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Magnetic properties of $Pr_2Co_{17-x}Al_x$ and $Y_2Co_{17-x}Al_x$

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Abstract

The magnetic properties of $Pr_2Co_{17-x}Al_x$ and $Y_2Co_{17-x}Al_x$ compounds with $0 \leq x \leq 4$ were studied by means of magnetic measurements. These measurements have shown that increasing Al concentration leads to a sign reversal of the magnetocrystalline Co-sublattice anisotropy from easy-plane anisotropy for low Al concentration to easy-axis anisotropy for higher Al concentration. In the $Pr_2Co_{17-x}Al_x$ compounds, the competition between the Pr- and Co-sublattice anisotropies leads to spin-reorientation transitions at temperatures that decrease strongly with increasing Al concentration. There is an almost linear decrease of the Curie temperature with Al concentration. Also the saturation moments at 5 K decrease strongly with Al concentration although this decrease is less strong in $Pr_2Co_{17-x}Al_x$ than in $Y_2Co_{17-x}Al_x$. © 1997 Elsevier Science S.A.

Keywords: Co-rich rare earth compounds; $R_2Co_{17-x}Al_x$; Magnetic properties; Spin reorientation transitions

1. Introduction

The intermetallic compounds of the type R_2T_{17} formed between rare-earth metals (R) and 3*d* transition metals (T) are of substantial technological and fundamental interest [1,2]. The R_2Fe_{17} compounds have the remarkable property that substitution of non-magnetic Al for Fe leads to initially strong increases in the magnetic ordering temperature [3]. Equally surprising is the behaviour of the Co compounds in which the substitution of non-magnetic Al for Co leads to a change in the character of the Co-sublattice anisotropy. Recent studies have shown that particularly interesting phenomena are observed in R_2Co_{17} compounds in which there is a competition between the R- and Co-sublattice anisotropies [4,5]. In the present study, we have extended this investigation to $Pr_2Co_{17-x}Al_x$ compounds because it can be expected that the uniaxial character is particularly strong for the Pr sublattice. In this investigation, we have included also $Y_2Co_{17-x}Al_x$ compounds in order to study the concentration dependence of the Co-sublattice anisotropy.

2. Experimental

$Y_2Co_{17-x}Al_x$ compounds with $x=2$, 3 and 4 and $Pr_2Co_{17-x}Al_x$ compounds with $x=1$, 1.5, 2, 3 and 4 were prepared by arc melting starting materials of at least 99.9% purity. Subsequently, the ingots were sealed into an evacuated quartz tube and annealed for three weeks at 900 °C. The X-ray diffraction diagrams showed that the annealed samples are all single phase and that their crystal structure corresponds to the rhombohedral Th_2Zn_{17}-structure type. No single-phase samples could be obtained for Al concentrations exceeding $x=4$.

The magnetic measurements were made on a SQUID magnetometer in the temperature range 5–300 K in magnetic fields up to 5 T. Measurements above 300 T were made on a home-built magnetometer based on the Faraday principle, using polycrystalline bulk samples in order to avoid oxidation at elevated temperatures as far as possible.

3. Results

X-ray diffraction studies, made on magnetically aligned $Y_2Co_{17-x}Al_x$ samples with $x=2$, 3 and 4, showed the easy magnetization direction at room temperature corresponds

