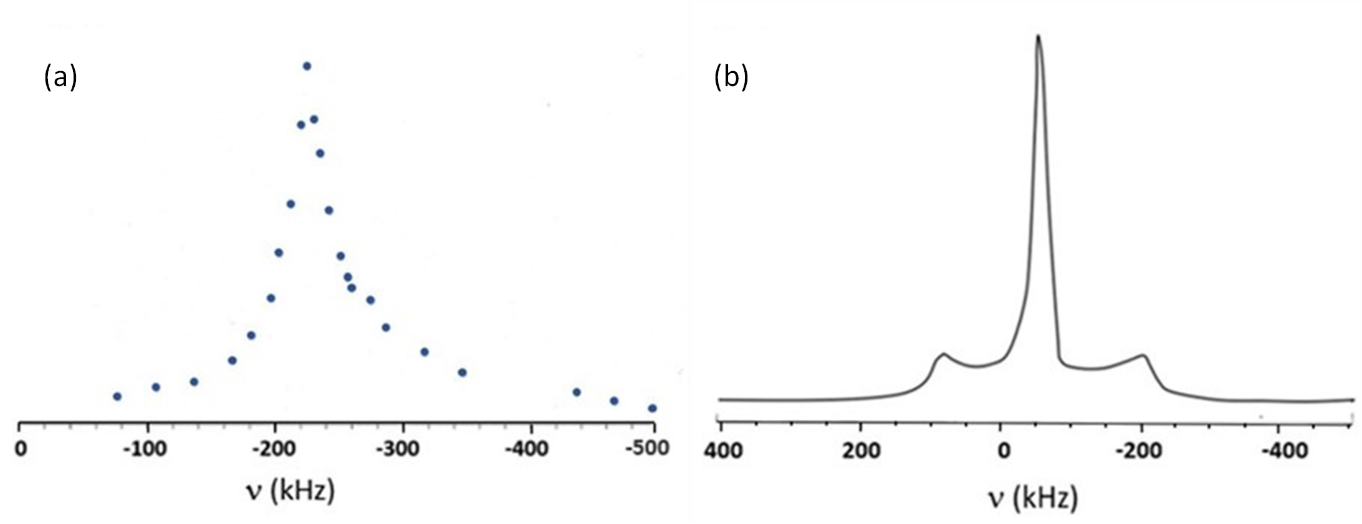
**Figure 2**. (a) Static 53Cr NMR data from Cr2N showing experimental (top) and simulated (bottom) central (1/2, −1/2) transition lineshape. Intensity values are shifted on the y axis for clarity. (b) Static 14N NMR spectrum of Cr2N.

The crystal structure [46] also indicates four N sites – one unoccupied, one fully occupied, and two partially occupied; however, a static pulsed 14N NMR spectrum (**Figure 2(b)**) of the specimen indicates a single line with 35 kHz width (fwhm) and a small negative shift diso = −200 ppm. The single narrow 14N NMR line is somewhat surprising considering (i) the site symmetry of all the N sites is no higher than , and (ii) 14N (I=1) is one of few quadrupolar nuclei with integer spin, and in non-cubic environments exhibits a first-order broadened 14N NMR lineshape [39]. The observed line possibly originates from the one fully occupied site. This single line may be due to vacancy assisted mobility of the nitrogen atoms meaning that only the permanently filled site will be detected. Low temperature NMR measurements may shed light on the origin of the 14N lineshape and are suggested as future work. From our room temperature lineshape, an upper limit value of CQ < 0.047 MHz can be estimated from the fwhm [49]. Bastow *et al.* [50] have previously reported 14N CQ values for other metal nitrides including AlN (CQ < 0.01 MHz). For AlN the 14N static spectrum was an approximately Gaussian lineshape with fwhm of 7.5 kHz which gave the upper limit CQ value ((4/3)fwhm) of < 0.01 MHz. This work has recently been revisited in a single crystal AlN specimen by Zeman *et al.* [51] reporting that CQ = 8.19 kHz; hence this method is found to be robust for estimating an upper limit for CQ within 20%.

*4.4 CrB2*

CrB2 has been established as a metal by single crystal measurements of (*inter alia*) electrical resistivity, Hall coefficient, and magnetic susceptibility [52] with weak itinerant antiferromagnetic ordering below the Néel temperature of 88 K [53]. The crystal structure [54] is hexagonal P6/mmm with Cr in 2a at (0,0,0) and B in 4d at (⅓,⅔,½), a = 2.969 Å, c=3.006 Å, both sites having axial symmetry and h = 0. The powder XRD [35] shows well crystallized CrB2 with Cr3B4 detected as a minor impurity.

The 53Cr NMR lineshape for CrB2 has not been previously reported. In the present work, frequency-stepped 53Cr NMR was used to delineate the lineshape for CrB2 at 295 K: a single narrowly peaked somewhat asymmetric lineshape (fwhm = 38 kHz) (**Figure 3(a)**) exhibiting a very large negative Knight shift: Kiso = −9982 ppm (−226 kHz at 9.4T). There is no quadrupolar structure, suggesting a relatively small CQ.



**Figure 3**. Static NMR data from CrB2 showing (a) the central (1/2, −1/2) transition for 53Cr and (b) the central as well as first-order quadrupole broadened (±3/2, ±1/2) transition for 11B.

The absence of a significant quadrupolar interaction in the 53Cr lineshape is somewhat unexpected given the substantial nuclear quadrupole interaction exhibited at the metal sites by the isostructural neighbouring group III and IV transition metal diborides ScB2, TiB2, and ZrB2 [36]. These diborides have sharp features for the second-order perturbed central line splitting and for the first-order perturbed satellite singularities allowing precise determination of CQ values. In CrB2, the narrow 53Cr NMR lineshape is presumably due to a fortuitous cancellation of all efg contributions. Attributing the observed, relatively narrow, 53Cr lineshape to a second-order perturbed quadrupolar linewidth (Eq. 3), with I=3/2 and the Larmor frequency νL = 22.66 MHz at 9.4 T, yields an estimate for νQ ≈ 1.285 MHz giving CQ ≈ 2.6 ± 0.5 MHz. This CQ value estimated for 53Cr compares reasonably well with the value of 3.05 MHz calculated *ab initio* by Schwarz *et al.* [55]. The broader underlying intensity is probably a result of some satellite transition intensity.

The 53CrB2 lineshape has presumably gone undetected for decades due to the large negative Knight shift making it difficult to know where to search for the resonance. The Knight shift for pure Cr metal is large and positive, 6870 ppm [4]. Although the transition metal monoborides and diborides formed the basis of substantial early work, the 53Cr resonance proved difficult to detect [56,57]. The present work may encourage 53Cr NMR study of the bonding and electronic structure in the stable chromium borides, e.g. Cr2B, Cr5B3, CrB, Cr3B4, CrB4 and CrB2 for comparison with theoretical predictions [58].

The 11B NMR spectrum at 295 K exhibits a first-order quadrupolar lineshape [59]. For 11B (I=3/2), the separation of the satellite transitions (±1/2, ±3/2) defines the quadrupolar frequency nQ (Eq. 3). For crystallographic sites with axial symmetry this equation simplifies as h = 0, and for 11B (I=3/2) therefore 2nQ = CQ. An 11B NMR spectrum at 295 K yielding a CQ of 0.58 MHz was measured as shown in **Figure 3(b)**. Schwarz *et al.* [55] calculated 11B CQ = 0.589 MHz in excellent agreement with this experimental value. The measured values of 11B CQ = 0.58 MHz and Knight shift = −390 ppm are in reasonable agreement with values first reported by Silver and Kushida [60] measured using continuous wave spectroscopy. The main 11B lineshape was reported to vanish below 88 K [61] and a transition to antiferromagnetism deduced. Subsequently Funahashi *et al.* [62], using neutron diffraction, observed a helical magnetic structure in CrB2 below 88 K. Bauer *et al.* [53] confirmed the incommensurate spin order reported by Funahashi *et al.* [62]. Recent *ab initio* calculations for two dimensional CrB2 have predicted a ferromagnetic half metal with TC=175K [63].

*4.5 CrO2*

In this ferromagnetic oxide the hyperfine interaction at the Cr site is sufficiently large that the 53Cr spectrum can be conveniently examined in zero applied field. This interaction is progressively thermally averaged to lower values as the temperature rises from 4.2 K to the Curie temperature TC = 395 K [17,64]. CrO2 has the tetragonal rutile structure and is ferromagnetic below TC. Until recently this compound was used as the magnetic coating for high quality magnetic tapes, and having a convenient Curie temperature relative to room temperature makes it attractive for use in flexible magnetic composite devices [64]. An SEM micrograph of the powder [35] displays a characteristic nanorod microstructure [19,20] with typical rod dimensions: length ~ 200 to 300 nm, diameter ~ 30 nm. The powder XRD pattern [35] indicates a well crystallized material with CrO(OH) (Guyanaite) detected as a minor impurity.

The rutile structure implies one distinguishable Cr site per unit cell, so that there should be only one central line visible in the 53Cr zero field NMR spectrum. However two widely separated narrow lines of approximately equal intensity at frequencies nlow and nhigh of 26.5 and 37.2 MHz, respectively, are observed at 4.2 K [16-18,20,21]. A self-doping mechanism has been tentatively suggested for the existence of two distinct Cr sites [17]. A hypothesis that the sites originate from intra-domain and domain wall Cr atoms, respectively, has been considered and experimentally discounted [17]. Recently, it has been hypothesized that the two different Cr sites have different 3d orbital occupation numbers [20]. Because CrO2 is a half metal with a Curie temperature above ambient temperature, it is being investigated for use in spintronic devices [65].

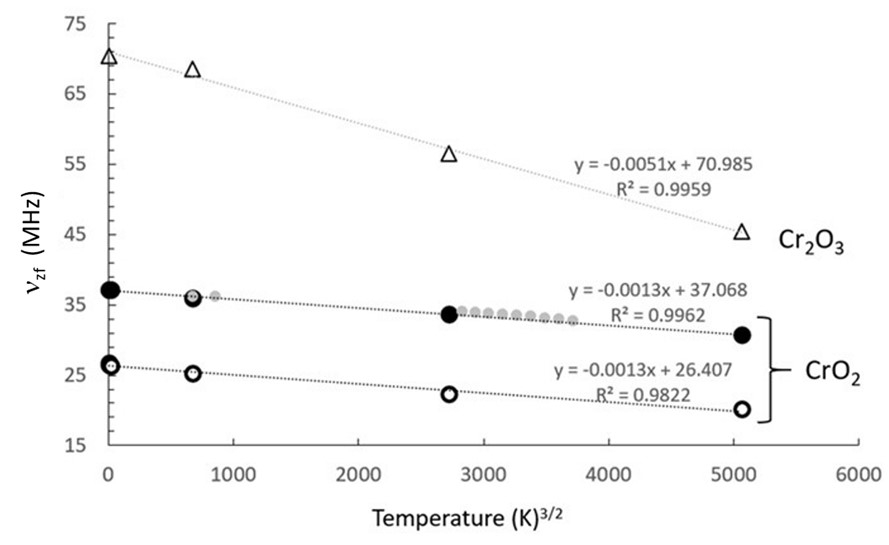
The frequencies, nlow and nhigh, for these two lines measured in this work at 77, 195 and 295 K (**Table 2**) were located by systematically searching frequencies below the reported values at 4.2 K. Increasing spin wave excitation as the temperature rises is presumably responsible for the steadily decreasing nzf(T) for the two Cr sites as the temperature rises (**Figure 4**). There is a correlation with Bloch ferromagnetic spin wave theory [9,11] that predicts a T3/2 decrease in magnetization. Using Bloch theory, the data in **Figure 4** for the two Cr sites predict resonance frequencies at 0 K of 26.407 MHz and 37.068 MHz, indicating hyperfine fields at the nuclei of 12.7 and 17.8 T, respectively. The relationship between the hyperfine parameters, the magnetic moment and the chromium valence is further discussed in Section 4.7, as is spin wave theory.

The 53Cr NMR linewidths diminish along with decreasing signal-to-noise ratio as the temperature rises towards the Curie temperature (**Table 2 and Figure 5**). Within experimental error, the frequency difference, (nhigh − nlow), remains essentially constant as the temperature rises from 4.2 K with an average value of 10.55 MHz. Shim *et al.* [17] have reported the saturation magnetization (measured using a magnetometer) in CrO2 from 10 to 380 K indicating a T3/2 decrease in magnetization by 50% up to approximately 375 K, followed by a rapid continuous decrease of the remaining 50% of the magnetization toward zero in the critical region at the Curie temperature of 395 K. Recently, Piskunov *et al.* [21] have measured 53Cr NMR data from 4.2 K to 365 K in high purity CrO2, giving values similar to those reported here.

It may be noted that there is no evidence of a quadrupole interaction in the 53CrO2 NMR spectrum in the published or present data. Compare TiO2 (also rutile structure) where the 49Ti nuclei see a substantial efg (CQ = 13.9 MHz, h = 0.19) [66] and a-VO2 (rutile) where the 51V CQ = 2.77 MHz and h = 0.86. [67]. It is possible that the broad 53Cr lines have a second-order quadrupole interaction folded in, which, since this quantity generally decreases with increasing temperature, would explain why the observed line widths decrease with increasing temperature. Takeda *et al.* [20] report single crystal 53CrO2 NMR measurements at 4.2 K, in an applied magnetic field of 0.3 T parallel to the c axis, giving fwhm for the low and high resonances as 190 kHz and 280 kHz, respectively. A rough estimate of the upper limit for CQ can be made from the narrowest linewidth that still obscures the quadrupolar splitting, where assuming h = 0 and perturbation theory still holds, a second-order perturbed quadrupolar linewidth Δ from Eq. 3 where I = 3/2, νL = 0.723 MHz at 0.3 T, then using the measured fwhm 190 kHz as Δ yields estimates for νQ ≈ 0.513 MHz and CQ ≈ 1.03 MHz. Our estimate of 0.513 MHz for νQ is in good agreement with a recent estimate of νQ ≈ 0.5 MHz [21]. It can be noted that a (hypothetical) value of h = 0.4 decreases CQ by only 2.6%. To the best of our knowledge *ab initio* calculations of the 53Cr efg in CrO2 have not been published.

