ELECTRONIC PROPERTIES OF TWO NEW ELEMENTAL FERROMAGNETS: fcc Pr AND Nd

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The fcc phases of Pr and Nd have been stabilized at room temperature and at liquid-helium temperatures and both prove to be ferromagnetic. The measured electronic properties of this new phase are discussed in the light of presently accepted phase diagrams. The existence of the fcc phase accounts for a variety of anomalous data reported for double-hcp Pr.

Pr and Nd are reported to exhibit a double-hcp (dhcp) structure below 798 and 868°C, respectively, with a bcc allotropic phase above these temperatures.[1,2] Recent studies show that in dhcp Pr the cubic sites have a crystal-field–quenched moment, whereas the hexagonal sites order antiferromagnetically at 25°K.[3,4] In dhcp Nd the hexagonal and cubic sites order antiferromagnetically at 19.0 and 7.5°K, respectively.[4] The present extensive study, especially of Pr and some of its alloys, was initiated for several reasons:

(1) Recent progress in generating very low temperatures by hyperfine-enhanced nuclear cooling in Van Vleck paramagnets[5] revealed the possibility that fcc Pr might be a most suitable candidate, since in dhcp Pr the cubic sites (with fcc symmetry to a first approximation) do not show a moment[3] and therefore exhibit strong Van Vleck paramagnetism at low temperatures.

(2) A study of fcc Th-Pr alloys[6] showed a strong increase in the ferromagnetic exchange interaction up to more than 96 at.% Pr but no ordering could be detected down to 1°K; therefore a hypothetical fcc Pr phase could present a unique case where the exchange J is close to the critical value J/Δ (Δ = crystal field splitting) where an exchange-induced spontaneous moment develops. At low temperatures interesting new phenomena have been predicted in such materials.[7]

(3) The study of polymorphic phases of rare earths such as Pr or Nd offers a valuable test for the reliability of band-structure calculations in predicting the nature of the magnetic ground state in these elements.[8]

(4) The lack of satisfactory explanations of the electronic properties of dhcp Pr[9,10] also suggest the possibility of contamination by a second phase, fcc being most likely.

Results on fcc Pr.—In two recently purchased high-purity Pr lots (Research Chemicals Corp.) referred to as lots 1 and 2 we were indeed able to retain the fcc phase at room temperature and below by quenching in the arc furnace. All samples exhibited reproducible properties. Cold working or filing converted them to the dhcp phase. The lattice constant determined from flakes which had been splat cooled in high-purity argon was 5.18_6 Å for fcc Pr at 23°C. This is somewhat higher than one would extrapolate from data contributed by various authors investigating the Th-Pr(fcc) system.[11-13] Contrary to their results we found complete solid solubility in the Th-Pr system in the fcc phase.

Several spectrographic analyses revealed the following impurities in lots 1 and 2 (in at. ppm) Ca, 50; Mn, Mg, 5; Cu, Fe, Si, C, 2-5; O_2, 2000; N_2,[14] 110; H_2,[14] 5000. A less pure lot (referred to as lot 3) analyzed as follows: Mg, 4000; Fe, 2000; Al, 600; C, 140; Ca, 50; Cu, Si, 2-5; O_2, 3000; N_2,[14] 130; and H_2,[14] 7000. The amount of other rare earths was <50 in all three lots. The fcc phase could not be retained in lot 3 by arc quenching presumably because of impurities. Splat cooling of lot 3 did however produce some faint fcc x-ray lines.

Differential thermal analysis (DTA) showed a sharp and reproducible phase transformation in lot 3 at 792°C, in contrast to lots 1 and 2 which showed a transition at 860°C. It is likely that the transition around 860°C (or possibly at 792°C) is actually a transition from an fcc to a bcc phase. The fcc-dhcp transition could not be detected in the DTA, suggesting that it must occur somewhere below these temperatures and/or is very sluggish in high-purity Pr. A lower limit may be 560°C because annealing at this temperature for 40 h did partially convert arc-quenched samples of lots 1 and 2 to the dhcp phase.

In Figs. 1 and 2 we show the magnetic properties of dhcp and fcc Pr. Contrary to our expectation from dhcp Pr,[3] fcc Pr becomes ferromagnetic at 8.7°K. The Curie temperature was determined by a mutual-induction method, recording the susceptibility in a field of 10 Oe as a function of temperature. The sharp peak occurring at 8.7°K is in reasonable agreement with the paramagnetic Curie temperature of 8°K which had been extrapolated from temperatures between

