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MAGNETIC PROPERTIES OF $PrCo_2$ AND ITS TERNARY HYDRIDE $PrCo_2H_4$

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Magnetization and susceptibility data on $PrCo_2$ and $PrCo_2H_4$ are presented. The ac susceptibility of $PrCo_2$ measured in zero dc field displays a sharp and high peak at $T_c = (39.9 \pm 0.2)$ K. The magnetization versus temperature curves show ferromagnetic behaviour for $B > 1$ T, but display a maximum at lower values of the applied field. These results, together with the behaviour of the hysteresis loops at different temperatures below T_c, indicate that $PrCo_2$ orders ferromagnetically, the magnetic hardness increasing strongly for $T \to 0$. The saturation moment at 4.2 K equals 3.9 μ_B per formula unit, as found from the magnetization curve measured in a pulsed-field magnet up to $B = 30$ T.

Similar experiments on $PrCo_2H_4$ provide evidence that the introduction of hydrogen in $PrCo_2$ not only destroys the long-range atomic order, but also considerably reduces the ferromagnetic interactions. Such an effect of the hydrogen is commonly observed in cobalt intermetallics. Part of the $PrCo_2H_4$ is found to have decomposed into PrH_2 and free Co. The clusters of free Co atoms give rise to a maximum in the zero-field ac susceptibility versus temperature curves, similar as observed in spin glasses or magnetic glasses. By increasing the ac frequency, the maximum shifts to higher temperatures. The behavior can be explained in terms of the Néel model for superparamagnetic particles with randomly oriented local anisotropy axes.

1. Introduction

Previous investigations of the magnetic properties of the compound $PrCo_2$ showed that the temperature dependence of the magnetization in 0.6 T has a pronounced maximum [1] near 30 K, indicating that the magnetic ordering is either antiferromagnetic (or ferrimagnetic), or that it is ferromagnetic with a magnetic hardness that increases strongly at low temperatures. The purpose of the present investigation was to obtain more experimental information on the magnetic properties of $PrCo_2$. Measurements of the temperature dependence of the magnetization (σ) in fields up to 1.8 T were therefore supplemented by measurements of hysteresis loops at various temperatures and by measurements of the temperature dependence of the ac susceptibility (χ) in zero field. In addition magnetization curves have been measured up to very high fields (30 T) in a pulsed-field magnet.

Like most of the intermetallic compounds between a rare earth element and a 3d transition metal, $PrCo_2$ is able to absorb large amounts of hydrogen [2], the ternary hydride having the formula composition $PrCo_2H_4$ [3]. Another reason for starting this investigation was to study the changes in magnetic properties resulting from the H_2 take-up. A similar set of experiments was therefore performed on the hydride.

The conclusions from the present study may be stated as follows. The data confirm that $PrCo_2$ orders ferromagnetically, the ordering temperature being found as $T_c = (39.9 \pm 0.2)$ K. The magnetic hardness is indeed observed to increase drastically for

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$T \to 0$. The saturation moment for $PrCo_2$ at 4.2 K is determined as $(3.9 \pm 0.1)\mu_B$ from the magnetization curve up to 30 T. This value agrees with a previous neutron diffraction determination.

Furthermore, the ferromagnetic interactions are found to be destroyed upon the introduction of hydrogen, as seems to be the rule in cobalt intermetallic compounds. X-ray data indicate an absence of long-range atomic order in $PrCo_2H_4$. The ac susceptibility data, measured at different frequencies, show a dependence on temperature similar to that observed for magnetic glasses. The behavior can be qualitatively explained on basis of the Néel model for superparamagnetic particles with local anisotropy axes randomly oriented in space. At low enough temperature the particle moments become frozen, leading to a maximum in the susceptibility versus temperature curve that depends on the frequency. From high-field magnetization studies at 4.2, 77 and 300 K, it was possible to identify the superparamagnetic particles with clusters of free Co atoms, resulting from (local) decomposition of $PrCo_2H_4$ into PrH_2 and free Co.