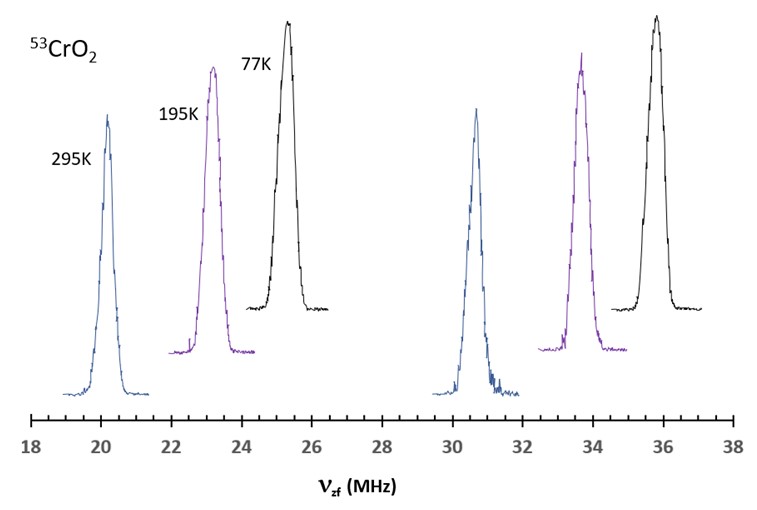
**Table 2** CrO2 53Cr zero field NMR line peak frequencies nhigh and nlow and linewidths Dv at various temperatures below TC.

|  |  |  |  |
| --- | --- | --- | --- |
| T(K) T3/2 (K3/2) | nlow (MHz) Dv (kHz) | nhigh (MHz) Dv (kHz) | Reference |
| 4.2 8.6 | 26.5 450 | 37.2 680 | [20] |
| 6.5 16.6 | 26.4 485 | 37.1 450 | [17] |
| 77 676 | 25.3 530 | 35.9 510 | present work |
| 195 2723 | 23.3 510 | 33.7 460 | present work |
| 295 5067 | 20.2 390 | 30.7 420 | present work |



**Figure 4**. 53Cr frequencies nhigh (•) and nlow (**O**) for CrO2 plotted as a function of T3/2. With best fit equation and R2 value displayed for the dotted line fits. Data of Yasuoka *et al.* [15] for 53CrO2 nhigh (•) included for information as described in the text. 53Cr frequency (Δ) for Cr2O3 plotted as a function of T3/2 with best fit displayed.

The resonance reported by Yasuoka *et al.* [15] in 1963 for CrO2 was detected using a marginal oscillator and a super-regenerative oscillator. The resonance, which can be attributed to nhigh, was reported for eleven temperatures over a range from 77 to 240K. These data were added to the data shown in **Figure 4** in order to further refine the fit to spin wave theory T3/2 and resulted in a best fit, y = −0.0012x + 37.104 (R2 = 0.9866), in excellent agreement with that obtained from frequencies measured using zero field pulsed NMR. It can be noted that neither a T2 fit nor a linear T fit to these data was as good as the T3/2 fit [11]. Comparison of the 53Cr zero applied field NMR frequency, nhigh, from the present work, Yasuoka *et al.* [15], and Piskunov *et al.* [21], with the saturation magnetization data of Shim *et al.* [17] as functions of temperature for CrO2, show agreement with Bloch spin wave theory to T = 340 K or T =0.86TC [35]. Data from 340 K to 365 K (up to 0.9TC) indicate a rapid continuous decrease of nhigh and nlow toward zero in the critical region near the Curie temperature of 395 K [21] although the values of nzf are still at the 40-50% level of decrease from 4.2 K when measured at 365 K [35]. It remains to be demonstrated whether the local 53Cr sublattice magnetization transition at TC = 395 K will be first order, i.e. a discontinuous drop to zero of spontaneous magnetization rather than a smooth transition to the paramagnetic state; i.e. zero magnetization. 53Cr NMR measurements up to and through TC (395 K) are suggested for future work.



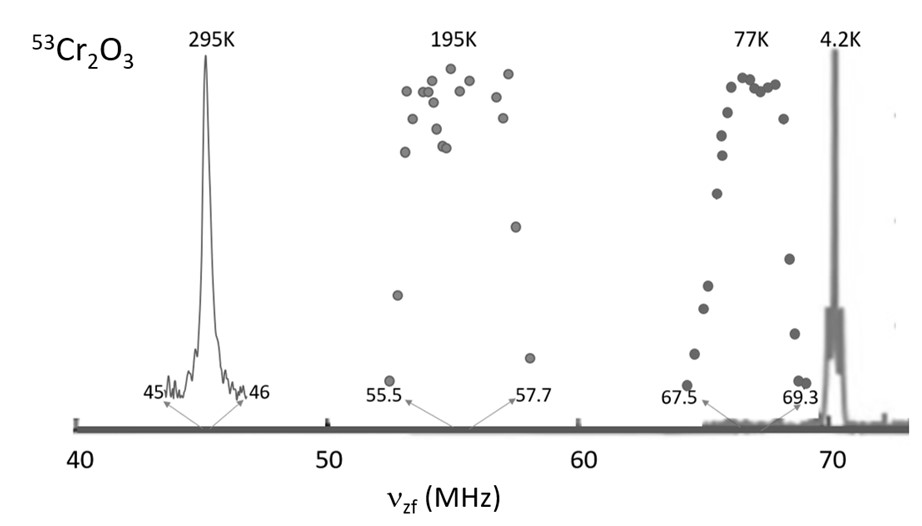
**Figure 5.** 53Cr NMR lineshapes for CrO2 at 295, 195 and 77 K. Intensity values are shifted on the y axis for clarity.

*4.6 Cr2O3*

This antiferromagnetic compound has the corundum (Al2O3) structure with one distinguishable Cr atom per unit cell at a site with axial symmetry so that any detectable second-order lineshape should indicate an efg with h = 0. An XRD spectrum [35] indicated good crystallinity with no trace of impurity. The antiferromagnetic to paramagnetic transition temperature, Néel temperature, TN = 307.9 ± 0.2 K, was measured using DSC. The DSC traces were made on two separate samples of the powder, and both measurements [35]indicate a lambda anomaly in specific heat at TN, characteristic of a second-order phase transition.

Antiferromagnetic ordering was established in Cr2O3 by Brockhouse in 1953 [68] and Corliss *et al.* [69,70]. Previous internal NMR, as discussed in Section 2, has been reported by Rubinstein *et al.* [14] using a super-regenerative oscillator detector, with a 53Cr 95% enriched specimen at temperatures from 1.6 to 16 K. Over this relatively small temperature range the NMR line was detected at a constant frequency of 70.43 MHz, with the signal disappearing into the noise above 16 K. The frequency separation of the satellites (53Cr, I=3/2) gave nQ = 0.525 MHz and CQ = 1.05 MHz using Eq. 4 for h=0. Takeda *et al.* [19] using a much later, spectroscopically more sophisticated, method, recently reported a similar value of nQ = 0.54 MHz. The 53Cr NMR spectrum of Takeda *et al.* [19] at 4.2 K is reproduced here in **Figure 6**; its sharp central line centred at 70.43 MHz with clear (±1/2, ±3/2) satellites measuring nQ = 0.54 MHz (CQ = 1.08 MHz) can be compared with the 53Cr spectra reported in the present work as described below.

In the present work, the 53Cr zero field NMR signal was searched for below 70.43 MHz, first at 77 K. This search revealed a surprisingly broad lineshape (**Figure 6)** centred at 68.5 MHz with width 1.7 MHz, delineated by frequency stepping. A search at 195 K located, again by frequency stepping, a somewhat broader essentially featureless lineshape of width 2.0 MHz centred at 56.5 MHz. At 295 K a single line at 45.5 MHz of fwhm = 0.16 MHz was measured. The 295 K measurement was repeated and verified the original result. Spectra taken at increasing positive and negative 50 kHz frequency offsets from this value confirmed a single absorption line at 45.5 MHz. It is unclear what line broadening mechanism is operating at 77 and 195 K and what is happening to remove this mechanism at 295 K. The specimen was studied over a wide temperature range (10-300 K) using synchrotron radiation powder XRD, and there was no indication of a phase transition. The DSC trace [35] starts upwards from 140 K and there are no transitions other than the Néel temperature at 307.9 K. Karnachev [71] studied the rare earth orthochromite Dy0.2Er0.8CrO3 (TN = 141K) over the temperature range 58-91 K using zero applied field NMR and observed line broadening attributed to efg inhomogeneity. We can find no other report of line broadening in Cr2O3 and suggest further exploration of the mechanism as potentially fruitful future experimental work and DFT calculation. **Figure 4** shows a plot of the central line frequency for 53Cr in Cr2O3 as a function of T3/2 consistent with spin wave theory, predicting a resonance frequency at 0 K of 70.985 MHz, indicating a hyperfine field at the nucleus of 34.1 T. A hyperfine magnetic field still exists at 19 T at approximately 10 K below the Néel temperature (**Figure 4**). Corliss *et al.* [69,70] showed that greater than 50% of the macroscopic magnetization decrease in Cr2O3 powder (measured using neutron diffraction) occurs in the critical region between 295 K and the Néel temperature [35]. The present work suggests that 53Cr studies of the magnetic sublattice in Cr2O3 over a wide temperature range inclusive of TN will be fruitful.



**Figure 6**. 53Cr NMR lineshapes for Cr2O3 in zero field over a range of temperatures. Spectrum at 4.2 K adapted from Takeda *et al.* [19].

*4.7 Compilation of 53Cr solid-state NMR in alloys and compounds*

Chromium exhibits seven valence states in its alloys and compounds with the most prevalent being Cr(0) for the metal, metallic alloys, and strong field ligand complexes, and Cr(III) and Cr(VI) for other compounds. The present work has reported NMR spectra for 3d6 Cr(0) paramagnetic (Cr2N) and 3d6 Cr(0) antiferromagnetic (CrB2) metals, a 3d3 Cr(III) antiferromagnetic (Cr2O3) semiconductor, a 3d2 Cr(IV) ferromagnetic half metal (CrO2), and 3d0 Cr(VI) diamagnetic (BaCrO4, (NH4)2CrO4) insulators. As discussed, 53Cr magnetic resonance data can be used to elucidate the bonding environment of Cr in materials. **Table 3** summarises the calculated integer valence and theoretical spin only magnetic moments expected for chromium in its compounds as compared to the range of reported low temperature measured magnetic moments [72-76]. **Table 4** comprehensively summarises 53Cr magnetic resonance data for the compounds reported here within the context of data from the literature on Cr alloys and compounds [77-116]. To the best of our knowledge, past 53Cr solid-state NMR studies have not been tabulated in one place since 1971 [117]. For the literature surveyed here, which covers 1961 to 2022, 73% of the compounds studied are magnetic compounds, with 27% of those having their critical magnetic ordering temperature (TC or TN) above 300 K. For these studies of magnetic materials, 89% report NMR data with zero applied magnetic field.

*4.7.1 Zero applied field NMR at low temperatures*

This section will first focus on magnetic 53Cr compounds and their NMR data at zero applied magnetic field. In **Table 4**, for zero field NMR reports, we include the low temperature resonance position of the central line(s); in reports where domain and wall resonances are distinguished, we have included only the data from domains; in reports where TC or TN > 77 K and measurements were made at both liquid helium and liquid nitrogen temperatures we have included those data for comparison purposes. For the spin echo technique, only domain signals are observed due to the short relaxation times of the broad resonance signals from walls. Three low temperature zero field NMR reports attribute separate resonances to domain and domain wall sites [3, 94, 118] for CrI3, EuCrO3, and CrBr3, respectively, with the domain wall resonances located from 0.89 MHz to 1.42 MHz below the domain resonances. Where possible, low temperature Cr valence is given and it should be noted that in some compounds (mixed valence or those with a phase transition), valence can change with temperature.

The background to the hyperfine interactions at zero applied magnetic field, where the center-line resonance, nzf, (in units of MHz) is a measure of the hyperfine field at the 53Cr nucleus, has been introduced in Section 4.1 (Eqs. 4 to 6) under the approximations noted above. NMR measurements as the temperature approaches 0 K (liquid helium temperatures) in zero field are necessary to minimize thermal effects on the value of the hyperfine constants derived from the data and for comparison with quantum chemical calculations of hyperfine interactions. The sublattice magnetization, and the resonance frequency will decrease as the temperature rises due to thermally excited spin waves. 53Cr zero applied field and magnetization measurements for CrO2 and Cr2O3 [35] illustrate the frequency-magnetization relationship, i.e., proportionality of nzf(T) and M(T), along with the T3/2 relationship for temperatures up to ~ 0.8 (TC or TN) (cf. **Figure 4**).

The absolute value of the hyperfine coupling constant |A| depends on the configuration and valence of the Cr ion in the compound, indicates the extent of delocalization of the unpaired electron, and can be calculated *ab initio* for the 3dn4s0 ions [119] or calculated from the measured values of nzf(0) and M(0) for a given compound [1]. Several authors [119-121] calculate A for the chromium 3dn4s0 ions, giving the core polarization hyperfine field per unpaired valence electron, within the Hartree Fock scheme as −12.5 T/mB. This value results from the approximation of (i) the magnetic hyperfine 3d exchange interaction transferred at the chromium nucleus (through covalency and overlap) as the Fermi contact interaction and (ii) the magnetic moment as the spin density at the nucleus. Values of A derived from low temperature experiment are compared with theory to ascertain the extent of delocalization or magnitude of the transferred field. Alternatively, theoretical values of A are used with measured values of nzf at low temperature to predict magnetization and valence. The ground state magnetization can also be calculated using *ab initio* DFT methods where the approximation of the exchange and correlation potential is the subject of much research in chromium compounds [122-125].

