# High-Field Magnetization of Light Rare-Earth Metals

McEwen, K.A.; Ørsted, H.C.; Cock, G.J.; Roeland, W.J.; Mackintosh, A.R.

*Published in:*
Physical Review Letters

*DOI:*
10.1103/PhysRevLett.30.287

# High-Field Magnetization of Light Rare-Earth Metals

K. A. McEwen
*H. C. Ørsted Institute, University of Copenhagen, Copenhagen, Denmark*

and

G. J. Cock and L. W. Roeland
*Natuurkundig Laboratorium der Universiteit van Amsterdam, Amsterdam, The Netherlands*

and

A. R. Mackintosh
*Danish Atomic Energy Commission Research Establishment, Risø, Denmark*
(Received 18 December 1972)

The magnetization of single crystals of Eu, Sm, Nd, Pr, and Pr-Nd alloys has been measured in fields up to 37 T (370 kG). The results give new information on the magnetic properties of these metals. Of particular interest is a first-order transition from a nonmagnetic to a metamagnetic phase in double-hexagonal close-packed Pr, due to the crossing of crystal-field levels, when a field of about 32 T is applied in the hard direction at low temperatures.

The magnetic properties of the light rare earths differ substantially from those of the heavy rare earths, principally because the effective exchange is much smaller, so that crystal-field effects are correspondingly more important.[1] The difficulty of preparing monocrystalline samples has limited the availability of experimental information on these materials; but recently, single-crystal studies of the magnetic structures,[2-4] the magnetization,[5,6] and the magnetic excitations[7,8] have been performed. In this Letter, we wish to report magnetization measurements on Eu, Sm, Nd, Pr, and Pr-Nd alloys in fields as great as 37 T. These results elucidate further the magnetic properties of the light rare earths.

The samples were monocrystalline spheres, spark cut from single-crystal ingots prepared either by pulling from the melt or by strain-anneal techniques.[9] The measurements were performed at the University of Amsterdam high-field magnet,[10] in which constant fields up to 38 T can be sustained for 0.1 sec by passing a large current through a copper coil cooled with liquid Ne. Magnetic moments can be measured[11] with a sensitivity of $10^{-5}$ A m$^2$ and an absolute accuracy of $10^{-4}$ A m$^2$. As explained elsewhere,[12] deviations from a linear behavior can be determined with a much higher accuracy. Measurements were made at a number of different temperatures obtained by using different refrigerant liquids and pumping on them, but we will here be concerned principally with the results obtained at 4.2 K, which are shown for the pure metals in Fig. 1.

Eu undergoes a first-order transition to a helical magnetic structure below 94 K, with a $\vec{Q}$ along a $\langle 100 \rangle$ direction in the bcc structure; and recent neutron-diffraction studies of single crystals[4] have shown that a magnetic field along [100] gives rise to a single domain with $\vec{Q}$ along the field. We have made high-field measurements for a number of different crystal orientations, and find that the results are all identical to within the accuracy of the method, in accordance with the earlier results in lower fields.[5] These results cannot readily be understood in terms of the standard theory for the helical structure,[13] since the susceptibility in the plane is predicted to be much lower than that along the axis. However, the $Eu^{++}$ ion has an $^8S_{7/2}$ ground state, and the magnetic anisotropy is therefore expected to be very small. It is therefore energetically favorable for the moments to turn normal to the direction of an applied field, rather than for the helix to distort in its plane, leaving $\vec{Q}$ fixed and forming a cycloidal structure. As the field is increased, the moments then bend towards the field direction, forming a modified conical structure, and ultimately a ferromagnetic structure along the field direction. The susceptibility is thus approximately independent of the direction of the field. This hypothesis will be further explored by means of neutron diffraction in a magnetic field. In our highest field, a moment of about $5\mu_B$/atom has developed, so that full alignment, with an ordered moment in excess of $7\mu_B$/