2. Experimental details

The $PrCo_2$ used in this investigation was prepared from 99.9% pure starting materials. After arc-melting, the alloy button was vacuum-annealed for 7 weeks at 600°C. X-ray diffraction showed the sample to be single phase (cubic Laves phase structure). The temperature dependence of the magnetization was determined in the range 4.2–300 K by means of an adaptation of the Faraday method. Magnetization isotherms at various temperatures were studied by means of a PAR vibrating sample magnetometer. The ac susceptibilities of the polycrystalline samples were measured as a function of temperature by an induction method in an apparatus described by Groenendijk et al. [4]. Data on $PrCo_2$ were taken at a fixed frequency of 166 Hz and in zero dc fields (the amplitude of the ac field was about 1–10 Oe). For $PrCo_2H_4$ the dependence of the susceptibility on the frequency of the oscillating field was also studied, the frequency range being 7 Hz–10 kHz. Lastly, magnetization isotherms at T = 4.2, 78 and 300 K up to very high fields (30 T) were measured using a pulsed-field magnet. The field pulse is of sinusoidal shape (half a period) and has a duration of about 15 ms. The magnetization is obtained by integrating the output of a compensated, pick-up coil system. By measuring the field with a separate pick-up coil both the magnetization and field are recorded as a function of time, yielding finally the required dependence of σ on B.

3. Results and analysis: $PrCo_2$

The temperature dependence of the magnetization as measured in applied fields of 0.3 and 1.8 T is shown in fig. 1. Other curves measured for $B > 1$ T were found to be similar to that for $B = 1.8$ T, and have a shape expected for a ferromagnetic material. The maximum in the curve for 0.3 T is similar to that reported previously for a field of 0.61 T [1]. As mentioned in the introduction, this effect may be ascribed to an increase in the magnetic hardness upon lowering of the temperature. This explanation had already been suggested by Titcomb et al. [1], and is confirmed by the temperature dependences of the ac susceptibility and of the hysteresis loop, which are given in figs. 2 and 3, respectively. In fig. 2 both the real (χ') and imaginary (χ'') part of the complex susceptibility $\chi = \chi' - i\chi''$ are shown. The dispersion reaches a relatively

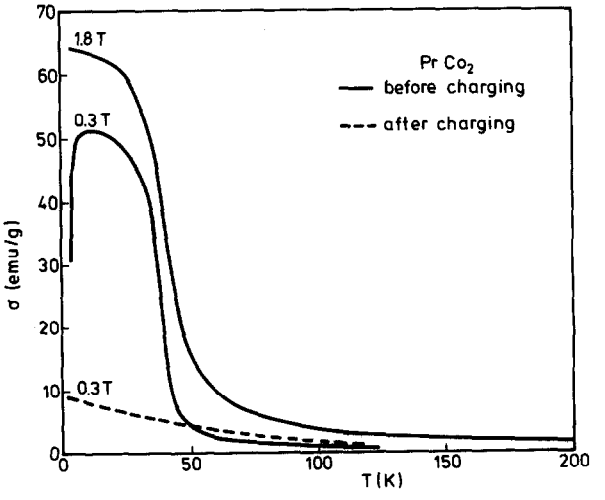

Fig. 1. Temperature dependence of the magnetization of $PrCo_2$ in an applied field of B = 0.3 and 1.8 T (solid curves). Broken curve shows the result found for $PrCo_2H_4$ in a field of 0.3 T.

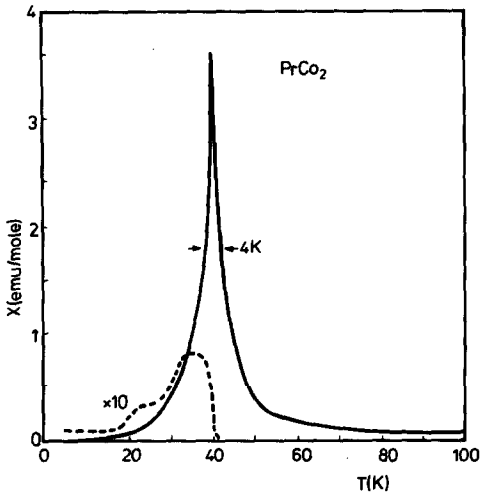

Fig. 2. Temperature dependence of the real part χ' (solid curve) and imaginary part χ'' (dashed curve) of the ac susceptibility $\chi = \chi' - i\chi''$. Note that χ'' is plotted on a ten times larger scale.