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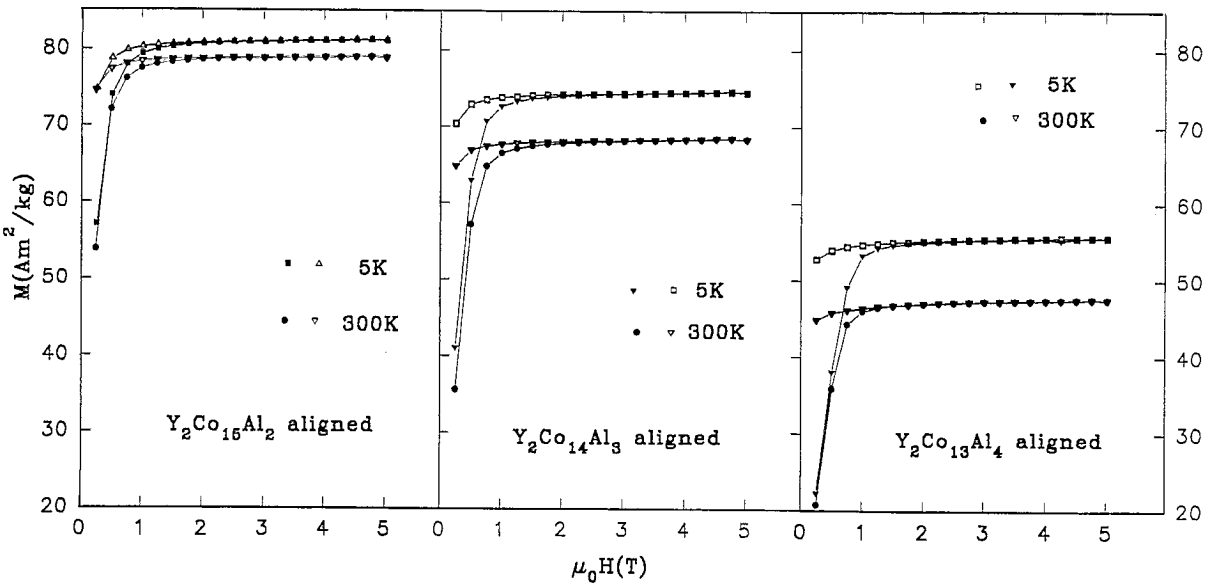

Fig. 1. Field dependence of the magnetization at 5 K and 300 K, measured on magnetically aligned $Y_2Co_{17-x}Al_x$ samples with the field applied parallel (open symbols) and perpendicular (full symbols) to the alignment direction.

to the c axis in these compounds. In order to study the changes of the magnetic anisotropy as a function of Al concentration, we have measured the field dependence of the magnetization on these samples after aligning the powder particles at room temperature. Results obtained at 5 K and room temperature with the field applied parallel and perpendicular to the alignment direction are shown in Fig. 1. These results show that the anisotropy field increases remarkably with increasing Al concentration.

As an example of the results of magnetic measurements made on the $Pr_2Co_{17-x}Al_x$ compounds, we show in Fig. 2 the temperature dependence of the magnetization for the compounds with $x=1$, 2 and 4. It follows from these results that the Curie temperature is above room temperature for all three compounds and that it decreases with

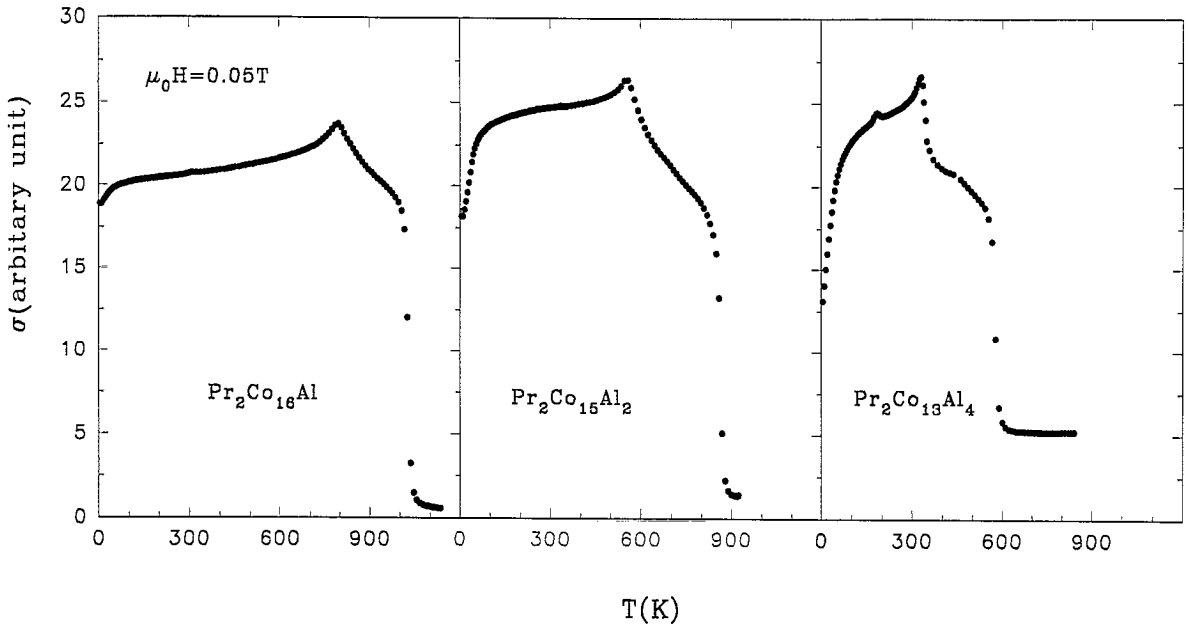

Fig. 2. Temperature dependence of the magnetization of various $Pr_2Co_{17-x}Al_x$ compounds measured in a field of 0.05 T.