Other methods for the calculation of the hyperfine coupling constant have been reported for 53Cr with values of |A| ranging from 8.3 to 12.2 T/mB [125-129]. The value A = −10 T/mB is often used, as this is the average value for the core polarization hyperfine field per unpaired valence electron for the 3d transition metals reported by Blugel *et al.* [128]. The value of |A| = 8.33 T/mB results from a first principles calculation of the contact field for Cr3+ [125]. Rubinstein *et al.* [14] first reported the measured value of A = −9.76 T/mB based on zero applied field measurements of 53Cr3+ in an octahedral environment of oxygen atoms in Cr2O3 with nzf = 70.43 MHz at 1.6 K and with M(0) assumed to be 3 mB per Cr atom. The theoretical value of |A| for an isolated Cr3+ ion (12.5 T/mB) has been shown to be very close to the measured values (11.3 to 12.4 T/mB) in Cr molecular rings and chains [10,104,105]. The theoretical values compare favourably with the range of measured (calculated from measurements on Cr compounds) values of |A| shown in **Table 3**.

**Table 3** is also useful for estimating the range of observed frequencies near 0 K for the 53Cr nucleus in various compounds. Using the range of |A| values and the spin only magnetic moment values, the anticipated range of 53Cr nzf(0) is 38-110 MHz; using the measured local magnetic moment values, the anticipated range is 10-114 MHz; as compared to the reported measured range of nzf in **Table 4** which is 13-79 MHz. This measured range of nzf(0) reported for each configuration in **Table 4** can be compared to the range calculated from **Table 3** in a form of Slater-Pauling-like curve (see **Figure 7**). The Slater-Pauling curve (magnetic moment M as a function of valence electron concentration) for 3d transition metal compounds has been calculated *ab initio* by Dederlichs *et al.* [129] for Fe, Ni, and Co based alloys. Such an *ab initio* calculation for Cr-based alloys has not been reported and is recommended as fruitful future work.

The theoretical value |A| = 8.33 T/mB, [125] along with the spin only magnetic moment values from **Table 3** for each valence, are used to calculate the theoretical internal field frequencies for each valence in **Figure 7 (b)**. **Figure 7** **(b)** shows that the value of the hyperfine interaction constant |A| has a great bearing on the goodness of fit between theory and experiment. It can be noted that a variation in |A| from 8.3 to 12.5 T/μB results in a variation of predicted resonance frequency (e.g. for Cr(III), using spin only M = 3 mB) from 60 to 90 MHz. In addition, it should be noted that in **Figure 7** **(b)** the mixed valence compounds are shown together at the boundaries of the integer valence values which may also affect goodness of fit.

Future work on *ab initio* calculations for magnetic Cr alloys and compounds would be useful and could help predict the mixed valence values for nzf(0). Mixed valence is thought to enable local double exchange mediated magnetic order [130] which, in topological insulators, is postulated as a pathway to room temperature quantum transport in zero magnetic field [131,132]. Also, *ab initio* calculations of nzf(0) would be helpful for locating Cr(I) and Cr(V) internal field resonances that, to the best of our knowledge, have not yet been reported by zero field NMR studies. In **Figure 7 (b)** we have indicated, with dashed line ellipses, where one might expect to find the low temperature 53Cr zero applied field NMR resonances for 3d5 low spin and 3d1 compounds in future experiments or calculations.

Some further comments on **Figure 7 (b)** are warranted as it is the first time the literature data for 53Cr have been compiled in such a format. As reviewed in this section, previous 53Cr reports have mainly focussed on a single material with a single Cr valence (predominantly Cr3+), with authors choosing either to fix the hyperfine coupling constant A or to fix the magnetic moment. The data in **Figure 7 (b)** now provide a summary of 53Cr nzf(0) values for a wide range of Cr compounds across the valences Cr(0) to Cr(IV) including mixed valence, high spin, low spin, octahedral and tetrahedral configurations, metals, semi metals, semiconductors, insulators, and varying crystal and magnetic structures. These data allow us to test our understanding of magnetism in Cr alloys and compounds. Cottenier [133] has noted the difficulty of DFT functionals in capturing the physics of the ground state for Cr alloys and compounds, making these alloys ideal testing grounds for improved DFT functionals. The data set may also prove helpful as a training set for a machine learning approach to property prediction as well as testing hypotheses and models.

1. It can be found in the literature that the covalency of the Cr-x bond increases as x=O is successively replaced by x=halides, x=S, and x=Se [120]. The “covalency school model” [120] expects the magnetic moment of the electron spins (and hence nzf) to decrease with decreasing electronegativity, i.e. with increasing covalency, which it does as shown in **Figure 7** **(b)** for d3 Cr(III)oct oxides, halides, sulphides and selenides.
2. The reported non-integer valence values for mixed valence compounds from **Table 4** have been plotted as an expanded section [35] and show the expected decrease in low temperature 53Cr internal magnetic field resonance frequency with valence from Cr3+ to Cr4+ for mixed valence chromium oxides.
3. The two Cr2+ high spin d4 Cr(II)oct compounds may appear as outliers; however, they are high spin and sit approximately 10 MHz lower than would be predicted using the spin only magnetic moment M = 4 and |A| = 8 .33 T/μB.

**Table 3.** Magnetic moment, integer valence, and ionic radius of chromium in its alloys and compounds.

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Configuration** | **Valence** | **Number of unpaired electrons, *n***  **Spin S=*n*/2** | **Spin Only Magnetic moment, M (mB) calc**  **M=√*n*(*n*+2)** | **Magnetic moment, M (mB) measured** [72]  **Octahedral** |**Tetrahedral** | | **Average Magnetic Moment, M (mB)**  **M = gmBS**  **(using g=2)** | **Hyperfine Coupling Constant**  |A|  **(T/mB)** | **Metallic or Ionic Radius**  **(pm)** [73,74] | **Cr Valence Reference Standard Compounds** [75,76] |
| Cr (0) [Ar]3d54s1  configuration is for a non-bonded isolated Cr | Cr | 6  S=3 | 6.93 | NA | NA | 6 | Theory  12.5 | 140 | NA |
| Cr (0) [Ar]3d64s0 | Cr | hs 4 ls 0  S=2 S=0 | 4.90 0 | ls 0.4-0.6 |  | 4 0 | Measured  11.3 - 13.9 | ls 128 | Cr, Cr(CO)6 |
| Cr (I) [Ar]3d54s0 | Cr+ | hs 5 ls 1  S= S= | 5.92 1.73 | ls 1.77 |  | 5 1 | 9.8 | ls 109 | (C6H6)2CrI |
| Cr (II) [Ar]3d4 | Cr2+ | hs 4 ls 2  S=2 S=1 | 4.90 2.83 | hs 4.0-5.0  ls 2.7-3.4 |  | 4 2 | 8.6  7.5 - 9.0 | hs 80  ls 73 | CrSe  CrCl2 |
| Cr (III) [Ar]3d3 | Cr3+ | 3  S= | 3.87 | 2.7-4.0 |  | 3 | 9.0 – 12.7 | 61.5 | CrCl3, Cr2O3 |
| Cr (IV) [Ar]3d2 | Cr4+ | 2  S=1 | 2.83 |  | 2.6-2.8 | 2 | 5.6 - 8.0 | 55 | CrO2 |
| Cr (V) [Ar]3d1 | Cr5+ | 1  S= | 1.73 |  | 1.7-1.8 | 1 | 7.4-7.8 | 49 | CrOCl3, YbCrO4, NdCrO4 |
| Cr (VI) [Ar]3d0 | Cr6+ | 0  S=0 | 0 |  | 0 | 0 | NA | 44 | CrO3, CaCrO4, K2CrO4, K2Cr2O7 |

hs=high spin, ls=low spin. The notation Cr (I, II, …) for oxidation state should not be confused with some authors’ use of this nomenclature for inequivalent Cr atom positions in a unit cell.

**Table 4**. 53Cr hyperfine interaction parameters of chromium compounds from magnetic resonance measurements. Cr valence expected at 0 K. Local magnetic moment near 0 K, when reported. Note the measurement temperature, as the chemical shift diso or Knight shift for metals, the zero applied field NMR center line frequency, the Cr sublattice magnetization, and the Cr ion valance can be functions of temperature. Material character and critical magnetic transition temperatures are given where known.