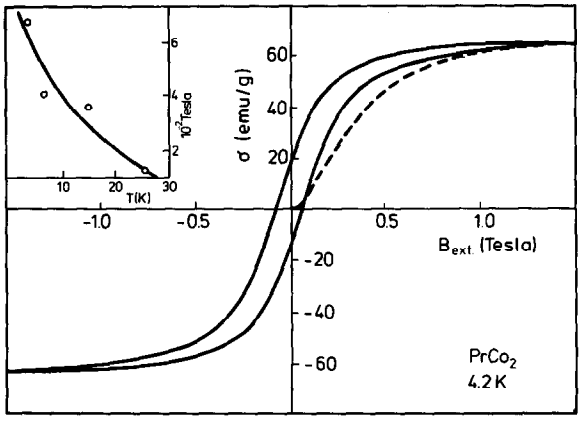

Fig. 3. Hysteresis loop of $PrCo_2$ at 4.2 K. The broken line shows the curve of initial magnetization. The inset shows the temperature dependence of the coercive force.

high value of $\chi' = 3.66$ emu/mol at the transition temperature, which is found to be $T_c = (39.9 \pm 0.2)$ K. Below T_c the susceptibility χ' drops sharply and the value found at 4.2 K is $\chi' = 0.030$ emu/mol only. At this temperature the absorption χ'' is about 30% of χ'. Similar sharp peaks have previously been reported for PrX_2 compounds with X = Rh, Ir, Ru and for Pt [5]. This behaviour is consistent with the model of a ferromagnet in which the domain walls become more and more blocked as the temperature is lowered, so that the ac field may only produce wall motions over very short distances around the equilibrium positions. As the temperature is raised to T_c both χ' and χ'' start to increase, indicating that the walls become more mobile, such that their movements may contribute to the susceptibility.

The temperature dependence of the magnetization isotherms is also in accordance with this explanation. The isotherm measured at 4.2 K is shown in fig. 3. Similar hysteresis loops were obtained at 7, 15 and 20 K. From the results of these measurements it can be derived that the magnetic hardness indeed decreases strongly with temperature. For instance, at 20 K the coercive field has become reduced by a factor of four from its value at 4.2 K. This strong decrease of the magnetic hardness with temperature leads to a corresponding reduction in the difference in magnetization values measured in low and high fields, respectively.

It is interesting to note that, in all but the lowest fields applied, the curve of initial magnetization (broken line) is situated substantially lower than the corresponding curve of the hysteresis loop. This is a rather unusual behaviour compared to that found in other ferromagnetic materials, where the whole curve of initial magnetization is confined to an area within the hysteresis loop. This behaviour indicates that reversal of magnetic domains via propagation of Bloch walls is much more difficult in the unmagnetized material than in magnetized $PrCo_2$. The conclusion seems to be that, even in the region of higher fields, the domain structure after a magnetization cycle is quite different from that in the original state. An explanation could be that in the unmagnetized, original state of the polycrystalline material each crystallite is separately divided into domains. When the field is lowered after the sample has been magnetized up to 1.8 T, a more macroscopic domain structure could possibly be formed, in which each domain comprises one or more crystallites. This would lower the total wall-energy and for the same value of the applied field the induced magnetization would be larger. Similar behaviour of the initial magnetization curve was also observed [10] in $PrIr_2$ and in $PrRu_2$; so it seems not to be restricted to the Co intermetallic compounds.