increasing Al concentration. The sharp cusp seen in the M(T) curves below the Curie temperature is indicative of the occurrence of a spin-reorientation transition. X-ray diffraction measurements were made on the sample with x=4 after magnetic alignment of the powder particles at room temperature. From these measurements, which were performed at a temperature just below the spin reorientation temperature, it is derived that the easy magnetization direction is perpendicular to the c axis. For this compound, there is a second, much smaller cusp at much lower temperatures which is not observed for the other compounds. This cusp is ascribed to a very small amount of $Pr(Co,Al)_5$, present in this compound because the x=4 composition may exceed the solid-solution limit of Al in the 2:17 phase. The presence of a small amount of $Pr(Co,Al)_5$ in the $Pr_2Co_{17-x}Al_x$ sample with x=4 has been confirmed also by X-ray diffraction. The concentration dependence of the spin-reorientation temperatures and the Curie temperatures is shown in Fig. 4. The concentration dependence of the magnetic moments at 5 K, derived from the data shown in Figs. 1 and 4, is displayed in Fig. 5.

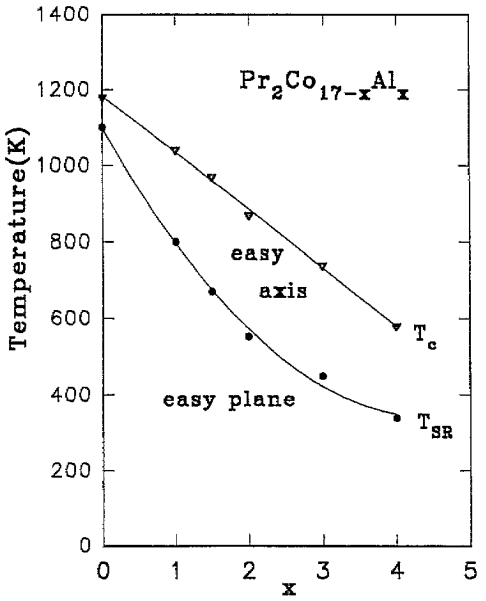

Fig. 4. Field dependence of the magnetic moment of the $Pr_2C_{17-x}Al_x$ compounds measured at 5 K with decreasing field.

4. Discussion

The Curie temperature is seen in Fig. 3 to decrease almost linearly with the Al concentration. This behaviour is in strong contrast with that observed in various $R_2Fe_{17-x}Al_x$ compounds where the Curie temperature first strongly increases with x before decreasing at higher x values (x>4). This difference in behaviour is probably associated with the fact that the magnetic coupling between the Co moments in metal systems is always ferromagnetic, independent of the Co moment and structure. Hence, antiferromagnetic types of 3d-moment interactions that could reduce the Curie temperature are absent. The latter feature is frequently involved to explain the abnor-

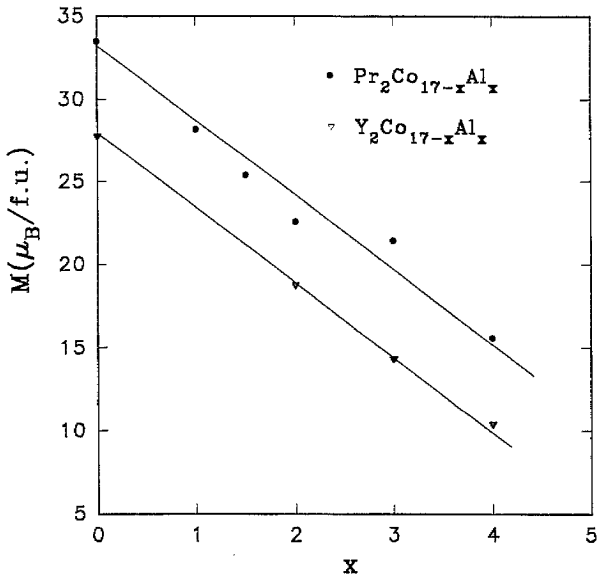

Fig. 3. Concentration dependence of the Curie temperature and spin-reorientation temperature of $Pr_2Co_{17-x}Al_x$ compounds. The open triangles represent the Curie temperatures and the filled circles the spin-reorientation temperatures.

