Magnetic Properties of Praseodymium in Magnetic Fields Determined from the Nuclear Heat Capacity and Applied to Nuclear Cooling

P. E. Gregers-Hansen,* M. Krusius, and G. R. Pickett†
Department of Technical Physics, Helsinki University of Technology, Otaniemi, Finland
(Received 25 May 1972)

The nuclear heat capacity of praseodymium in fields from 0 to 18.6 kOe has been measured from 16 to 300 mK. In zero field the metal was found to be ordered with average magnetic moments of $0.62\mu_B$ and $0.05\mu_B$ on the two inequivalent lattice sites. Above 10 kOe the Van Vleck behavior dominates and an induced moment appears on both sites. The corresponding induced hyperfine field has been employed for nuclear cooling.

There is considerable interest at present in whether the rare-earth metal praseodymium is magnetically ordered at low temperatures. Several neutron diffraction measurements on single crystals[1-3] have shown no ordering, the lowest measurements being made down to 1.8 K,[3] whereas similar measurements on polycrystals[4,5] and calorimetric measurements on all types of material[6,7] indicate magnetic order at low temperatures on at least half of the sites, with a wide variation in the ordered moment between specimens. In this paper[8] we report detailed measurements of the nuclear heat capacity of polycrystalline praseodymium metal in fields up to 18 kOe, from which we are able to determine the separate variation with field of the electronic moments on the two lattice sites. We have also been able to perform hyperfine-enhanced nuclear cooling with praseodymium, using the information gained from the heat-capacity measurements.

Praseodymium has a double hexagonal close-packed crystal structure, with stacking sequence *ABAC*, giving successive hexagonal planes with alternately cubic and hexagonal nearest-neighbor environments. The Pr^{3+} ion with a $^3H_4$ ground state has an integral total angular momentum J, and the different crystal fields at the two sites both give rise to nonmagnetic singlet ground states.[9] In the presence of a magnetic field the crystal-field ground state includes admixtures from higher levels and a small moment is induced, the well-known phenomenon of Van Vleck paramagnetism. Exchange interactions can also spontaneously admix higher levels, inducing a moment, provided that the ratio of the exchange parameter to the energy gap separating the ground state from the first excited level exceeds a critical value. This ratio for praseodymium appears to be extremely close to the critical value.

The hyperfine interaction Hamiltonian, in terms of the nuclear spin I, can be written

$$\mathcal{H} = a' I_z + P[I_z^2 - \tfrac{1}{3}I(I+1)], \quad (1)$$

where the first term represents the magnetic-dipole interaction and the second the electric-quadrupole interaction. In the rare earths both these interactions are generally dominated by the host-ion unfilled $4f$ shell, and we therefore expect a' to be proportional to $\langle J_z \rangle$ (and thus also proportional to the electronic moment). The effect of the quadrupole term is likely to be negligible in the case of the double hcp praseodymium structure.[9] There is only one stable isotope with $I = \frac{5}{2}$. Bleaney[10] has estimated from EPR data on praseodymium salts the value of a' for the metal, assuming the saturated $4f$ moment of $g_J J = 3.2\mu_B$. By fitting the observed heat-capacity anomaly arising from the thermal depopulation of the nuclear spin levels, we obtain experimental values of a' for the two different lattice sites. Using Bleaney's value of a' corresponding to full J, we can determine the ordered moments on the two sites.

The measurements were made in an adiabatic demagnetization cryostat. The temperature was measured by a cerium-magnesium-nitrate thermometer calibrated against He^3 vapor pressure. The specimen was a 1.53-g polycrystalline sphere cut from a larger sample measured earlier by Lounasmaa[11] and by Holmström, Anderson, and Krusius.[6] Magnetic fields up to 18.6 kOe with homogeneity of 0.5% over the sample could be applied with a superconducting split-coil magnet. A second pair of reversed coils compensated the field to zero at the cerium-magnesium-nitrate thermometer and at the heat switch.