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Compound** | **Chromium Valence**  **Local Magnetic Moment** | **diso or Knight shift (ppm)\*** | **Center line frequency (MHz)** | **CQ (MHz)** | **h** | **Temperature**  **(K)** | **Character**  **AFM =** antiferromagnetic  **FM =** ferromagnetic  **PM =** paramagnetic | **Reference** |
| Cr | Cr(0)  0.5mB/Cr | 6870 | 16.60 |  |  | 314 to 387  314 | Metallic, AFM below TN = 313K, PM above | [4]  [31] |
| Cr1-xVx (x = 0.25 to 3 at%) | Cr(0) | 6850 to 6990 |  |  |  | 300 | Metallic, AFM below TN = 287K (0.25 at% V) to 65K (3 at% V), PM above | [4,5] |
| Fe1-xCrx (x = 0.25 to 26.3 at%) | Cr(0)  0.46mB/Cr |  | 15.85 to 17 |  |  | 1.2 | Metallic, FM below TC = 1050K (0.25 at% Cr) to 920K (26.3 at% Cr), PM above | [77] |
| Cr1-xMox (x = 12.9 to 22.6 at%) | Cr(0) | 6800 |  |  |  | 1.4 | Metallic, AFM below TN = 146K (12.9 at% Mo) to 20K (22.6 at% Mo), PM above | [28] |
| Cr3AsN (2 inequivalent sites) | Cr(0)  0.5mB/Cr |  | 13.66, 14.51 |  | 0  0 | 4  4 | Metallic, itinerant AFM below TN = 255K, PM above | [78] |
| CrH0.93 and CrH0.97 (hexagonal) | Cr(0) | 5300 |  |  |  | 3 to 300 | Metallic, paramagnetic | [27] |
| CrH0.93 and CrH0.97(cubic) | Cr(0) | 3000 |  |  |  | 3 to 300 | Metallic, paramagnetic | [27] |
| Al1-xCrx (x = 0.1 and 0.5 at%) | Cr(0) | −3800 |  |  |  | 1 to 4 | Metallic, dilute substitutional site | [79] |
| Pt1-xCrx (x = 0.1 and 0.5 at%) | Cr(0) | −8200 |  |  |  | 1 to 4 | Metallic, dilute substitutional site | [80] |
| CrB2 | Cr(0) | −9982 |  | 2.57a | 0 | 295 | Metallic, weak itinerant AFM below TN = 88K, PM above | present work |
| Cr2N | Cr(0) | −1900 |  | 6.3 | 0.15 | 295 | Metallic, paramagnetic | present work |
| Cr(CO)6 | Cr(0) | −1814\*\* |  | 0.348 | 0.48 | 295 | Insulator, diamagnetic | [44] |
| Rb2CrCl4 | Cr(II)oct  4mB/Cr |  | 82.3  67.4b | 3.2 |  | 4.2 | Semiconductor, FM below TC = 52K, PM above | [81] |
| SrCr2As2 | Cr(II)oct  1.9mB/Cr |  | 71 | c |  | 1.6 | Metallic, AFM below TN = 615K, PM above | [82] |
| Cr3Te4 (2 inequivalent sites) | Cr(II), Cr(III)  1.79mB/Cr or  2.35mB/Cr |  | 57.5, 45.3  56.0, 44.5  55.2, 44.8  50.0, 36.9  47.0, 36.5 |  |  | 4.2  4.2  20  77  77 | Metallic, FM below TC = 329K, PM above | [83]  [84]  [85]  [84] |
| Cr5Te6 (2 inequivalent sites) | Cr(II), Cr(III)  2.5mB/Cr |  | 53.0, 41.0 |  |  | 77 | Metallic, FM below TC = 327K, PM above | [84] |
| Cr7Te8 (2 inequivalent sites) | Cr(II), Cr(III)  1.8mB/Cr |  | 58.2, 45.1  52.6, 40.8 |  |  | 4.2  77 | Metallic, FM below TC = 350K, PM above | [86] |
| CrTe (2 inequivalent sites) | Cr(II), Cr(III)  2.4mB/Cr |  | 54.0, 42.2  55.2, 45.1 |  |  | 77  77 | Metallic, FM belowTC = 340K, PM above | [85,87]  [84] |
| Y3Fe4.57Cr0.43O12 | Cr(III) |  | 78.8  78.0 |  |  | 4.2  77 | Insulator, ferrimagnetic below TC = 500K, PM above | [88] |
| CrCl3 | Cr(III)  2.9mB/Cr |  | 62.42  62.32 | 0.882  0.9 | 0 | 1.23  1.4 | Semiconductor, AFM below TN = 16.8K, PM above | [2]  [13] |
| CrBr3 | Cr(III)  2.99mB/Cr |  | 58.038 | 1.184 | 0 | 1.34 | Semiconductor, FM below TC = 37K, PM above | [1] |
| CrI3 | Cr(III)  3.1mB/Cr |  | 49.392 | 0.744 | 0 | 1.65 | Semiconductor, FM below TC = 68K, PM above | [3] |
| CuCrO2 | Cr(III)  2.8mB/Cr |  | 63.8 to 66.0 |  |  | 4.2 | Insulator, AFM below TN = 24.3K, TN = 23.6K, PM above | [89] |
| Cr2O3 | Cr(III)  2.48mB/Cr |  | 70.43  70.43  68.5 | 1.05  1.08 | 0 | 1.6  4.2  77 | Semiconductor, AFM below TN = 308K, PM above | [14]  [19]  Present work |
| Dy0.2Er0.8CrO3 | Cr(III) |  | 63.6 | 4.4 | 0 | 69 | Semiconductor, AFM below TN = 141K, PM above | [71] |
| GdCrO3  (2 magnetic sublattices) | Cr(III) |  | 68.8  68.3 | 4.4  1.88 | 0 | 4  10 | Insulator, AFM below TN = 170K, PM above | [90] |
| ErCrO3 (low T AFM phase, higher T weakly FM phase) | Cr(III) |  | 68.97  67.6 | 2.7  1.8 | 0  0 | 4.2 (AFM)  37 (weakly FM) | Insulator, weakly FM below TC = 133K, PM above | [91]  [92] |
| TmCrO3  (2 magnetic sublattices) | Cr(III) |  | 68.9  69.1 | 1.36  3.52 | 0  0 | 1.8 to 5.6  1.8 to 65 | Insulator, AFM below TN = 125K, PM above | [93] |
| LuCrO3 | Cr(III) |  |  | 2.92 | 0 | 4.2 | Insulator, AFM below TN = 120K, PM above | [94] |
| EuCrO3 | Cr(III) |  | 68.7 | 2.76 | 0 | 14.3 | Insulator, AFM below TN = 140K, PM above | [94] |
| LaCrO3 | Cr(III) |  | 68.63 |  |  | 4.2 | Semiconductor, AFM below TN = 290K, PM above | [95] |
| MnCr2O4 | Cr(III) |  | 66.5  66.2 |  |  | 4.5  6.5 | Insulator, ferrimagnetic below TC = 41K, PM above | [96]  [97] |
| CuCr2O4 | Cr(III) |  | 63  63.2  59.4 |  |  | 5  0  77 | Insulator, ferrimagnetic below TC = 135K, PM above | [98]  [99] |
| FeCr2O4 | Cr(III) |  | 50.8  46.8 |  |  | 0  77 | Insulator, ferrimagnetic below TC = 80K, PM above | [87] |
| FeCr2S4 | Cr(III) |  | 50.8  46.8 |  |  | 0  77 | Metallic, ferrimagnetic below TC = 180K, semiconductor PM above | [99] |
| CoCr2S4 | Cr(III)  2.7mB/Cr |  | 49.3  47.4 |  |  | 0  77 | Semiconductor, ferrimagnetic below TC = 222K, PM above | [87] |
| MnxZn1-xCr2O4 (x>0.7) | Cr(III) |  | 65.5 |  |  | 1.8 | Insulator, ferrimagnetic below TC = 41K, PM above | [100] |
| Ga0.2Fe0.8NiCrO4 | Cr(III) |  | 75 |  |  | 4.2 | Insulator, frustrated ferrimagnetic below TC = 480K, PM above | [101] |
| NaCrS2 | Cr(III) |  | 53.45 | 0.2 |  | 1.5 | Semiconductor, AFM below TN = 17K, PM above | [102] |
| Cr3As2 | Cr(III) |  | 56.0  55.8 |  |  | 77  81.4 | Insulator, ferrimagnetic below TC = 243K, PM above | [103] |
| Cr7Ni | Cr(III) |  |  |  |  | 1.6 | Semiconductor, AFM ring | [104] |
| Cr7Cd (3 inequivalent sites) | Cr(III) |  | (44, 46, 57)b |  |  | 1.6 | Semiconductor, AFM ring | [105] |
| Cr8Cd | Cr(III) |  |  |  |  | 1.6 | Semiconductor, AFM ring | [8] |
| YCrO3 | Cr(III) |  | 68.73  68.74 | 1.99  2.0  1.52 | 0  0  0 | 4.2  4.2  77 | Insulator, AFM below TN = 140K, PM above | [106]  [19]  [94] |
| NaCr2O4 | Cr(III), Cr(IV):  Cr3.5+ |  | 52 |  |  | 4.2 | Insulator, AFM below TN = 125K, PM above | [107] |
| K2Cr8O16  (4 inequivalent sites: A,B,C,D) | Cr(III), Cr(IV):  Cr3.75+ 2.25mB/Cr |  | A 46,56  B 46,56  C 43,53  D 39,49 |  |  | 4.2 | Half metal, FM below TC = 180K PM above, metal-insulator transition TMI = 95K | [19] |
| SrRu1−xCrxO3  (x = 0.05, 0.12) | Cr(III), Cr(IV):  Cr3.75+ 2.4mB/Cr |  | 60.8 (x = 0.05) 60.3 (x = 0.12) |  |  | 1.3 | Insulator, itinerant FM below TC = 175 to 186K (x = 0.05, 0.12), PM above | [108] |
| CuCr2Te4 | Cr(III), Cr(IV) |  | 34.9 |  |  | 77 | Semiconductor, FM below TC = 326K, PM above | [109] |
| CuCr2Se4 | Cr(III), Cr(IV) |  | 38.2 | 0.39 |  | 77 | Semiconductor, FM below TC = 430K, PM above | [109]  [110] |
| ZnCr2Se4 | Cr(III), Cr(IV) |  | 46.7  44.75 | 1.48 |  | 1.4  6 | Semiconductor, AFM below TN = 20K, PM above | [111]  [6] |
| CuCr2S4 | Cr(III), Cr(IV)  2.67mB/Cr |  | 39.8  38.9  27 | 1.8  1.8 | 0 | 4.2  77  300 | Metallic, FM below TC = 420K, semiconductor PM above | [112]  [87] |
| CuCr2-xSbxS4  (x=0, 0.02, 0.07) | Cr(III), Cr(IV) |  | 39.5  39.3  39.4 | 1.8  1.8  1.8 | 0  0.1  0.2 | 77  77  77 | Metallic, FM below TC = 420K, semiconductor PM above | [110] |
| Cd1-xAgxCr2Se4  (x=0, 0.001, 0.005, 0.015) | Cr(III), Cr(IV) |  | 44.05 | 3.68 |  | 4.2 | Semiconductor, FM below TC = 130K, semiconductor PM above | [113,114] |
| CdCr2Se4 | Cr(III), Cr(IV) |  | 44.06  34.8 | 3.52 | 0 | 4.2  77 | Semiconductor, FM below TC = 129K, PM above | [115]  [109] |
| CdCr2S4 | Cr(III), Cr(IV) |  | 46.02  45.97 | 3.80 | 0 | 1.4  4.2 | Insulator, FM below TC = 87K, PM above | [111]  [115] |
| HgCr2Se4 | Cr(III), Cr(IV) |  | 43.07  42.97 | 3.92 | 0 | 1.4  4.2 | Semiconductor, FM below TC = 105K, PM above | [111]  [115] |
| HgCr2S4 | Cr(III), Cr(IV) |  | 45.68 | 3.8 |  | 1.4 | Semiconductor, AFM below TN = 22K, PM above | [111]  [110] |
| Cr0.33NbSe2 (2 inequivalent sites) | Cr(III), Cr(IV)  2.3mB/Cr |  | 49.98  53.44 | 2.48  7.64 |  | 4.2 | Semiconductor, FM below TC = 82K, PM above | [7] |
| Cr0.5NbSe2 | Cr(III), Cr(IV)  1.9mB/Cr |  | 54.31 | 7.64 |  | 4.2 | Semiconductor, AFM below TN = 53K, PM above | [7] |
| Cr0.33NbS2 (2 inequivalent sites) | Cr(III), Cr(IV)  2.82mB/Cr  2.1mB/Cr |  | 65.3-66.6,  49.9-50.2  55.5-56.8  38.3-38.7 | 2.46  2.16  2.46  2.16 |  | 4.2  77 | Semiconductor, FM below TC = 127K, PM above | [116] |
| CrO2 (1 site but 2 frequencies, see text in Section 4.5) | Cr(IV)  1.94mB/Cr |  | 26.5, 37.2  26.3, 37.1  26.4, 37.1  25.3, 36.2  25.3, 35.9 | 1.03 a  1a | 0 | 4.2  6.5  77  77 | Half metal, FM below TC = 395K PM above | [19]  [21]  [17]  [21]  present work |
| Li2CrO4 (dihydrate) | Cr(VI) | −62\*\* |  | 4.00 | 0.30 | 295 | Insulator, diamagnetic | [22] |
| Li2CrO4 (anhydrous) | Cr(VI) | −17\*\* |  | 1.80 | 0.15 | 295 | Insulator, diamagnetic | [22] |
| K2CrO4 | Cr(VI) | −35\*\*  −32\*\* |  | 1.76  1.75 | 0.43  0.40 | 295  295 | Insulator, diamagnetic | [22]  [44] |
| Rb2CrO4 | Cr(VI) | −24\*\* |  | 1.28 | 0.80 | 295 | Insulator, diamagnetic | [22] |
| Cs2CrO4 | Cr(VI) | −19\*\*  −22\*\* |  | 1.23  1.17 | 0.23  0 | 295 | Insulator, diamagnetic | [22]  [44] |
| Ag2CrO4 | Cr(VI) | 188\*\* |  | 4.10 | 0.28 | 295 | Insulator, diamagnetic | [22] |
| (NH4)2CrO4 | Cr(VI) | 0 |  | 3.1 | 0.58 | 295 | Insulator, diamagnetic | present work |
| MgCrO4 (dihydrate) | Cr(VI) | −67\*\* |  | 2.62 | 0.38 | 295 | Insulator, diamagnetic | [22] |
| CaCrO4 | Cr(VI) | −117\*\* |  | 4.55 | 0 | 295 | Insulator, diamagnetic | [22] |
| SrCrO4 | Cr(VI) | -27\*\* |  | 5.0 | 0.68 | 295 | Insulator, diamagnetic | [22] |
| BaCrO4 | Cr(VI) | 0  −47\*\* |  | 4.9  5.00 | 0.16  0.14 | 295  295 | Insulator, diamagnetic | present work  [22] |
| PbCrO4 | Cr(VI) | 68\*\* |  | 4.4 | 0.85 | 295 | Insulator, diamagnetic | [22] |
| Cs2Cr2­O7 | Cr(VI) | −17\*\* |  | 7.25 | 0.30 | 295 | Insulator, diamagnetic | [22] |
| aK2Cr2O7  (2 inequivalent sites) | Cr(VI) | −22\*\*  −67\*\* |  | 7.48  8.28 | 0.30  0.21 | 295 | Insulator, diamagnetic | [22] |

\* shift with respect to saturated aqueous solution of alkali chromate (Na2CrO4 or (NH4)2CrO4)

\*\* originally reported with respect to Cr(CO)6 in chloroform solution (the difference is −1797 ppm, i.e., aq Cr(CO)6 is 0 ppm wrt itself or −1797 ppm wrt aq Na2CrO4)

a no singularities, upper limit estimate of CQ using fwhm of Gaussian peak as D

b extrapolation from field dependent data using g = 2.406 MHz/T

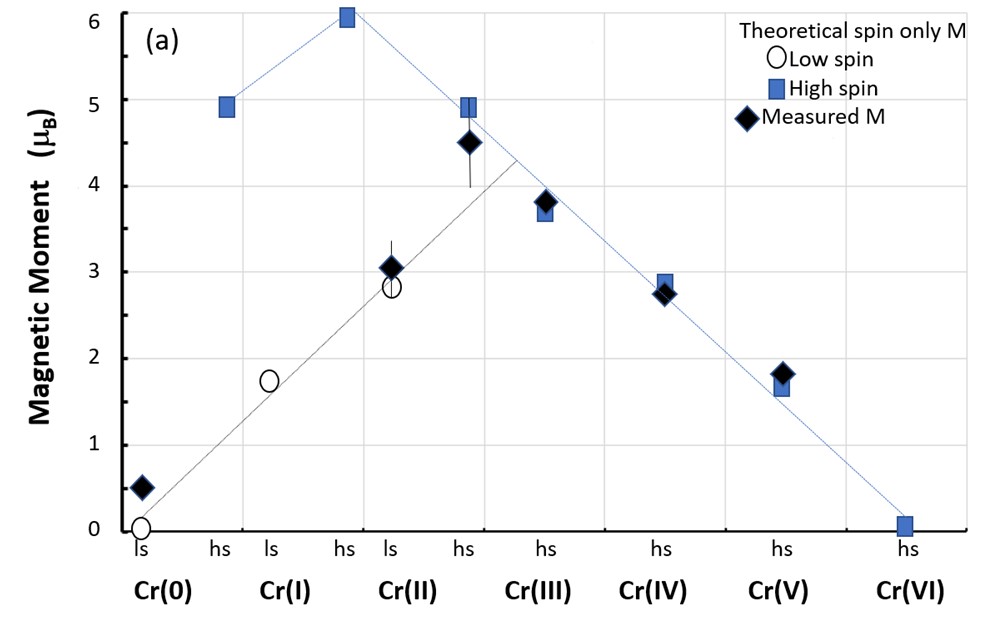
c Ding *et al.* [82] estimate a value for nQ but it appears to be inconsistent with the spectrum.

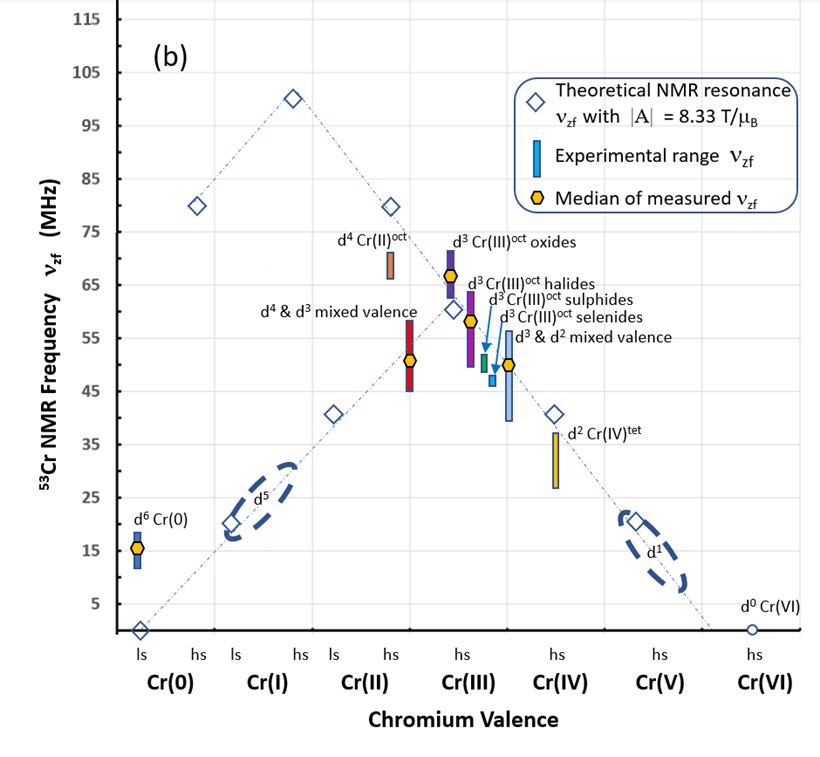
antiferromagnetic=AFM; ferromagnetic=FM; paramagnetic=PM

The reader should consult the references to ascertain XRD structure, phase purity, annealing state, and other experimental factors.