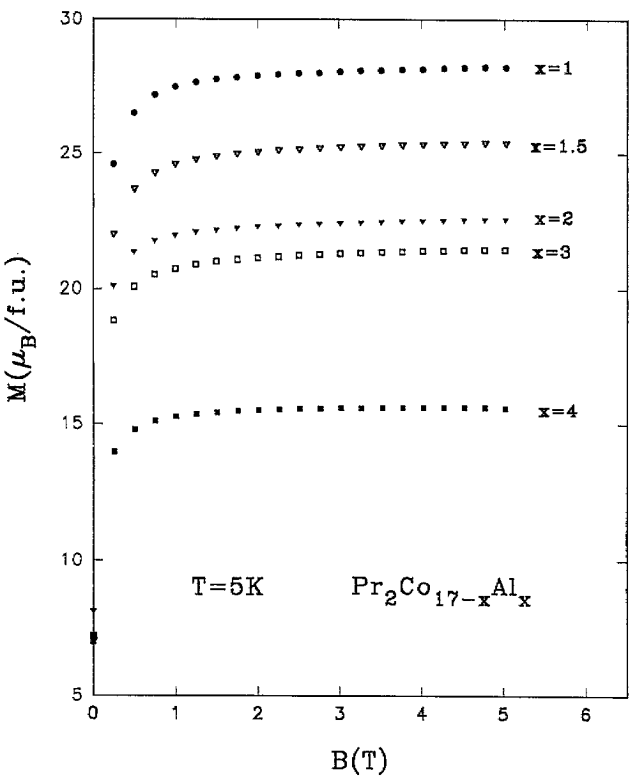

Fig. 5. Concentration dependence of the saturation moment in $Y_2Co_{17-x}Al_x$ and $Pr_2Co_{17-x}Al_x$ compounds. The lines are guides for the eye.

mally low Curie temperature of R_2Fe_{17} compounds and their enhancement by Al substitution.

One of the characteristic features of the crystal structure of R–Co compounds of the type R_2Co_{17} is the presence of the so-called dumb-bell pairs of Co atoms. These Co atoms occupy the crystallographic 6*c* position. Apparently, these Co atoms have an important effect on the magneto-crystalline anisotropy in this class of materials, as may be derived from investigations by Yajima and Hamano [6] and Desportes et al. [7]. These authors showed that the presence of the dumb-bell atoms is most likely responsible for the easy-plane anisotropy of the Co sublattice in the R_2Co_{17} compounds, where the Co dumb-bell atoms are absent.

The refinement results of the neutron-powder-diffraction patterns obtained recently on the isotypic compound series $Nd_2Co_{17-x}Al_x$ have shown that the preference for the Al atoms to occupy one of the four available Co sites in the rhombohedral Th_2Zn_{17} structure decreases in the sequence $18h > 6c > 18f > 9d$. In fact, the 9*d* site is completely avoided by the Al atoms. It can be derived from our results on compounds of the $Y_2Co_{17-x}Al_x$ series, that an easy-axis room-temperature anisotropy is found for $2 \leq x \leq 4$. Apparently, the effect of the 6*c*-site substitution overcompensates the effect on the Co-sublattice of the Al atoms that partially occupy the other sites, opening the possibility that the Co-sublattice anisotropy becomes of easy-axis type at sufficiently high Al concentrations.