The measured heat capacity for several values of applied field is plotted in Fig. 1 together with the lowest measurements by Lounasmaa[11] in zero field. No hysteresis was observed after thermal or magnetic cycling. Figure 1 can best be under-

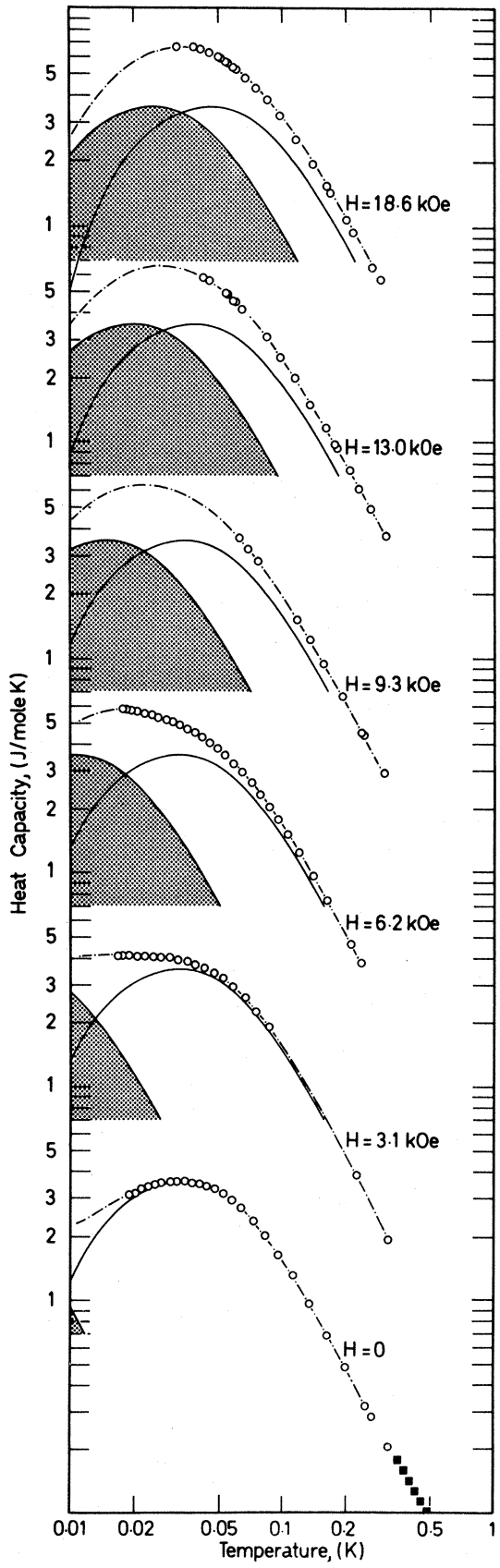

FIG. 1. Heat capacity of praseodymium in various fields. For successive fields the ordinate is stepped one decade for clarity. For each field the stippled Schottky anomaly corresponds to the cubic sites and the unstippled to the hexagonal sites. The best-fitting sum of these two components is indicated by the dot-dashed line. The closed squares are the measured points of Lounasmaa, Ref. 11, on the same specimen in zero field.

stood by noting that the zero-field data fit very closely a single Schottky anomaly, indicated by the solid line in the diagram, corresponding to an electronic moment of $\sim 0.6\mu_B$ on only half the sites (in fact, those with hexagonal symmetry). At the lowest temperatures the measured points fall somewhat above this Schottky curve because of the influence of the high-temperature tail of a second anomaly at much lower temperatures corresponding to the other half of the sites (those with cubic symmetry). This second anomaly, stippled in the figure, moves up rapidly in temperature as the field is increased. This is a very clear demonstration of Van Vleck paramagnetism in that the nuclear anomaly moves up in temperature proportionately with the increasing electronic-host moment induced by the field. The hexagonal sites also show a moment increasing at the higher fields but which remains unchanged below about 10 kOe, indicating that exchange interactions are strong enough to stabilize a sizable moment for this symmetry.

In more quantitative terms, the experimental points, for any single value of the applied magnetic field, can be fitted by a sum of two Schottky anomalies, each corresponding to a single value of the interaction parameter a' of Eq. (1), neglecting the quadrupole interaction. As the specimen is polycrystalline, a distribution of a' values, allowing for the random orientations of the crystallites, would be more appropriate. However, we have made fits using a distribution of a' for the two sites corresponding to the anisotropies from the neutron-diffraction measurements of Lebech and Rainford,[2] but no improvement in the fit was obtained. The hexagonal sites which dominate the heat capacity have an ordered moment at the lower fields and the anisotropy will only be manifest in the increase of the moment with field. The 1 : 4 anisotropy found by neutron diffraction for the cubic sites does not influence the high-temperature tail of the Schottky anomaly enough for the difference to be significant in our temperature range. Consequently we have preferred to