**Table 5**. 53Cr centre-line zero applied field magnetic resonance frequency data nzf(T) modelled using Bloch spin-wave theory.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Compound | Bloch spin wave formulation  nzf = nzf(0) − c(**T/TCrit)3/2** | R2  goodness of fit | Valence | Critical Transition (Néel or Curie) Temperature TCrit (K) | Spin Wave Stiffness D  (meV Å2) | Reference |
| Dy0.2Er0.8CrO3 | nzf = 74.401 − 32.371(**T/TCrit)3/2** | 0.995 | d3 Cr(III) oct | 141 | 34.8 | [71] |
| Cr2O3 | nzf = 70.985 − 27.436(**T/TCrit)3/2** | 0.996 | d3 Cr(III) oct | 308 | 76.3 | present work |
| MnCr2O4 | nzf = 66.657 − 5.198(**T/TCrit)3/2** | 0.990 | d3 Cr(III) oct | 41 | 39.7 | [96] |
| CuCr2O4 | nzf = 63.254 − 8.343(**T/TCrit)3/2** | 0.985 | d3 Cr(III) oct | 135 | 88.7 | [98] |
| CrCl3 | nzf = 63.111 − 39.731(**T/TCrit)3/2** | 0.999 | d3 Cr(III) oct | 16.8 | 4.7 | [2,135] |
| Cr3As2 | nzf = 58.621 − 14.110(**T/TCrit)3/2** | 0.904 | d3 Cr(III) oct | 243 | 164 | [103] |
| CrBr3 | nzf = 58.229 − 20.265(**T/TCrit)3/2** | 0.998 | d3 Cr(III) oct | 37 | 18.4 | [1] |
| NaCrS2 | nzf = 54.072 − 12.092(**T/TCrit)3/2** | 0.988 | d3 Cr(III) oct | 17 | 8.0 | [102] |
| FeCr2S4 | nzf = 51.381 − 14.145(**T/TCrit)3/2** | 0.988 | d3 Cr(III) oct | 180 | 107 | [99] |
| CrI3 | nzf = 49.596 − 15.368(**T/TCrit)3/2** | 0.987 | d3 Cr(III) oct | 68 | 32.5 | [3] |
| ZnCr2Se4 | nzf = 46.657 − 11.115(**T/TCrit)3/2** | 0.988 | d3 Cr(III) oct | 20 | 14.1 | [6] |
| K2Cr8O16  Sites A and B  Site C | nzf = 46.484 − 23.074(**T/TCrit)3/2**  nzf = 42.963 − 21.332(**T/TCrit)3/2** | 0.998  0.998 | mixed valence  d2 Cr(IV) and  d3 Cr(III) | 180 | 142  151 | [19] |
| CdCr2Se4 | nzf = 44.179 − 20.103(**T/TCrit)3/2** | NA | mixed valence  d2 Cr(IV) and d3 Cr(III) | 129 | 65 | [111,115] |
| CuCr2S4 | nzf = 40.188 − 21.756(**T/TCrit)3/2** | 0.997 | mixed valence  d2 Cr(IV) and d3 Cr(III) | 420 | 137 | [87,112] |
| CrO2 nhigh    CrO2 nhigh  nlow | nzf = 37.038 − 8.681(**T/TCrit)3/2**  nzf = 37.068 − 9.882(**T/TCrit)3/2**  nzf = 26.407 − 10.151(**T/TCrit)3/2** | 0.993  0.996  0.982 | d2 Cr(IV) tet | 395 | 127  113  90.4 | [15]  present work  present work |
| Cr3AsN | nzf = 14.504 − 2.397(**T/TCrit)3/2** | 0.992 | d6 Cr(0) low spin | 255 | 410 | [78] |



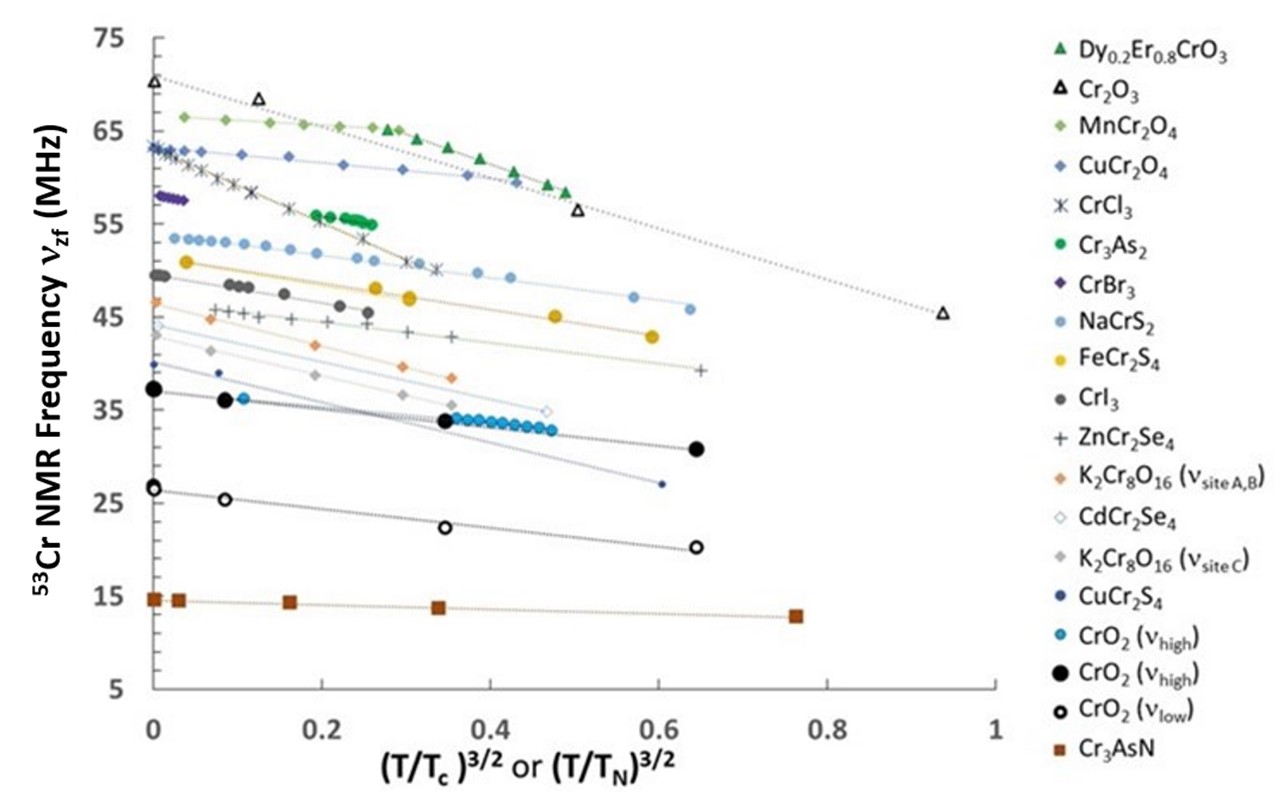


**Figure 7.** (a) Magnetic moment as a function of valence for Cr compounds, and (b) the 53Cr zero applied field magnetic resonance frequency near 0 K as a function of Cr valence.

Hence the internal field data near 0 K can be used to gain knowledge of the local internal field at the 53Cr nucleus in the ground state and can be used to understand the valence state. As discussed in the next section, the temperature dependence of the magnetic resonance central frequency for systems adequately modelled by spin wave theory can also prove useful for understanding magnetic stability.

*4.7.2 Zero applied field NMR as a function of temperature*

As discussed in Section 4.5, the internal field data as a function of temperature well below the critical temperature region (< 0.8TCrit) may be modelled using the Bloch T3/2 relation which is valid for any crystal structure [134]. **Table 5** provides data for Cr compounds (in addition to CrO2 and Cr2O3) where the magnetization (antiferromagnetic, ferromagnetic and ferrimagnetic) can be modelled to a first approximation by Bloch spin wave theory. The magnetic resonance data for these sixteen compounds are summarised in **Figure 8**.



**Figure 8.** Bloch spin wave theory applied to internal field NMR centre-line frequency, nzf, data for sixteen compounds using data adapted from the literature cited in **Table 5**.

Bastow *et al.* [136,137] have shown that experimental Debye-Waller factors for a range of crystalline solids also have a T3/2 dependency attributed to the variation of the mean square amplitude of vibration of atoms in crystals over a temperature range from the Debye temperature to close to the melting point. As the data in **Figure 8** are for crystalline compounds far below their Debye temperature, the T3/2 dependency can be attributed to the fundamental magnetization behaviour described by spin wave theory [11]. The goodness of fit values for these data (**Table 5** and **SI Table S7a**) support further investigation of parameters that can be extracted from the Bloch spin wave relationship for the temperature dependence of the magnetization M at T < TCrit as follows [11,134]:

M(T)/M(0) = 1 – a3/2(T)3/2 (Eq. 8)

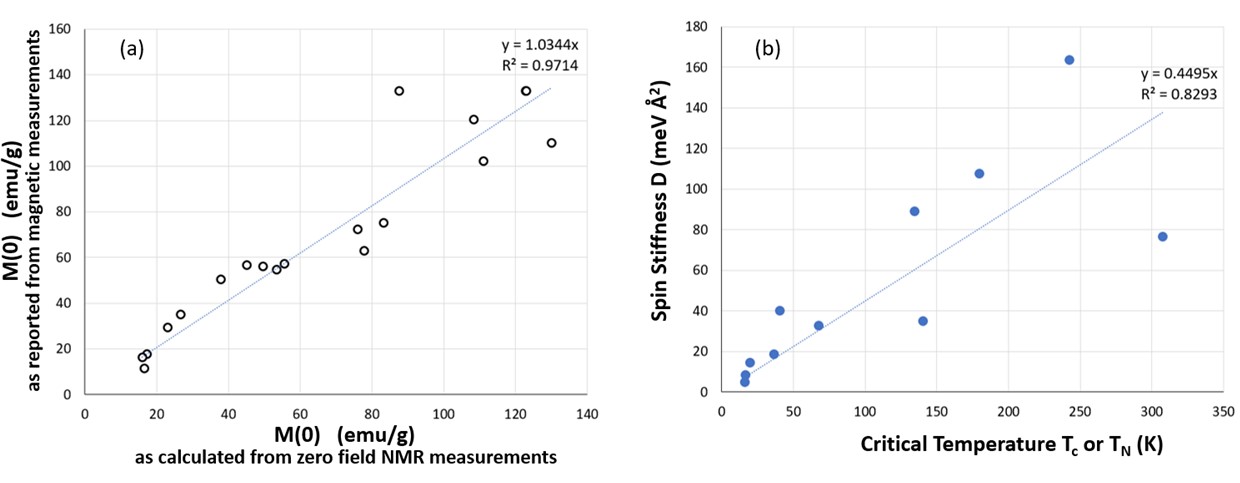
where a3/2 has units of K−3/2 and is related to the spin stiffness in zero field, D, using the relationship [134]:

a3/2 = [2.612(gmB)/(rM(0))][kB/(4pD)]3/2 (Eq. 9)

where g is the dimensionless Lande g factor, r is the density in kg/m3, mB = 9.27x10−24 J/T, kB = 8.617 x 10−5 eV/K, and M(0) is the saturation magnetization at 0 K in J/(Tkg). Rewriting Eq. 8 using the relationship between nzf and M in Eq. 7 and as presented in **Table 5**, gives

nzf(T) = nzf(0) – c(T/Tcrit)3/2  (Eq. 10)

where nzf(0) is related to the electronic and magnetic properties, and the slope, c = a3/2nzf(0)(Tcrit)3/2 with the parameter a3/2 related to the lattice geometry and magnetic exchange interaction. Since the data are well fitted to the Bloch T3/2 relationship, the spin wave excitation gap can be considered negligible [138]. For the sixteen compounds in **Table 5**, values of a3/2, density, and low temperature saturation magnetization are given in [35] and used to calculate spin stiffness D. **Figure 9 (a)** shows that the low temperature saturation magnetization values reported in the literature for these Cr compounds as compared to values calculated from nzf(0) are in very good agreement, in support of the validity of Eq. 7 for these compounds. As shown in **Table 5**, the compound with the highest slope c, CrCl3 has the lowest spin stiffness of 4.7 meV Å2. The compound with the lowest slope c, Cr3AsN has the highest spin stiffness of 410 meV Å2. Only two of the sixteen compounds have published values for D from magnetic measurements or theory, and these are CrI3 D = 27±6 meV Å2 [138], where the error bars of ~20% reflect the population standard deviation for different samples, and CrO2 D = 91 meV Å2 [139]. Both published D values for these ferromagnetic compounds compare well (within ~15%) with the values calculated from the internal field data as shown in **Table 5**. Calculation of D from magnetization data for the antiferromagnetic semiconductor ZnCr2Se4 [140] gives D = 13.7 meV Å2 within 3 % of the value D = 14.1 meV Å2 calculated from the internal field data. Calculation of D from magnetization data for the antiferromagnetic semiconductor Cr2O3 [69] gives D = 61.2 meV Å2 within 20 % of the value D = 76.3 meV Å2 calculated from the internal field data. The D value calculated for Cr3AsN can be compared with D values for other metals. Lowde [141] has published D values for the metallic CrFe system in the range 100-300 meV Å2, and Lewis [142] has reported D = 284±40 meV Å2 for metallic ferrimagnetic Pt3Cr; all values are the same order of magnitude as the value calculated for metallic ferrimagnetic Cr3AsN in **Table 5**, noting that an analysis of published magnetic measurements of Cr3AsN [78] suggests D = 229 meV Å2 which is ~40% lower than the value from internal field magnetic resonance data. Thus, the values of D in **Table 5** appear reasonable for ferro- ferri- and antiferromagnetic chromium compounds, and this tabulation can be useful for comparison with magnetic measurements or density functional approaches to the calculation of spin stiffness in Cr alloys and compounds. **Figure 9 (b)** shows the relationship between spin stiffness and critical transition temperature for the Cr(III) d3oct subset of compounds from **Table 5**. This relationship, D = (0.45 meV Å2/K)TCrit resembles that reported for a family of magnetic cobalt Heusler alloys of D = (0.36 meV Å2/K)TCrit [143]. The relationship between spin stiffness D and Tcrit, for all Cr alloys and compounds from **Table 5**, is D = (0.37 meV Å2/K)TCrit [35].