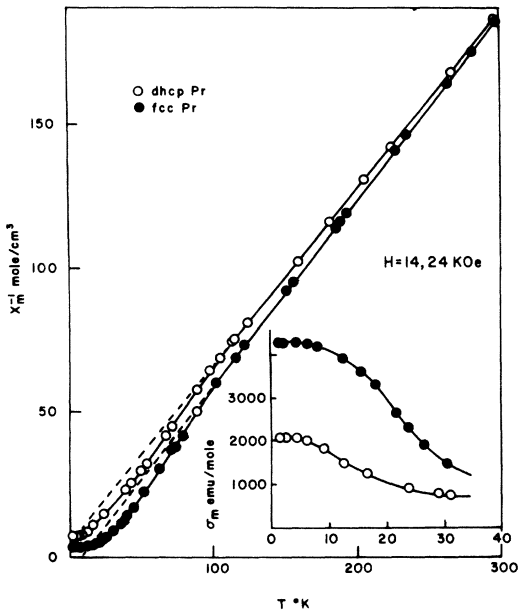

FIG. 1. Inverse molar susceptibility versus temperature between 1.43 and 300°K for dhcp and fcc Pr.

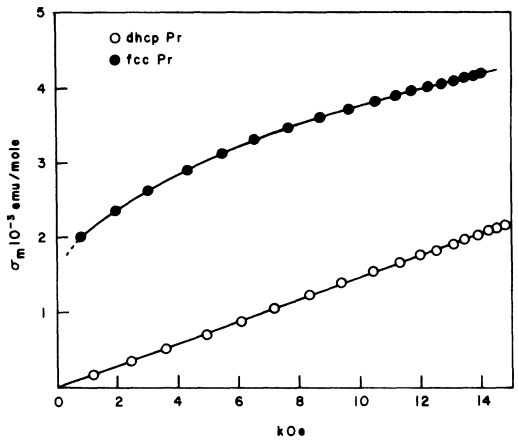

FIG. 2. Molar magnetization σ_m versus field at 1.43°K for dhcp and fcc Pr. (Both curves are corrected for the demagnetization factor for the spherical sample.)

100 and 300°K in Fig. 1. In the absence of exchange interaction the crystal-field theory would predict a nonmagnetic singlet ground state for the fcc[9,15] and dhcp phases.[9] In the latter phase, the moment is exchange induced only on the hexagonal sites (because of their smaller crystal-field splitting compared with the cubic sites) and the coupling of the exchange-induced moments is antiferromagnetic.[4] Considering the nonmagnetic ground state of the cubic sites in the dhcp phase, it is remarkable that in the fcc Pr we have an exchange-induced ferromagnetic ground state. The different magnetic ground states must be due to a change in the shape of the Fermi surface, since the exchange is due to the conduction electrons. The small difference in atomic volume, of slightly less than 1%, is not expected to introduce a drastic change in the crystal-field splitting on the cubic sites. The total magnetization at 15 kG and 1.43°K corresponds to $0.76\mu_B$, about 24% of the saturation value, given by $g_J\mu_B J$. On the other hand, our analysis of the low-temperature specific heat yields a hyperfine term A/T^2, where A is only about 4.9% of the maximum value which would be found if the Pr atom were fully magnetized, assuming a hyperfine constant of 1093 MHz.[16] This leads to a zero-field ground-state moment of only 22% of the saturation moment since $A \sim H_{hf}^2 \sim \langle J \rangle^2$ and H_{hf} is the effective hyperfine field in zero external field. The close agreement between these two numbers suggests that we probably have a true ferromagnet with parallel alignment of the moments.

At the ferromagnetic transition temperature T_C no specific-heat anomaly could be detected. This can easily be understood since at $T = T_C$ most of the entropy has been removed by the crystal-field splitting if all crystal-field levels are much higher in energy compared with kT_C. Then the ordering of the exchange-induced moments is no longer associated with a large reduction in entropy. For a simple two-singlet-level system the specific heat jump ΔC can easily be calculated:

$$\Delta C(T = T_C) = 2Rx^3 e^{-2x}[1 + 2(x-1)e^{-x} + O(e^{-2x})], \quad (1)$$

where $x = \Delta/kT_C$ and Δ is the splitting between the singlets. Expression (1) is valid in the molecular-field approximation if $x \gg 1$. Plotting $\ln(C_{Pr} - C_{La})T^2$ vs $1/T$ between 10 and 23°K we find $\Delta = 69 \pm 4$°K. C_{Pr} and C_{La} are the total specific heats of fcc Pr and fcc La, respectively. It is assumed, of course, that both the electronic and the lattice terms are identical in Pr and La over the whole temperature range considered. Therefore (1) would predict a specific heat jump of only 0.92 mJ/°K mole, i.e., ≈0.05% of the total specific heat at this temperature which is far beyond our detectable limit. The singlet-triplet case is not expected to be significantly different.

It is interesting at this point to compare our result on Δ with the results given by the molecular-field theory. Extending Bleaney's[17] calculation

Table I. Electronic properties of fcc and dhcp Pr and Nd. (The values given in brackets are reference values).