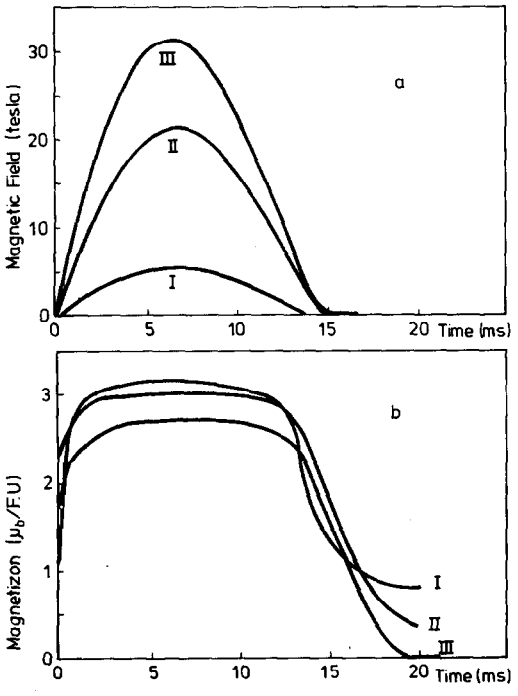

Fig. 4. Variation with time of the field (top part) and magnetization signal (bottom part) for $PrCo_2$ as measured in the pulsed-field magnet at 4.2 K in a sequence of three pulses I, II and III. The magnetization in the bottom part is given in Bohr magnetons per formula unit.

The presence of a remanence and of a coercive force again shows that the magnetic interactions in $PrCo_2$ are predominantly ferromagnetic. From the magnetization curve in fig. 3 the saturation moment at 4.2 K is found to be $2.7\mu_B$ per formula unit. This is in agreement with the value $2.9\mu_B$ and $3.2\mu_B$ reported by Crangle and Ross [6] and by Farrell and Wallace [7], respectively, from similar measurements. It is pointed out that both the Pr and the Co atoms contribute to the total magnetic moment. From neutron diffraction studies Schweizer [8] has deduced $\mu_{Pr} = (2.7 \pm 0.20)\mu_B$ and $\mu_{Co} = (0.50 \pm 0.25)\mu_B$, giving a total moment of $(3.7 \pm 0.7)\mu_B$. The value for μ_{Pr} differs from that found [9] from the hyperfine specific heat, $\mu_{Pr} = (2.18 \pm 0.05)\mu_B$. Evidently, the value of $3.7\mu_B$ for the total moment exceeds by far that found from the low-field magnetization studies.

Indeed, the present high-field magnetization data show that fields of the order of 10–20 T are needed to saturate the sample. Even the remanent moment is found to be still field-dependent up to such high values of the applied field. In fig. 4 the variation with time of the field and the magnetization is shown as measured in the pulse-field magnetometer for a sequence of three pulses with maximum field values of 5.2, 21.1 and 31.5 T, corresponding to the curves labelled I, II and III, respectively. Starting with the low-field pulse I, the sample was in its virginal state, and a remanent moment of about $0.82\mu_B$ is seen to remain at the end of the pulse. This value is of the same order as that observed in fig. 3. For the next pulse II, the magnetization starts for $B = 0$ at this value, and since σ is obtained by integration of the differential susceptibility $\chi = \partial\sigma/\partial B$, we have to add the remanent moment of pulse I to all the magnetization values measured in pulse II. Nevertheless, at the end of pulse II the magnetization is still different from zero (at $0.4\mu_B$), meaning that the remanent moment has still increased. Only after the third pulse III one observes $\sigma = 0$ at the end of the pulse.

By adding up the remanent moments of pulses I and II to pulse III, the final magnetization curve for $PrCo_2$ at 4.2 K is obtained, which is shown in fig. 5 together with the measurements at 77 K (at which temperature the above difficulties due to remanence are absent. The 4.2 K curve is fairly constant for $B > 20$ T, and indicates a saturation value of $(3.9 \pm 0.1)\mu_B$, in excellent agreement with the neutron diffraction results of $(3.7 \pm 0.7)\mu_B$. Apparently, a field of 10 T is sufficient to overcome the magnetic anisotropy in $PrCo_2$. The difference with the value of about $2.18\mu_B$ found for μ_{Pr} from the hyperfine specific heat remains as yet unexplained, unless μ_{Co} is as large as $0.85\mu_B$.