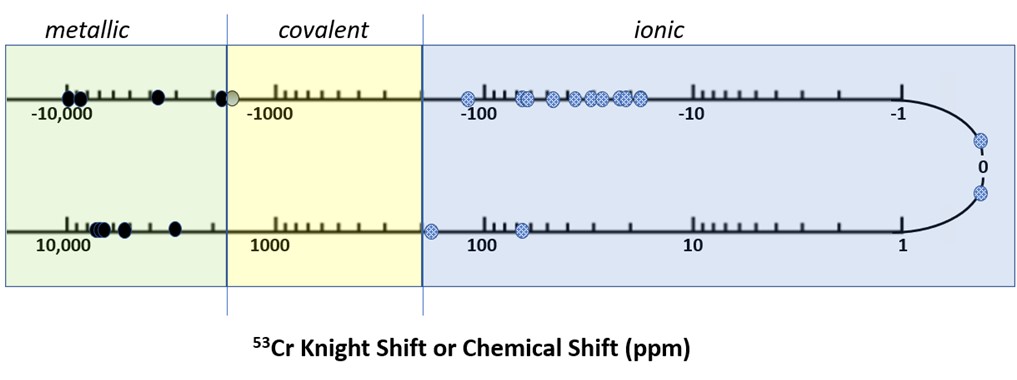
**Figure 9**. (a) Comparison of spontaneous magnetization at low temperature as reported from magnetic measurements and as calculated from internal field magnetic resonance data. (b) Spin stiffness and critical temperature for the d3 Cr(III)oct compounds in Table 5, including ferromagnetic, antiferromagnetic, and ferrimagnetic compounds.

*4.7.3 External field NMR*

The second focus of Section 4.7 is inclusive of non-magnetic Cr compounds. Two recent solid-state NMR reviews have commented on the challenges of recording 53Cr solid-state NMR spectra, citing only three reports on 53Cr NMR of the diamagnetic octahedral Cr(0) d6 compound Cr(CO)6 and diamagnetic tetrahedral Cr(VI) d0 chromates and dichromates [23,24]. The comprehensive up to date summary of magnetic and non-magnetic compounds presented in **Table 4** permits an expanded discussion of the 53Cr solid-state NMR characteristics of interest to experimentalists and theorists. The range of CQ observed for these compounds (Cr(0), Cr(II), Cr(III), Cr(IV), mixed valence, and Cr(VI)) is 0.2 MHz < CQ < 8.28 MHz. The range reported in diamagnetic alkali earth chromate and dichromate compounds alone is 1.28 MHz < CQ < 8.28 MHz [22,44], all with Cr(VI) electron configuration. Some generalizations can be made based on the data in **Table 4** – the Cr compounds with CQ ≤ ~ 1 MHz tend to be semiconductors. Insulating compounds have CQ values ranging from 1.3 to 4.4 MHz. The compounds with CQ > 4 MHz tend to be semiconductors and metals. These observations provide some general guidelines for the likely magnitude of CQ to be found in such materials. These are some of the parameters that could feature in an NMR crystallography approach to detailed local structural characterisation.

As discussed in Section 4.1, DFT calculations of Knight shifts and chemical shifts in transition metal compounds require orbital and spin contributions to accurately reproduce the experimental values. Knight shifts for the 53Cr compounds in **Table 4** range from −9982 to 6990 ppm and can be temperature dependent. As shifts are reported relative to the Cr ion in solution, ionic compounds typically have shifts near 0 ppm, i.e. −100 ppm < d < 100 ppm (see **Figure 10**). As (CO)6 is a strong field ligand, the Cr(0) complex Cr(CO)6 is more shielded (−1814 ppm) than the chromate salts. As bonding covalency increases leading finally to metallic conduction, the shielding also increases and the Fermi contact term dominates the contribution to the shift. As shown in **Table 4**, the present work, to the best of our knowledge, has measured the largest Cr(0) Knight shift (−9982 ppm for CrB2) for any chromium-containing metallic material reported to date. **Figure 10** illustrates the range of chemical and Knight shifts for 53Cr alloys and compounds.

The hyperfine coupling constant A, or the core polarization hyperfine field per unpaired valence electron for the 3d transition metal 53Cr, plays a role in the shielding of the nucleus or the magnetic shift away from the Larmor frequency that can be measured by NMR. The exchange polarization between d electrons on the Fermi surface and s electrons in the core orbitals dominates the Knight shift and leads to the large observed Knights shifts in metallic Cr compounds shown in **Figure 10** [31]. In Section 4.7.1 we have shown that the value of |A| of 8.33 T/mB reasonably describes Cr alloys across the range of crystal structures. Assuming A is independent of temperature, the Knight shift should be proportional to the magnetic susceptibility, such that a large Knight shift is indicative of a large Pauli spin susceptibility χP per Cr atom (Eq. 4). The experimental magnetic susceptibility of CrB2 at room temperature in the paramagnetic state has been reported in a range from 0.485 to 0.795 (10−3 cm3/mol) [144-147]. Using this range for susceptibility and the measured 53Cr Knight shift value of −0.9982 % reported here, the Clogston-Jaccarino [148] analysis can be applied [35], assuming negligible orbital contribution to the Knight shift and negligible transferred hyperfine field, resulting in a range of values for |A| from 7.0 to 11.5 T/mB, in agreement with the treatment presented in Section 4.7.1. *Ab initio* calculation of the magnetic susceptibility for CrB2 metal in the paramagnetic state suggests that the magnetic susceptibility is dominated by the spin contribution, χspin = 0.703 (10−3 cm3/mol) in agreement with experimental results [145]. It can be noted that Laskowski and Blaha [37] have calculated the Knight shift and magnetic susceptibility for Cr metal including orbital and spin contributions, with their theoretical values coming within 10% of the measured values. Our results suggest that theoretical calculation of the Knight shift for CrB2 should be the subject of fruitful future work.



**Figure 10.** Knight shift or chemical shift for 53Cr compounds from Table 4.

*4.7.4 Hyperfine interactions as a guide to the production of novel materials*

A theme of the discussion thus far has been the ability of magnetic resonance to determine parameters that can be useful to check theoretical models and their predictions in magnetic and non-magnetic Cr alloys and compounds. In addition, it is suggested that the hyperfine interactions probed by magnetic resonance are useful guides for the selection and production of novel materials for industrial applications. The multivalent nature of chromium makes for a variety of stable compounds with diverse magnetic properties. The ability to tune and control room temperature accessible magnetic states makes chromium alloys and compounds prime candidates for quantum engineering devices, and NMR adds to the ways these states can be probed. The results presented here have shown a correlation between the critical transition temperature (TC or TN) and the spin stiffness in zero field, D, calculated from magnetic resonance data for Cr alloys and compounds. The local, site specific nature of magnetic resonance as a probe technique means that this approach can be used across a range of valences, including mixed valence, various crystal structures, and ferro-, ferri-, antiferro- magnetic order. D is a measure of the resistance of the spin lattice to thermal disturbance, hence the magnetic resonance parameters enable an indirect test of the robustness of spin polarization in Cr alloys and compounds. The data presented here can also guide the discovery of technologically important ferro-, ferri-, and antiferro- magnetic materials with high critical temperatures and stable properties given the correlations that have been developed here. A number of approximations are involved in the treatment of these compounds using Bloch spin wave theory including (i) dominance of spin rather than spin orbital contributions, (ii) same treatment for all crystal and magnetic structures, (iii) temperature independent and valence independent hyperfine coupling constant, (iv) an isotropic Fermi contact interaction, and (v) a dominant core polarisation contribution to the hyperfine field, such that the treatment points to some key features as drivers of behaviour in these systems. With the accumulation of experimental data for training sets, it is hoped that these key features will be able to be investigated using machine learning. Extending this approach, one might speculate what local site properties at chromium could be related directly to the macroscopic properties needed, such as the size of the efg as a characteristic of the local site distortion and the impact on quantum switching. In low-dimensional spin systems hyperfine fields contribute to decoherence in the system leading to limitation in the performance of potential quantum devices [125].

*5. Summary*

This study encompassing new experimental observations and a comprehensive survey of magnetic resonance parameters collected on 53Cr shows it can be quite a receptive nucleus for NMR with an external field or zero field. Therefore 53Cr NMR can be used to characterize a range of important materials including metals, half metals, insulators, semiconductors, ferromagnetic, antiferromagnetic, and diamagnetic materials. The 53Cr solid-state NMR work to date of relevance to the new observations here has been summarised and put into context. The work presented here has established quadrupolar coupling constants and chemical/Knight shifts for the first time for several important compounds. The T3/2 behaviour of the sublattice magnetization of CrO2 and Cr2O3 measured via 53Cr zero applied field NMR are reported here over a wide temperature range from liquid He temperature to room temperature. The large negative Knight shift of 53Cr in the transition metal intermetallic CrB2 has been measured. Unexplained lineshapes have been reported here for high purity Cr2O3, and these should be the subject of future verification and elucidation. Also, as in the case of AlN, it may take careful single crystal work or enriched specimens or both to pinpoint singularities and CQ values in some of the Cr compounds discussed here where only an upper limit on CQ could be estimated.

The first comprehensive summary of 53Cr NMR interaction parameters for chromium compounds reported from 1961 to 2022 has been tabulated. Here is shown how low temperature internal field central frequencies have been correlated with valence state, and spin stiffness has been calculated for sixteen chromium compounds. The local information provided from 53Cr NMR complements bulk measurements. Therefore, such NMR data can help determine whether new materials show promising characteristics, and if one could go further and relate these characteristics directly to site parameters (e.g. shift, anisotropy, efg) then one could have a direct measure of desirable properties. Additional theoretical and computational studies have been suggested based on current gaps in the data for 53Cr NMR parameters. Knowledge of these parameters will enable further progress in understanding and capturing the benefits from electronic and magnetic structure-property-function relationships in Cr compounds.

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**Author Contributions**

TJB devised the experimental plan, contributed the overall supervision of this work, and performed NMR measurements, data analysis, and co-wrote the manuscript. AJH assisted in data collection and analysis and co-wrote the manuscript. KMN and MES assisted in data analysis and editing of the manuscript.

**Competing interests statement:** The authors declare no competing interests.

See Supplemental Material at [35] <http://link.aps.org/supplemental>... for NMR probe, XRD spectra, SEM image, DSC scans, internal field NMR data, mixed valence data, spin stiffness data, and Clogston-Jaccarino analysis. URL will be inserted by publisher.

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**Supporting Information**

**53Cr Solid-State Nuclear Magnetic Resonance: New Observations and Comprehensive Correlations as a Probe of Valence and Magnetic States**

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**Contents**

1. Figure S1 Internal field NMR probe used in this study

2. Figure S2 XRD spectrum of Cr2N

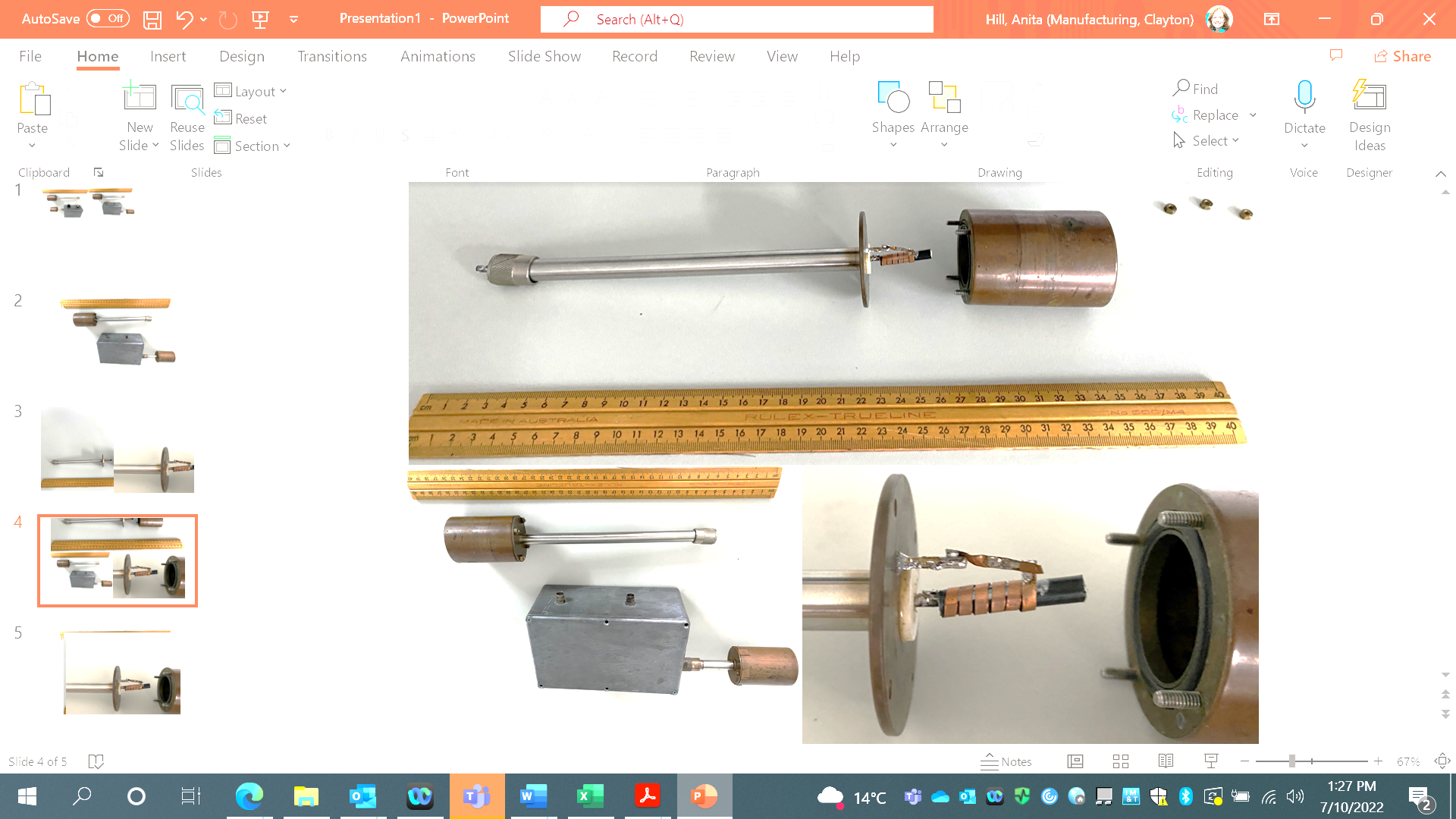
3. Figure S3 XRD spectrum of CrB2

4. CrO2: Figure S4a SEM micrograph of CrO2 powder, Figure S4b XRD spectrum of CrO2 and Figure S4c comparison of 53Cr internal field NMR frequency, νzf, values from Figure 4 (main text) and magnetization as function of temperature.