	Pr		Nd	
	fcc	dhcp	fcc	dhcp
Lattice constants (Å) at 296°K	5.18_6	a= 3.67_2[a] c=11.83_5	--	a= 3.65_8[a] c=11.80_0
Transformationpoint (°C) to bcc phase		860(798)[b] 792[b]		870(868)[b]
Curie-or Néel Temp. (°K)	8.7	23(25)[c]	29	7.0, 19.5(7.5, 19.0)[c]
σ_m/H at 1.43°K in 15 kOe (cm^3/mole)	0.285	0.145 (0.190)[d] (0.217)[e] (0.28)[f]	--	.215, 0.142[g] (0.153)[d]
Crystal field splitting Γ_1-Γ_4(°K) (in molecular field approximation)	69±4	87[h]	--	--

[a]In agreement with Ref. 1.
[b]Ref. 2, lower transition temperature for impure Pr (lot 3).
[c]Ref. 4.
[d]Ref. 23.
[e]Ref. 20.
[f]Ref. 22.
[g]This work: low-field value ($H \leq 5$ kOe).
[h]Ref. 9.

to the singlet-triplet case we find

$$\Delta = kT_c \ln \frac{1+3[1-(M_0/m)^2]^{1/2}}{1-[1-(M_0/m)^2]^{1/2}},$$

where M_0 is the zero-field moment ($\sim \frac{1}{5} g_J \mu_B J$) and $m = g_J \mu_B \langle \Gamma_4 | J_z | \Gamma_1 \rangle$. Expression (2) leads to $\Delta = 38$°K, obviously too low. Compared with T_c, M_0 is much too large. This is indicative of the difficulty in extending molecular-field theory to finite temperatures since T_c cannot simply be derived from the static exchange $J(\vec{k}=0)$.

It now also becomes evident why earlier attempts to explain the specific heat and the susceptibility of dhcp Pr failed.[9,10,18] The results were obviously affected by the presence of various amounts of ferromagnetic clusters of fcc Pr as well as by impurities. This explains nonlinearities in the magnetization curves,[19] too large susceptibilities,[9,19-22] anomalously high hyperfine specific-heat terms,[18,23,24] and possibly a magnetic specific-heat anomaly.[10,18] The susceptibility of dhcp Pr is now found to be considerably smaller than reported earlier[19-22] (see Table I). On the other hand, the linear term of the specific heat in fcc Pr[25] is even larger than in dhcp Pr[18] and strongly field dependent. This means that the linear term does not reflect the density of states. The whole curve is extremely difficult to analyze because of the many contributions. A detailed analysis of the specific heat will be published later.

Results on Nd.– X-ray analysis of splat-cooled Nd flakes showed only the dhcp structure with faint additional lines.[26] The low-field susceptibility (25 G) however showed a reproducible strong ferromagnetic peak at 29°K and a weak anomaly at 46 and 7°K, the latter due to the presence of the dhcp phase.[4] A magnetization curve taken at 1.43°K up to 15 kG however showed that the flake contained only about 8-9% of the ferromagnetic phase (calculated from the moment of the ground-state Γ_6 doublet which we would expect in a fcc phase). Although we do not have a direct x-ray proof for the fcc phase, there is little doubt that the ferromagnetic peak at 29°K is due to this phase, firstly from the comparison with Pr and secondly from the recently found ferromagnetism in fcc Th-Nd alloys.[27] Therefore we conclude that by analogy with Pr there must be a fcc phase below the transformation point to the bcc phase in Nd.

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EXPERIMENTAL LIMIT ON THE PROTON ELECTRIC DIPOLE MOMENT

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A high-precision molecular-beam-resonance experiment has been carried out to look for a violation of P and T invariances in a molecule. The null result can be interpreted in terms of the electric dipole moment of the proton to give $|d_p| = (7 \pm 9) \times 10^{-21} e$ cm.

The presence of an electric dipole moment (edm) on an elementary particle is strictly forbidden if either P or T invariance is valid. Interest in the experimental search for an edm has intensified since the discovery of the CP-nonconserving $K_L^0 \rightarrow 2\pi$ decay.[1] While the CP nonconservation implies through the CPT theorem that T invariance is violated, there is as yet no direct experimental evidence.

Ramsey and his co-workers[2] have carried out a series of very precise beam-resonance experiments to look for an edm on the free neutron; their current limit is $d_n \leq 4 \times 10^{-23} e$ cm. An independent limit on the edm of the proton is obviously of interest but is very much harder to obtain because the proton is charged. For this reason an experiment on the free proton similar to that of Ramsey is not possible. There is also a very general theorem (see, e.g., Schiff[3]) that a charged particle in equilibrium under electrostatic forces has no term in the energy linear in the electric dipole moment. This would at first sight appear to rule out experiments in which the proton is bound in a neutral molecule; however, Schiff points out that this theorem is inadequate to the extent that the nucleus of an atom has finite size and structure. Using Schiff's theory one of us[4] has shown that a useful test for an edm on the proton is possible in a suitable molecular beam resonance experiment. In this Letter we report