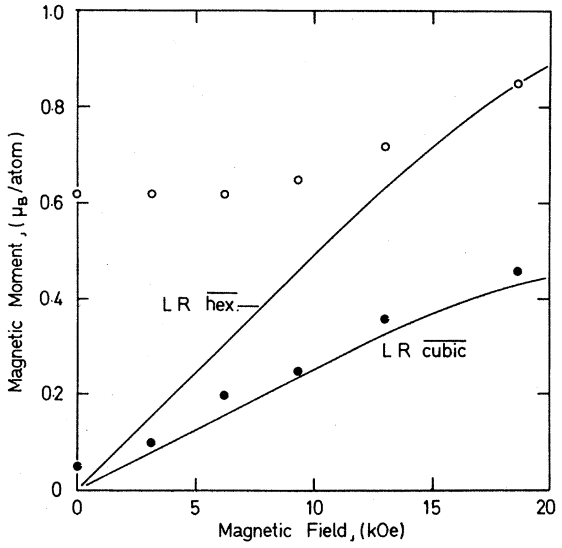

FIG. 2. Magnetic moment on the two lattice sites in praseodymium as a function of field. Solid lines, values averaged over all orientations of the neutron diffraction measurements at 4.2 K of Lebech and Rainford, Ref. 2.

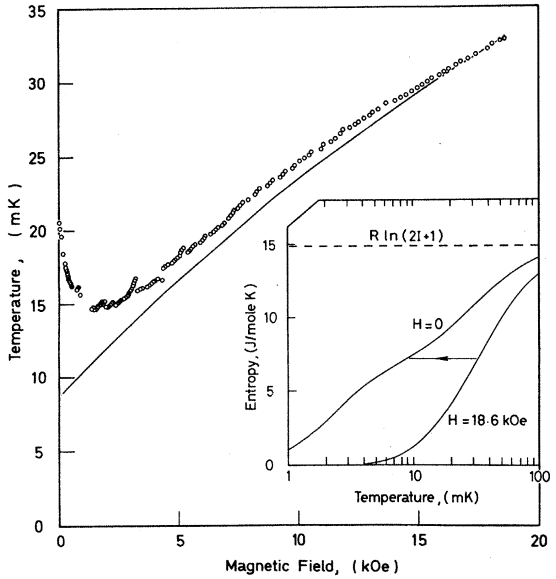

FIG. 3. Nuclear demagnetization of praseodymium. Sudden jumps up in temperature with decreasing field are due to heating from flux jumps in the magnet. A similar jump down in temperature is a pause in demagnetization. Solid line, ideal adiabatic process calculated from the heat capacities. Inset, molar entropy in fields of 0 and 18.6 kOe. The arrow represents the same adiabatic process.

use single-valued anomalies to present the data.

From the fitted values of a' we have calculated the electronic magnetic moments on the host ions using Bleaney's value of a' for full J. The results are shown in Fig. 2. Since the moments plotted represent an average over all orientations, we have calculated, for comparison, similar averages for the two sites from the neutron diffraction measurements of Ref. 2. These are shown in the figure by solid lines. The agreement between the two results for the cubic sites is good. The hexagonal results approach agreement at the higher fields but diverge at the lower fields where our specimen orders. It is this correspondence with the neutron diffraction results which enables us to identify our experimental moments with the appropriate lattice positions. The agreement at high fields between the two methods of measurement is gratifying and seems to indicate that disagreement between earlier measurements in zero field is a function of the variation from specimen to specimen of the moment, stabilized on the hexagonal sites. With regard to speculation as to whether the effective field experienced by the nuclei arises from a real ordered moment or, as has been suggested, from the nuclei relaxing fast enough to respond to crystal-field-level excitations, or even to indirect nuclear-nuclear interactions, it is worth emphasizing that the effective internal field seen by the hexagonal-site nuclei is independent of temperature from 0.5 down to at least 0.03 K. This implies that the order is real.

The fact that the ions on the cubic sites exhibit a strong Van Vleck polarizability suggested the use of praseodymium metal as a material for hyperfine-enhanced nuclear cooling of the type suggested by Al'tshuler[12] and investigated in several intermetallic sompounds by Andres and Bucher.[13] The ratio of the effective field at the nuclei generated by the induced electronic moment to the externally applied field, the hyperfine enhancement factor, is 26 for the cubic sites at 20 kOe (and of the order of 50 for the hexagonal sites beyond the ordering regime). The entropy change on applying a field is correspondingly higher than for "brute force" nuclear refrigeration materials such as copper. For copper in 18.5 kOe, 50% of the nuclear entropy is removed at 0.7 mK, whereas in the same field this level is reached in praseodymium at 30 mK. By demagnetizing our specimen from these starting conditions we have been able to reach 12 mK, and in fact all the hear-capacity data below 30 mK were taken after a cooling demagnetization of this type. Figure 3 shows a demagnetization,