5. Cr2O3: Figure S5a XRD spectrum of Cr2O3, Figure S5b DSC thermograms for two separate samples and Figure S5c comparison of 53Cr internal field frequency, νzf, values from Figure 4 (main text) and magnetization as function of temperature.

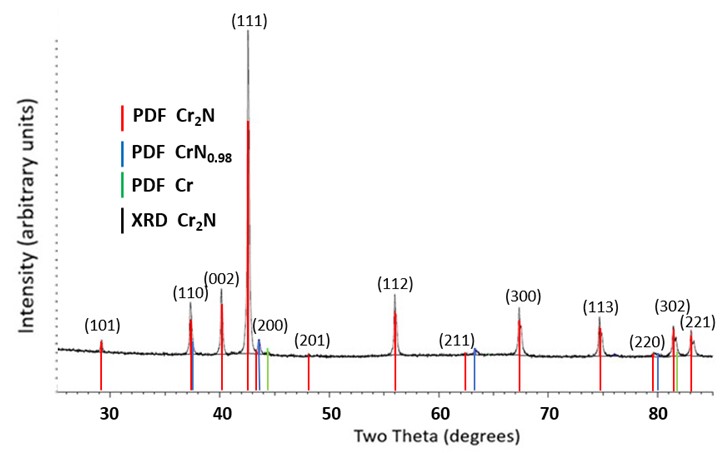
6. Figure S6a. Trends (dotted lines) for two values of the hyperfine coupling constant |A| for 53Cr for different valence. Figure S6b Copy of Figure 7 (main text) (left) with expanded area (right) showing 53Cr internal field frequency range, νzf, reported for Cr3+ and Cr4+ and mixed valence chromium oxides.

7. Table S7a Internal field NMR data and fits in the form νzf(T) = νzf(0)[1 – a3/2(T)3/2]. Table S7b Values of a3/2 calculated from internal field NMR data of Table 5 (main text) where a3/2 = c/( νzf(0)(Tcrit)3/2), values of density r and saturation magnetization M(0) from literature reports, used to calculate the spin stiffness parameter D in Table 5 (main text). Figure S7a Values of spin stiffness D and Tcrit for all Cr compounds in Table 5. Figure S7b 53Cr Knight shift versus magnetic susceptibility for CrB2 showing the Clogston-Jaccarino analysis.



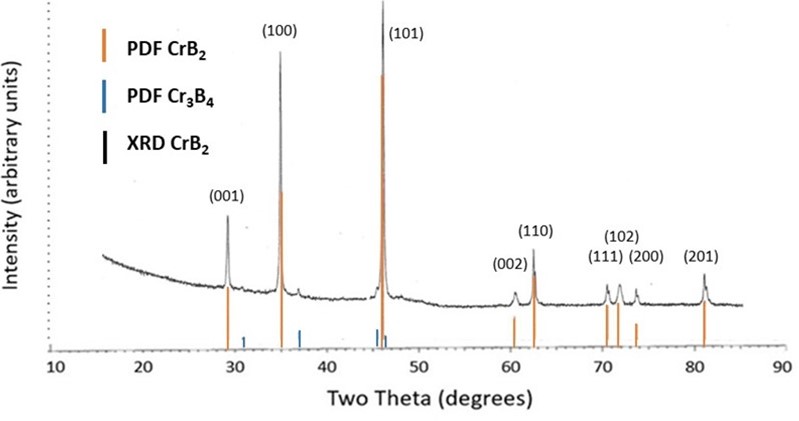
**Figure S1**. Top: 8 cm long cylindrical copper pot, detached from transmission line to show sample and enamelled wire wound coil. Bottom (left): copper pot and transmission line attached to a home-built matching circuit. Bottom (right): close up of sample and enamelled wire wound coil.

S2 Cr2N powder sample

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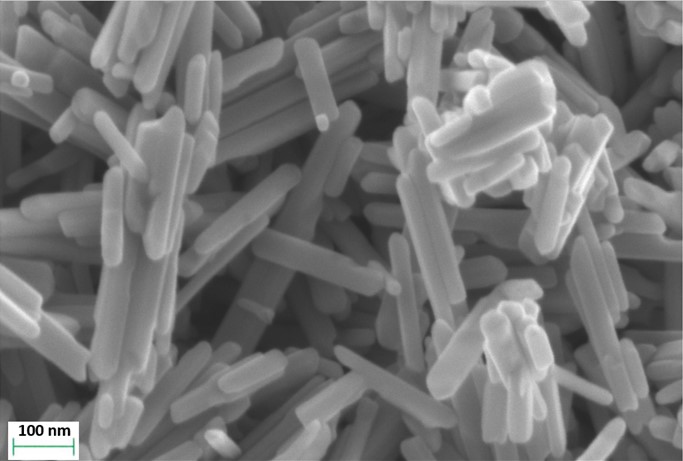
**Figure S2**. XRD spectrum of Cr2N including powder diffraction file (PDF) peak positions. The Cr2N diffraction peaks are indexed.

S3 CrB2 powder sample

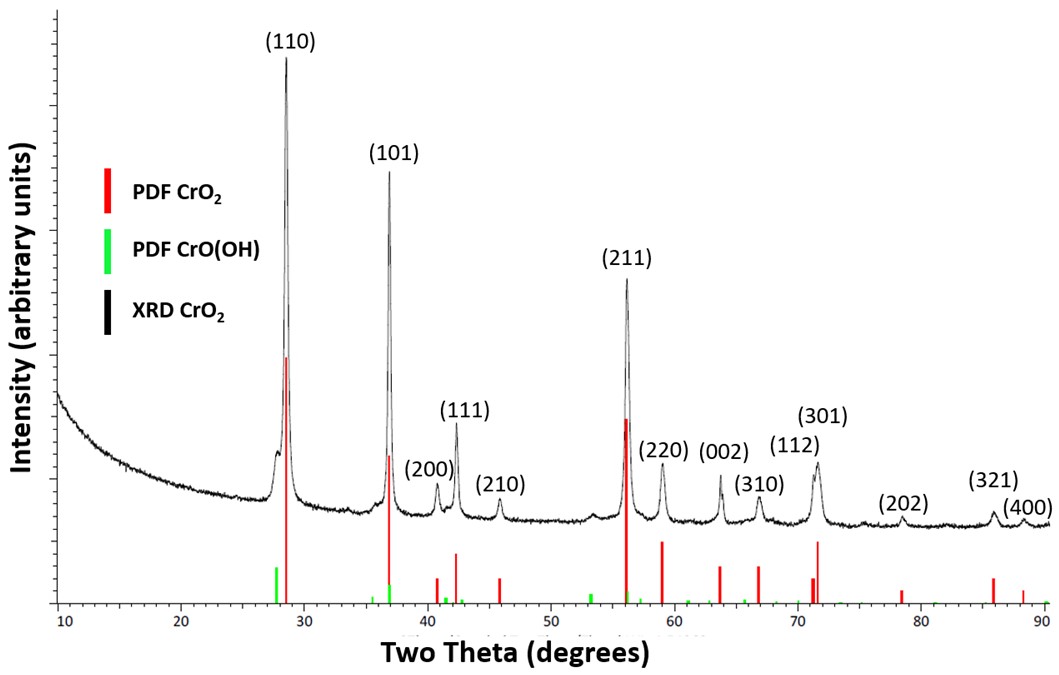


**Figure S3**. XRD spectrum of CrB2 including powder diffraction file (PDF) peak positions. The CrB2 diffraction peaks are indexed.

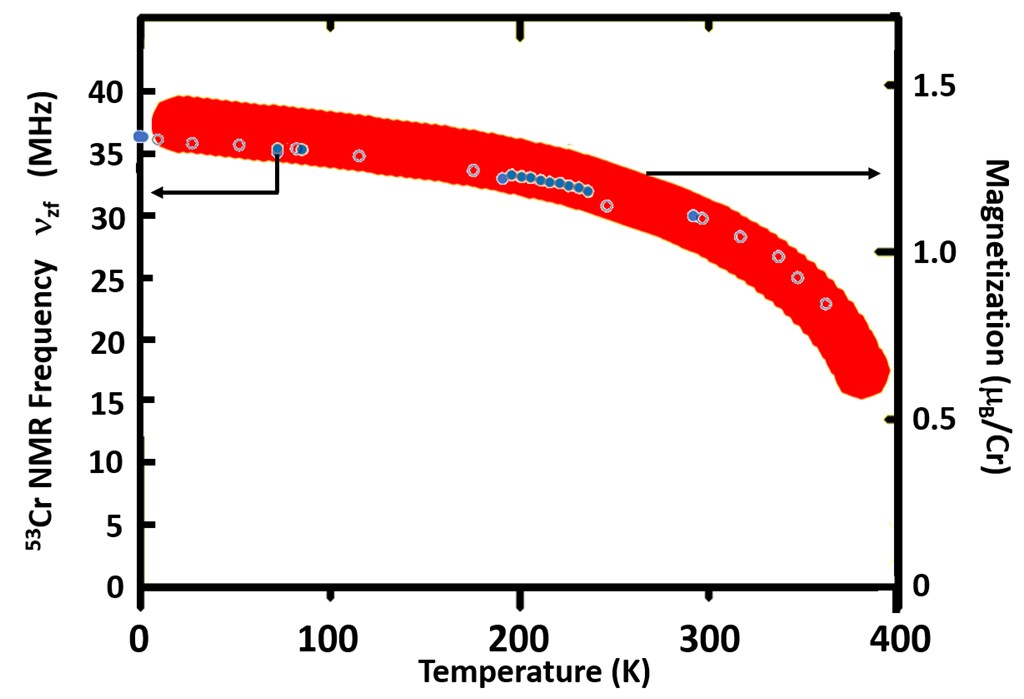
S4 CrO2 powder sample



**Figure S4a.** SEM micrograph of CrO2 powder.

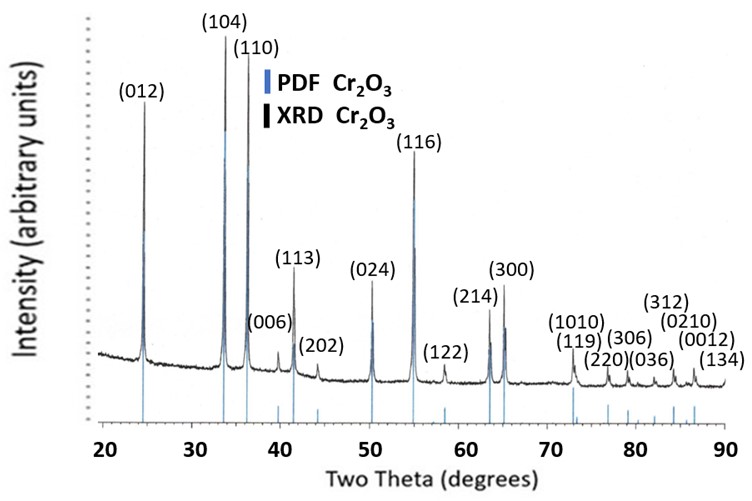


**Figure S4b.** XRD spectrum of CrO2 including powder diffraction file (PDF) peak positions. The CrO2 diffraction peaks are indexed.

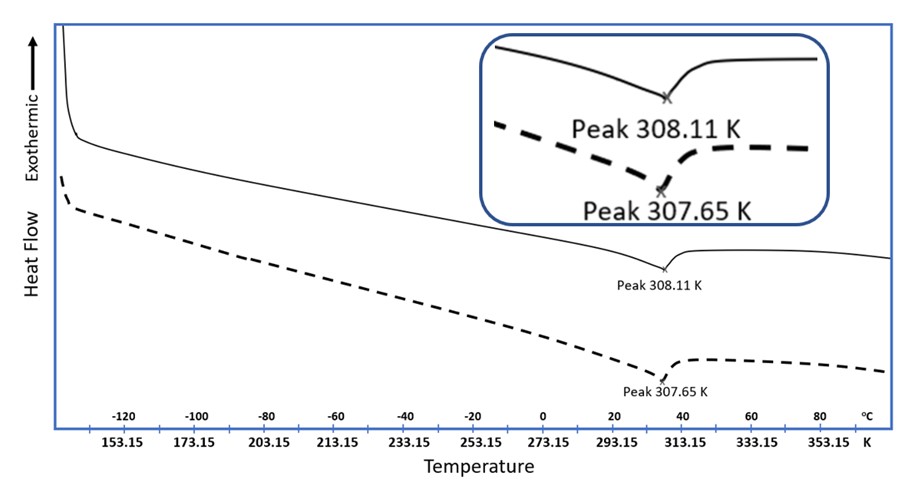


**Figure S4c**. Comparison of 53Cr internal field NMR frequency, nhigh, values from Figure 4 (main text), closed circles, for present work and Yasuoka *et al.* [1963], and from Piskunov *et al.* [2022], open circles, and magnetization at 0.2 T, octagons (10 – 380 K), (adapted from Shim *et al.* [2007]) for CrO2 as functions of temperature. Piskunov *et al.* suggest that data up to approximately 300 K (or ~0.76TC) can be fitted with a T3/2 dependence, their data for nhigh decrease by ~20% (from 37.1 MHz to 30.5 MHz) up to 300 K and fit well with the T3/2 dependence from Figure 4 (main text). The fit to spin wave theory T3/2 for their results from 4.2 to 300K gives a best fit, y = −0.0013x + 37.089 (R2 = 0.9863). The data of Piskunov *et al.* deviate from the T3/2 relationship at ~ 350 K, similar to the magnetization data, which may indicate a first order transition at 395K; however, to date there has been no report of 53Cr NMR data up to TC for CrO2.