In concluding the discussion of the $PrCo_2$ data the following remarks seem to be in order. Firstly, the value $T_c = 39.85$ K found for $PrCo_2$ is not exceptionally high when compared with those for other Laves phase compounds for Pr. Although $PrNi_2$ does not appear to have electronic magnetic order at temperatures above 1 K, ordering temperatures T_c of 7.7, 7.9, 9.9 and 11.2 K have previously been reported for $PrPt_2$, $PrRh_2$, $PrMg_2$ and $PrIr_2$, respectively [5,10,11]. For $PrRu_2$ we even found $T_c = 33.9$ K, a value quite comparable with that for $PrCo_2$, as well as with $T_c = 32$ K, reported for $PrAl_2$ [12]. Thus, in order to explain the value for T_c in $PrCo_2$ the presence of a partially depleted 3d band need not be essential,

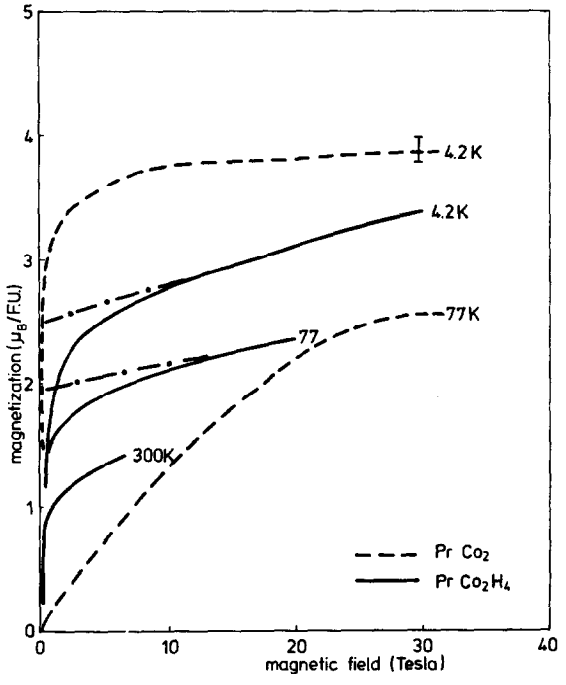

Fig. 5. High-field magnetization curves obtained for $PrCo_2$ at 4.2 K and at 77 K (dashed curves) and for $PrCo_2H_4$ at 4.2, 77 and 300 K (solid curves). Dash–dotted curves indicate the extrapolations to $H = 0$.

although the Pr–Co exchange interactions will certainly also be present. In our opinion it is more likely that the variation of T_c through this series of PrX_2 compounds results primarily from a competition between the Pr–Pr exchange interactions and the crystal field splittings of the Pr^{3+} electronic energy levels, since in these materials the Pr^{3+} groundstate is thought [10] to be either the singlet Γ_1 or the (non-magnetic) doublet Γ_3 level.

Lastly we mention that the specific heat data reported [13] for $PrCo_2$ show a double-peaked structure, the origin of which is as yet unexplained. The temperature of the lower peak, $T_c \approx 39.3$ K, agrees quite well with the present determination from the susceptibility. However, a second somewhat broader maximum was found in the specific heat at about $T_c \approx 43.4$ K. Such a double structure is not seen in our χ data. We plan to investigate this particular problem more extensively, including a reinvestigation of the specific heat near T_c.

4. Results and analysis: $PrCo_2H_4$

Charging of $PrCo_2$ with H_2 gas leads to the disappearance of all reflection lines in the X-ray diagram. This means that long-range atomic order is lost upon H_2 take-up. Similar observations have previously been reported [3] and can be explained in terms of the onset of phase separation during the absorption process, resulting from the metastable nature of the ternary hydrides [14]. It was shown elsewhere that the charged materials can be classified as microcrystalline rather than as amorphous [15]. The temperature dependence of the magnetization in 0.3 T after H_2 absorption is shown by means of the broken line in fig. 1. Compared to the magnetization for the uncharged compound in the same field there is a considerable reduction in magnetization at the lowest temperatures. It seems that the ferromagnetic character present in uncharged $PrCo_2$ below $T_c = 40$ K is lost upon charging. The present finding is contrary to that of Tittcomb et al. [1], who assume that their $PrCo_2$ contains actually some absorbed hydrogen which was removed by degassing in vacuum at 950°C. Tittcomb et al. [1] suggest that weakening of the exchange occurs upon removal rather than upon introduction of the hydrogen. However, our own results are in agreement with the behaviour observed quite uniformly in intermetallics of cobalt. In all cases investigated up till now, hydrogen absorption has been found to decrease the Co moment and to lower the ordering temperature [16].