which, although not the best cooling, is the best recorded. The time taken to reduce the field to zero was about 2 h. As is clear from Fig. 1 at the lower fields, the hexagonal nuclei act as a considerable thermal load on the cooling and thus H/T is not constant. The solid line in Fig. 3 represents the ideal isoentropic cooling curve calculated from the heat-capacity data. The experimental points follow this line reasonably well except at the lowest temperatures where flux jumps in the magnet, and too fast a demagnetization rate caused considerable heating. The inset shows the entropy of the system for 0 and 18.6 kOe. With starting conditions of 65 kOe and 20 mK it should be possible to reach 1 mK. After such a demagnetization the warmup times will be extremely long as the heat capacity at 1 mK is ~2 J/mole K, and by virtue of the ordered hexagonal sites does not fall below 1 J/mole K for more than two decades in temperature.

*Permanent address: Physics Laboratory I, H. C. Ørsted Institute, University of Copenhagen, Copenhagen, Denmark.

†Present address: Department of Physics, University of Lancaster, Lancaster, U. K.

[1]T. Johansson, B. Lebech, M. Nielsen, H. Bjerrum Møller, and A. R. Mackintosh, Phys. Rev. Lett. 25, 524 (1970).

[2]B. Lebech and B. D. Rainford, J. Phys. (Paris), Colloq. 32, C1-370 (1971).

[3]B. Lebech and B. D. Rainford, private communication.

[4]J. W. Cable, R. M. Moon, W. C. Koehler, and E. O. Wollan, Phys. Rev. Lett. 12, 553 (1964).

[5]F. A. Wedgewood and B. D. Rainford, unpublished.

[6]B. Holmström, A. C. Anderson, and M. Krusius, Phys. Rev. 188, 888 (1969).

[7]K. Andres, E. Bucher, J. P. Maita, L. D. Longinotti, and R. Flukiger, to be published.

[8]A preliminary report of the present measurements was presented in *Proceedings of the Twelfth International Conference on Low Temperature Physics, Kyoto, Japan, 1970*, edited by E. Kanda (Keigaku Publishing Co., Tokyo, 1971), p. 715.

[9]B. Bleaney, Proc. Roy. Soc., Ser. A 276, 39 (1963).

[10]B. Bleaney, J. Appl. Phys. 34, 1024 (1963).

[11]O. V. Lounasmaa, Phys. Rev. 133, A211 (1964).

[12]S. A. Al'tshuler, Zh. Eksp. Teor. Fiz., Pis'ma Red. 3, 177 (1966) [JETP Lett. 3, 112 (1966)].

[13]K. Andres and E. Bucher, Phys. Rev. Lett. 24, 1181 (1970).

Side-Jump Mechanism for Ferromagnetic Hall Effect*

S. K. Lyo and T. Holstein
Department of Physics, University of California, Los Angeles, California 90024
(Received 26 June 1972)

We show the equivalence of the side-jump model of the ferromagnetic Hall effect recently proposed by Berger and the anomalous velocity contribution obtained by Luttinger and others. Specifically, starting from the cited anomalous velocity expression, we give a derivation (to the lowest Born order) of the (vector) side jump which an electron undergoes during a collision with an impurity for a system of ferromagnetically polarized free electrons, each interacting with the impurity centers, together with the concomitant spin-orbit interaction. The side jump obtained is independent of the strength and form of the impurity potential and agrees with the result of Berger.

There have been two main approaches to the anomalous Hall effect of ferromagnetic metals and alloys, namely, an itinerant electron model of Smit[1] and Luttinger,[2] and a localized electron model of Kondo[3] and Maranzana.[3] In this paper we confine ourselves to the former model; we assume that the conduction electrons are ferromagnetically polarized. In particular, we will consider the scattering by impurity centers only.

There are two important contributions to the anomalous Hall effect; one is the skew scattering[1,2] contribution which can be explained according to the Boltzmann equation by extending the collision kernel to higher Born orders. The other is the nonclassical anomalous velocity[2,4] contribution which has no classical interpretation in terms of the Boltzmann equation. In either case, the transverse Hall current is caused by the spin-orbit interaction. The anomalous velocity contribution was first obtained by Luttinger[2] (his Eq. 3.26) using rigorous quantum transport theory.[5] However, there has been no simple intuitive picture of the underlying physical mechanism for this contribution. Recently, Berger[6] proposed a