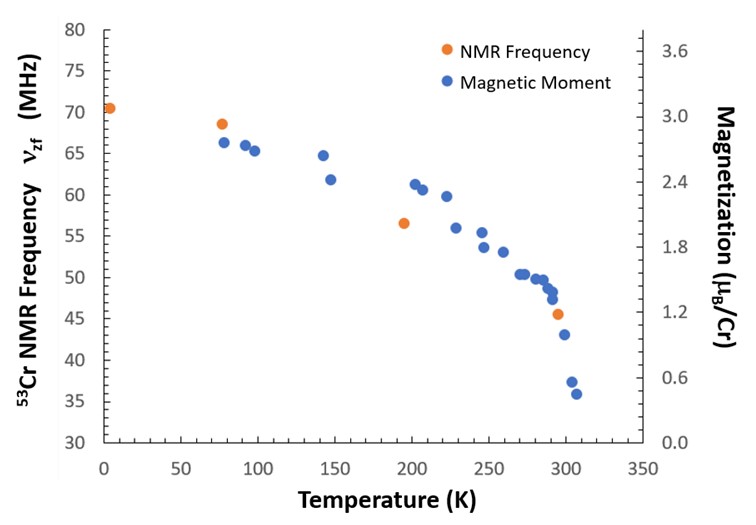
S5 Cr2O3 powder sample



**Figure S5a**. XRD spectrum of Cr2O3 including powder diffraction file (PDF) peak positions.

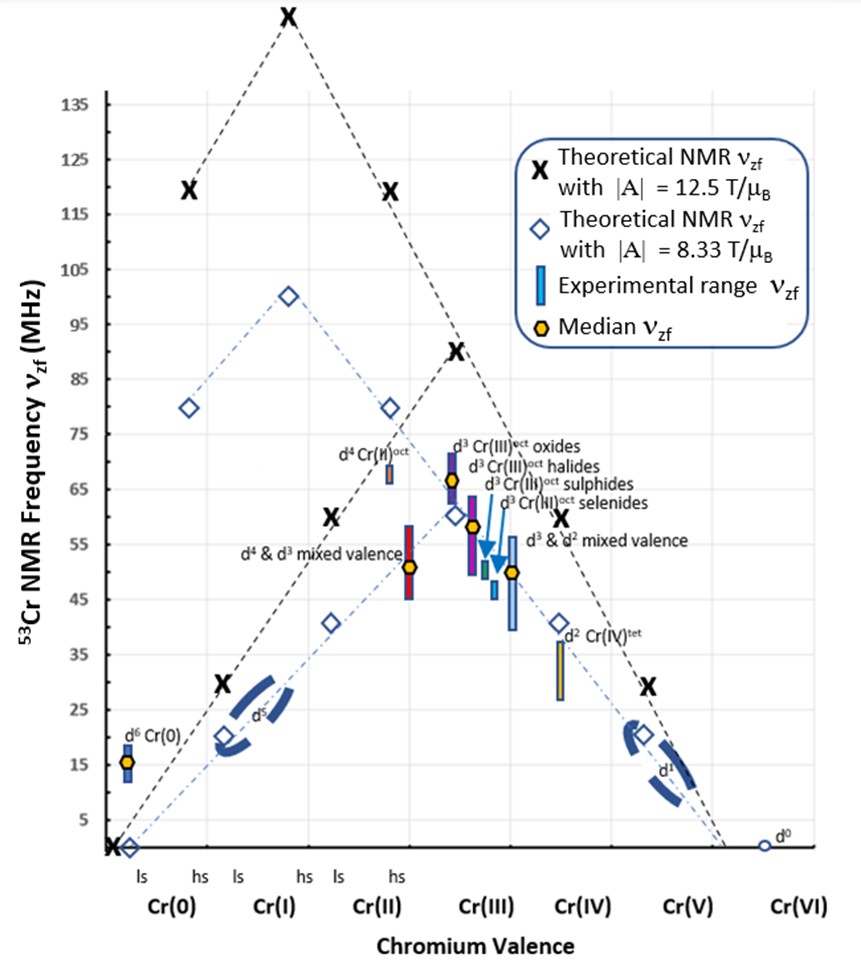


**Figure S5b**. DSC thermograms for two separate samples of Cr2O3 during heating showing TN. Inset is a magnification of TN.

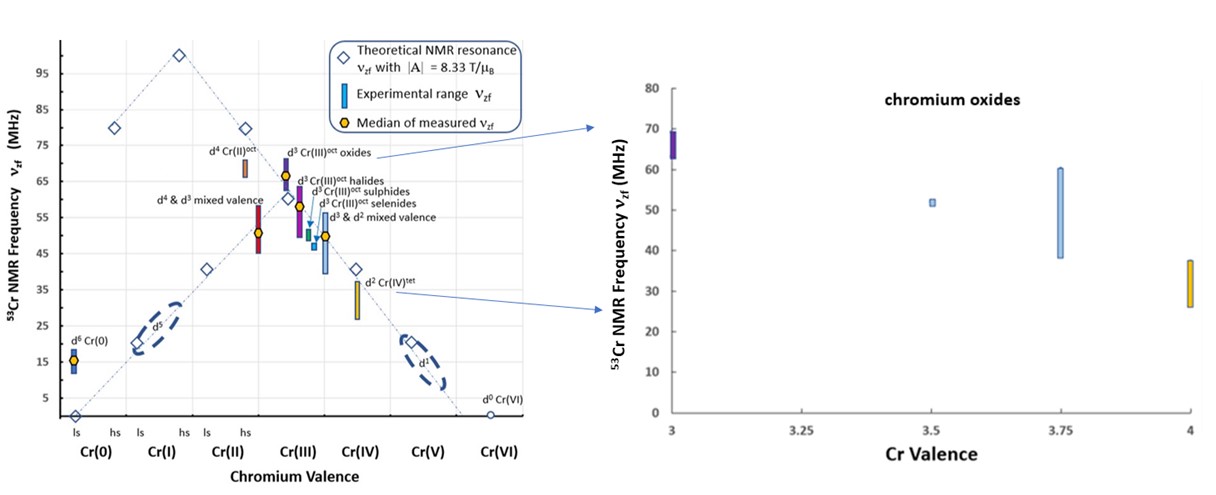
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**Figure S5c**. Comparison of 53Cr internal field frequency, nzf, values from Figure 4 (main text) and magnetization (adapted from [Corliss 1964]) for Cr2O3 as functions of temperature.

S6 53Cr internal field frequency – valence relationship



**Figure S6a**. Copy of Figure 7 from main text including trends (dotted lines) for two values of the hyperfine coupling constant |A| for 53Cr.

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**Figure S6b**. Copy of Figure 7 from main text (left) with expanded area (right) showing 53Cr internal field frequency range, nzf, reported for Cr3+ and Cr4+ and mixed valence chromium oxides.

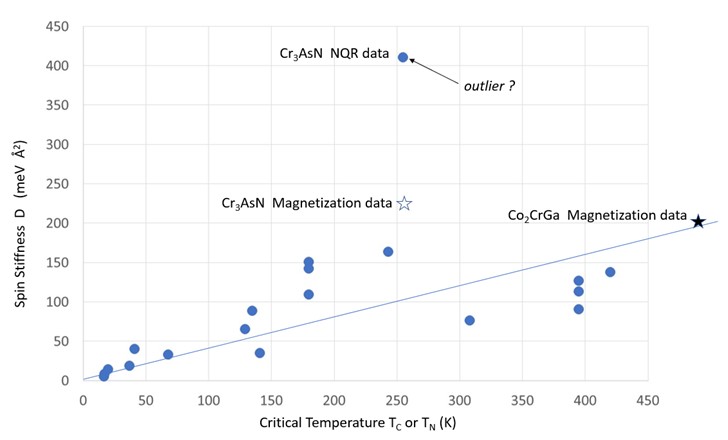
S7 Spin Wave Analysis of 53Cr internal field NMR Data

**Table S7a**. Internal field NMR data and fits in the form nzf(T) = nzf(0)[1 – a3/2(T)3/2]

|  |  |  |  |
| --- | --- | --- | --- |
| Compound | Bloch spin wave formulation  nzf = nzf(0) - nzf (0)a3/2(**T)3/2** | R2  goodness  of fit | a3/2  (x10-3 K-3/2) |
| Dy0.2Er0.8CrO3 | nzf = 74.401 - 0.0193(**T)3/2** | 0.995 | 0.2594 |
| Cr2O3 | nzf = 70.985 - 0.0051(**T)3/2** | 0.996 | 0.0718 |
| MnCr2O4 | nzf = 66.657 - 0.0198(**T)3/2** | 0.990 | 0.2970 |
| CuCr2O4 | nzf = 63.254 - 0.0053(**T)3/2** | 0.985 | 0.0838 |
| CrCl3 | nzf = 63.111 - 0.5770(**T)3/2** | 0.999 | 9.1426 |
| Cr3As2 | nzf = 58.621 - 0.0037(**T)3/2** | 0.904 | 0.0631 |
| CrBr3 | nzf = 58.229 - 0.0900(**T)3/2** | 0.998 | 1.5456 |
| NaCrS2 | nzf = 54.072 - 0.1717(**T)3/2** | 0.988 | 3.1754 |
| FeCr2S4 | nzf = 51.381 - 0.0064(**T)3/2** | 0.988 | 0.1114 |
| CrI3 | nzf = 49.596 - 0.0274(**T)3/2** | 0.987 | 0.5524 |
| ZnCr2Se4 | nzf = 46.657 - 0.1243(**T)3/2** | 0.988 | 2.6641 |
| K2Cr8O16  Sites A and B  Site C | nzf = 46.484 - 0.0096(**T)3/2**  nzf = 42.963 - 0.0088(**T)3/2** | 0.998  0.998 | 0.2065  0.2048 |
| CdCr2Se4 | nzf = 44.179 - 0.0139(**T)3/2** | NA | 0.3146 |
| CuCr2S4 | nzf = 40.188 - 0.0025(**T)3/2** | 0.997 | 0.0622 |
| CrO2 nhigh    CrO2 nhigh  nlow | nzf = 37.038 - 0.0011(**T)3/2**  nzf = 37.068 - 0.0013(**T)3/2**  nzf = 26.407 - 0.0013(**T)3/2** | 0.993  0.996  0.982 | 0.0297  0.0351  0.0492 |
| Cr3AsN | nzf = 14.504 - 0.0006(**T)3/2** | 0.992 | 0.0414 |

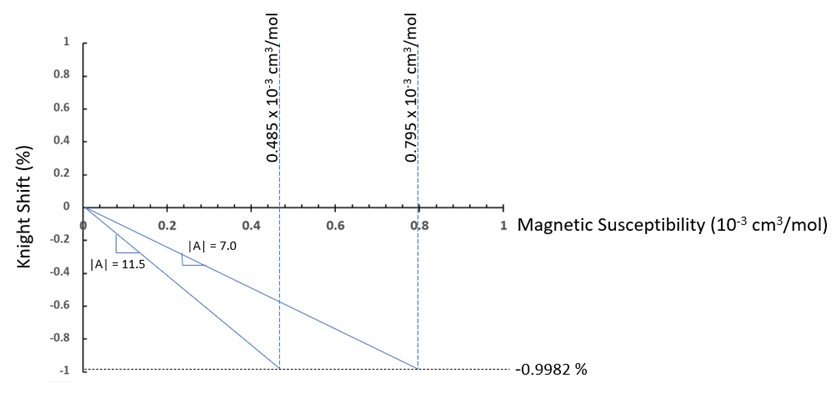
**Table S7b**. Values of a3/2 calculated from internal field NMR data of Table 5 (main text) where a3/2 = c/(nzf(0)(Tcrit)3/2), values of density r and saturation magnetization M(0) from literature reports, used to calculate the spin stiffness parameter D in Table 5 (main text).

|  |  |  |  |
| --- | --- | --- | --- |
| **Compound** | **Bloch Spin Wave Coefficient a3/2**  **(x10−3 K-3/2)** | **Density r**  **(kg/m3)** | **Saturation Magnetization M(0)**  **(emu/g)** |
| Dy0.2Er0.8CrO3 | 0.259405 | 8198 | 62.9 |
| Cr2O3 | 0.071846 | 5210 | 110 |
| MnCr2O4 | 0.297043 | 4930 | 75.2 |
| CuCr2O4 | 0.083789 | 5430 | 72.4 |
| CrCl3 | 9.142622 | 2870 | 102 |
| Cr3As2 | 0.063117 | 3804 | 54.8 |
| CrBr3 | 1.545622 | 3940 | 57.2 |
| NaCrS2 | 3.175396 | 3180 | 120 |
| FeCr2S4 | 0.111400 | 3854 | 56.2 |
| CrI3 | 0.552464 | 4740 | 56.6 |
| ZnCr2Se4 | 2.664123 | 5550 | 35.0 |
| K2Cr8O16  Sites A and B  Site C | 0.206523  0.204827 | 4450  4450 | 17.6  16.3 |
| CdCr2Se4 | 0.314629 | 5680 | 29.4 |
| CuCr2S4 | 0.062207 | 5440 | 50.4 |
| CrO2 nhigh  CrO2 nhigh  nlow | 0.029699  0.035071  0.049229 | 4890  4890  4890 | 133  133  133 |
| Cr3AsN | 0.041368 | 7015 | 11.4 |



**Cr3AsN internal field data**

**Figure S7a**. Values of spin stiffness D and Tcrit for all Cr compounds in Table 5 (main text). The star symbols are for D values from magnetization measurements [Waki 2017, Umetsu 2011]. The solid line is the best fit from Figure 9 (b) for the Cr(III)oct d3 subset of Cr compounds. If the outlier (Cr3AsN) is removed, the best fit equation is D = (0.37 meV Å2/K)TCrit with R2 = 0.8181 for all Cr compounds in Table 5 (main text).



**Figure S7b**. Illustration of the Clogston-Jaccarino [1961] analysis, with negligible orbital contribution to the 53Cr Knight shift, to extract a range of values for |A| from the range of reported magnetic susceptibility values for CrB2 with the measured value for the 53Cr Knight shift, using the relationship in Eq. 4 (main text).

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Clogston AM, Jaccarino V. Susceptibilities and negative Knight shifts of intermetallic compounds. Phys Rev. 1961; 121(5): 1357-1362.