A closer inspection of fig. 1 shows that in the region above 50 K the magnetization curve for $PrCo_2H_4$ lies above that measured for $PrCo_2$. In case the hydrogen absorption would merely destroy all ferromagnetic interactions (on a microscopic scale), this result is somewhat surprising. Therefore, it was decided to study in addition the initial susceptibility (for $B = 0$) as a function of temperature with the mutual inductance technique. Representative results of such measurements are shown in fig. 6 for different measuring frequencies. One observes that both χ' and χ'' display rather broad maxima in the range 25–30 K. The temperature of the maximum in χ'' is in all cases below that of the maximum in χ', and appears to coincide with an inflection point in the χ' versus T curve. Both the maxima in χ' and χ'' are seen to shift to higher temperatures as the frequency of the ac field is increased.

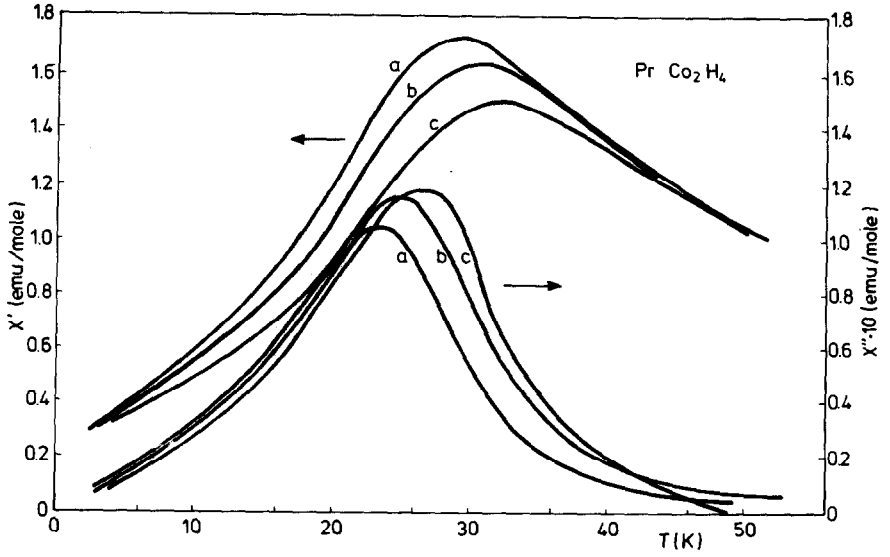

Fig. 6. Temperature dependence of the real part χ' (top part) and imaginary part χ'' (bottom part) of the ac-susceptibility of $PrCo_2H_4$ at various values of the frequency of the oscillating field. The frequencies applied are: 7.32, 117 and 1875 Hz for curves a, b and c, respectively.

The susceptibility behavior in fig. 6 is qualitatively similar to that observed in spin glasses or in magnetic glasses [17]. It is well explained in terms of the Néel model [18] for superparamagnetic particles or clusters: Within each cluster, the moments are ferromagnetically aligned along the local anisotropy axis. Reorientation along these axes will involve a relaxation time $\tau = \tau_0 \exp(E_0/k_BT)$ where E_0 is the anisotropy energy. Although both τ_0 and E_0 will depend e.g. on the size of the cluster and on the temperature, we may disregard such details for the sake of the argument. It follows that for $k_BT >> E_0$ the susceptibility of the assembly of clusters will follow a Curie law, since the direction of the local anisotropy axis of each cluster will be randomly distributed in space. However, with lowering temperature the relaxation time will increase exponentially, and eventually for $\tau >> \omega^{-1}$ the ac susceptibility will become very low-valued, since the time variation of the applied field becomes very short to that needed to establish internal equilibrium in the magnetic system. This will lead to a maximum in the ac susceptibility measured as a function of temperature, which defines a freezing temperature, T_f, in the sense that the cluster moments become blocked for $T < T_f$ (at the frequency considered). We may approximately define T_f as the temperature where $\omega\tau \approx 1$. The variation of T_f with ω is then given by $k_BT_f = -E_0/\ln \omega\tau_0$. Furthermore, if we assume that, after a field variation, the magnetization of the system reaches equilibrium according to an exponential decay $M(t) = M_0 \exp(-t/\tau)$ with the same relaxation time τ, then the real and imaginary parts of the ac susceptibility can be written as:

$$\chi' = \chi_{\text{Curie}}/(1 + \omega^2\tau^2) ,$$

$$\chi'' = \chi_{\text{Curie}}\, \omega\tau/(1 + \omega^2\tau^2) .$$

Here $\chi_{\text{Curie}} \propto 1/T$ denotes the Curie-susceptibility of the superparamagnetic particles.