The results obtained on the $Y_2Co_{17-x}Al_x$ compounds mean that the Co sublattice has a positive anisotropy constant K_1^{Co} in the very concentration range where we have observed spin-reorientation transitions in the $Pr_2Co_{17-x}Al_x$ series. The occurrence of these latter transitions can be explained when considering the anisotropy constant of the total lattice, being the sum of the Co sublattice and the R sublattice.

$$K_1^{tot} = K_1^{Co} + K_1^{R} = K_1^{Co} - 3/2\alpha_j < r^2 > < O_2^0 > A_2^0 \quad (1)$$

The anisotropy of the R sublattice is crystal-field induced, and in lowest-order approximation it can be given by the last term of Eq. (1), where the second-order crystal-field parameter A_2^0 depends on the crystal structure and the composition of a given compound. For the underlying crystal structure A_2^0 is negative [5] and together with the negative sign of the second-order Stevens constant α_j for Pr one finds that K_1^R is negative and hence of opposite sign to the positive value of K_1^{Co} associated with the easy-axis anisotropy of the Co sublattice. The temperature dependence of the anisotropy constant K_1^R is determined by the strong decrease with the temperature of the expectation value of $O_2^0 = <3J_z^2 - J(J+1)>$, while the temperature dependence of the anisotropy constant K_1^{Co} is comparatively small for temperatures well below the Curie temperature, as can be derived from the results shown in Fig. 1.

The occurrence of a spin reorientation with decreasing temperature can therefore be understood as follows. When going from the Curie temperatures to lower temperature, the crystal-field-induced R-sublattice anisotropy grows in importance due to the strong temperature dependence of the $<3J_z^2 - J(J+1)>$ term. This means that when lowering the temperature, the easy-axis Co-sublattice anisotropy has to compete with the Pr-sublattice anisotropy favouring a preferred moment direction perpendicular to the *c*-axis. The spin-reorientation transition marks the temperature at which both sublattice contributions have become of equal magnitude.

It can be seen in Fig. 3 that the spin-reorientation temperature decreases strongly with increasing Al concentration. This can most easily be explained by an increase of the Co-sublattice anisotropy with increasing Al substitution. An estimate of the concentration dependence of K_1^{Co} can be obtained from the results shown in Fig. 1 by means of the expression $K_1^{Co} = B_a M_s/2$, where M_s is the saturation magnetization of the Co sublattice and B_a the anisotropy field. Values of the former quantity are plotted as a function of concentration in Fig. 5. Values of the anisotropy field can generally be obtained from the intersection point of the magnetic isotherms measured on magnetically aligned powder samples with the field applied parallel and perpendicular to the alignment direction. The Co-sublattice anisotropy fields are, however, fairly small in the $Y_2Co_{17-x}Al_x$ compounds and the alignment is not perfect. This strongly hampers the determination of B_a values from the isotherms shown in Fig. 1, although it is clear from these results that the anisotropy field increases with *x*. This increase of the anisotropy field with *x* may, however, for a large part be compensated by the simultaneous strong decrease of M_S. This makes it questionable whether the decrease of the spin-reorientation temperature in Fig. 3 can be explained exclusively on the basis of K_1^{Co}.

A further mechanism responsible for the concentration-dependent decrease of the spin-reorientation temperature may be a decrease of the Pr-sublattice anisotropy with increasing Al concentration. This may, of course, be due to a decrease of the absolute value of A_2^0 with increasing Al concentration but also be the result of a less strong coupling of the Pr-sublattice to the Co-sublattice. In the latter case, one has to bear in mind that the Pr-sublattice magnetization, owing to a negligible Pr intrasublattice coupling, is primarily determined by the Pr–Co intersublattice coupling. At a given temperature, it is the strength of this intersublattice coupling constant J_{PrCo} and the value of the Co-sublattice moment that determine the molecular field experienced by the Pr moments and hence the value of $<3J_z^2\text{-}J(J+1)>$. Previous studies have shown that the intersublattice coupling strength is not very concentration dependent [8].

However, it can be derived from the results shown in Fig. 5 that the Co-sublattice moment strongly decreases with Al concentration. Consequently, the molecular field experienced by the Pr moments and the concomitant value

of $<3J_z^2 - J(J+1)>$ at a given temperature become reduced.

Concluding, we have investigated the effect of the magnetic dilution of the Co-sublattice in Pr_2Co_{17} by substitution of Al for Co. Although the Pr sublattice as well as the Co sublattice in this compound favour an easy magnetization direction perpendicular to the c axis, we observed spin-reorientation phenomena upon Al substitution. This behaviour has been attributed to a change in sign of the Co-sublattice anisotropy with Al substitution, as has been observed also in the $Y_2Co_{17-x}Al_x$ compounds. We have observed that the spin-reorientation temperature decreases strongly with Al concentration which we attribute mainly to a decrease of the Pr-sublattice anisotropy with increasing Al substitution.

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