Although the theory summarized in the above gives a qualitative explanation of the χ data, quantitative agreement is very poor. For instance, from the ω dependence of T_f, the unrealistically high value of $E_0/k_B \approx 1.6 \times 10^3$ K is estimated. Furthermore, the ω dependence of χ' and χ'' at constant temperature cannot be fitted with the above Debije formulae. We attribute this to deviations from the model in its simplest form e.g. to the fact that τ and E_0 will depend, among other things, on the size of the clusters and on the temperature.

We have not attempted to pursue this problem any further, but instead have tried to identify the nature of the superparamagnetic particles. Since $PrCo_2H_4$ is itself probably microcrystalline, an obvious possibility would be that the clusters are in fact weakly coupled $PrCo_2H_4$ particles. Another possible explanation, however, would be the presence of clusters of free cobalt atoms, resulting from local dissociation of $PrCo_2H_4$ into PrH_2 and Co. This dissociation could be initiated by the large reaction enthalpy (87 kJ/mol H_2) resulting from the absorption of hydrogen gas: $PrCo_2 + 2H_2 \rightarrow PrCo_2H_4$.

The latter possibility seems to be the most probable one for the following reason. For the Néel model to hold, it is necessary for the ferromagnetic interactions within each of the (otherwise weakly coupled) clusters to be quite strong, i.e. the associated ordering temperature T_c to be quite large compared to the freezing temperature. If the clusters would contain free cobalt this condition is easily met since for pure cobalt T_c = 1388 K. In case the clusters were $PrCo_2H_4$ particles, the implication would be that the ferromagnetic interactions in $PrCo_2H_4$ would be very much stronger than in $PrCo_2$, so that the absence of ferromagnetic ordering in $PrCo_2H_4$ would not be due to a lack of ferromagnetic interactions, but the result of the amorphous or microcrystalline nature of the compound.

By performing high-field magnetization studies, we have been able to solve this problem, and the results at 4.2, 77 and 300 K are shown in fig. 5, where they may be compared with those for $PrCo_2$ at 4.2 and 77 K. The data for $PrCo_2H_4$ at all temperatures show the presence of a rapidly saturating component plus what appears to be a paramagnetic contribution in the higher-field range ($B > 5$ T). The first contribution gives rise to the same hysteretic phenomena in the pulsed-field curves as discussed in connection with fig. 4, but in this case not only at 4.2 K but also at 77 K and even at 300 K.

We are therefore inclined to attribute the rapidly saturating component to the presence of cobalt clusters, noting that the saturation field for cobalt at 300 K is of the order of 0.5 T, in agreement with what is observed in fig. 5. We note that the pulsed field experiment at 4.2 K evidenced a remanent moment of about $1\mu_B$, which relaxed with a time constant of about 30 min. The experiments at 77 and 300 K did not show this long-time relaxation phenomenon. This irreversible high-field saturation effect occurring at low temperatures may also be understood in terms of the exponential dependence of the relaxation time on the temperature within the above cited Néel model.

The amount of free cobalt present in the sample may be estimated by extrapolating the experimental magnetization curves in the high-field region to $H = 0$ (see fig. 5). At $T = 4.2$ K this yields about $2.5\mu_B$/f.u. for the cobalt clusters. Since free cobalt has a moment of $1.7\mu_B$/Co, this would imply that about 70% of the cobalt atoms are present in the form of clusters. In fig. 5 one also observes that these interceptions decrease rather strongly with temperature. A fit to a Brillouin curve would yield a Curie temperature of the order of T_c = 350 K. This is of course quite low compared to T_c (cobalt) $\approx$ 1400 K. On the other hand in clusters of (sub) microscopic size a considerable reduction of the ordering temperature owing to the size effect is indeed to be expected.

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