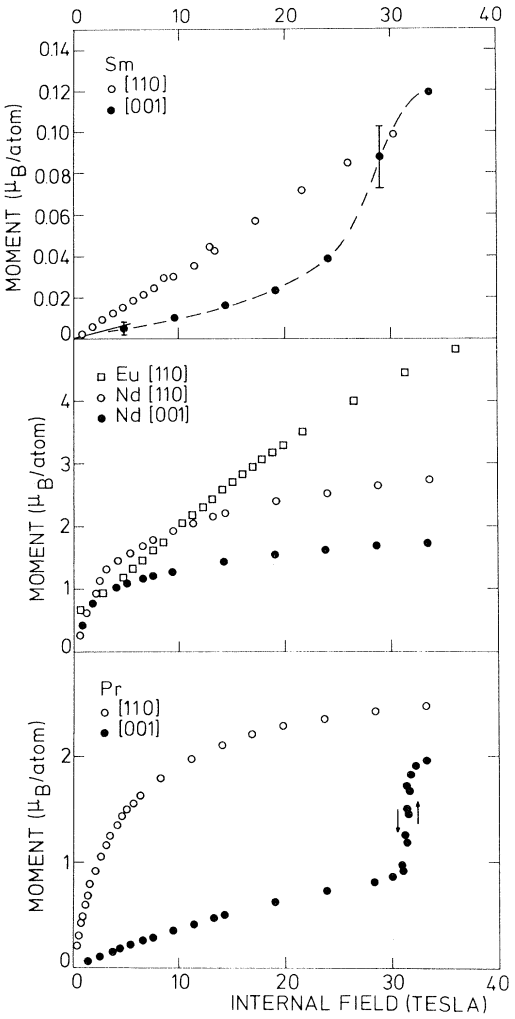


FIG. 1. High-field magnetization data for some light rare-earth metals in various directions at 4.2 K. The data have been fitted with more accurate low-field data, except for those for the [001] direction of Sm, which were matched to the point at 29 T, obtained by averaging four measurements. The low-field data obtained with a Foner magnetometer are shown as a solid line. The arrows for the [001] direction in Pr draw attention to the observed hysteresis of 0.2 T.

atom, might be anticipated at roughly 100 T.

The structure of Sm is fairly complicated, with atomic sites corresponding to two types of local symmetry, and the magnetic ordering has recently been studied by neutron diffraction.[3] At low temperatures, both the hexagonal and cubic sites form relatively simple antiferromagnetic structures, with the moments aligned parallel or antiparallel to the $c$ axis. On the hexagonal sites, the ferromagnetic sheets are normal to the $c$ axis, while on the cubic sites they are parallel to (101) planes. As may be seen in Fig. 1, the [110] basal-plane moment is linear with field but only a small fraction of the free ion moment ($\frac{5}{7}\mu_B$) is developed at 30 T. The [001] direction is magnetically hard at low fields, in agreement with previous results.[6] Since the sample magnetization at 5 T is so small ($\sim 10^{-4}$ A m$^2$), considerable difficulty was experienced in fitting these data with our low-field results, obtained in a more sensitive Foner magnetometer. We therefore averaged several measurements of the magnetization at 29 T and fitted each data set with this value. The results thus obtained at 5 T are consistent with those obtained with the Foner magnetometer, as illustrated in Fig. 1.

The [001] magnetization exhibits a rapid rise between 20 and 30 T which reduces the anisotropy to a value comparable with the statistical accuracy of the measurements. This rise may be due to a rotation of the moments on the cubic sites into the plane normal to the field direction. Such a rotation involves no change in the isotropic exchange energy, but it is necessary for the Zeeman energy to overcome the magnetic anisotropy.

Nd and Pr have double-hexagonal close-packed structures, and the sites may again be classified according to their local symmetry. At low temperatures, Nd forms complex periodic magnetic structures on both types of site.[14] Intermediate-field magnetization[5] and neutron-diffraction studies have previously established that the cubic sites are ordered ferromagnetically in a field of about 3 T applied in the [110] direction, while an antiferromagnetic moment persists on the hexagonal sites up to at least 5 T. The structure in the low-field results for this field direction shown in Fig. 1 is in agreement with previous measurements, while at high fields the magnetization attains a value somewhat less than the free-ion value of $3.27\mu_B$/atom. The $c$-axis susceptibility rises smoothly towards a value considerably lower than the free-ion limit, as a result of the crystal fields, and the anisotropy at high fields, although relatively modest, is considerably greater than at low fields.

The crystal fields have an even more profound effect on the magnetic properties of Pr. The ionic ground states on both the cubic and hexagonal sites are singlets and the exchange is sufficiently weak that there is no sign of magnetic ordering at temperatures as low as 1.8 K in a monocrystalline sample,[2] although it appears that an ordered state is formed at lower temperatures.[15]

As illustrated in Fig. 1, the magnetic moment increases smoothly with field applied in the easy [110] direction, although at 35 T it is still some way below the free-ion value of $3.20\mu_B$/atom. The effect of a field in the hard [001] direction is more striking. Neutron-diffraction[2] and susceptibility[5] measurements at intermediate fields have earlier shown that the total moment in this case is developed on the cubic sites, while the hexagonal sites are completely nonmagnetic. However, as shown in Fig. 1, there is an abrupt increase in the magnetization at $31.5 \pm 0.2$ T, which we ascribe to a first-order transition on the hexagonal sites from a nonmagnetic to a metamagnetic phase.[16] The transition is sharp to within about 0.01 T at 1.8 K, which is an order of magnitude smaller than the change in the internal field, and somewhat broader at 4.2 K. There is a pronounced hysteresis of about 0.2 T at 4.2 K, which increases as the temperature is lowered. At 14 K, there is no sharp transition but the moment rises smoothly by about $0.6\mu_B$ per hexagonal site over a field range of about 8 T, while at 65 K, all signs of the anomaly in the magnetization have disappeared.

It is believed[7] that the ground state of the hexagonal ions is $|M_J\rangle = |0\rangle$, while the first excited state is the $|\pm 1\rangle$ doublet. An applied field in the $c$ direction then reduces the energy of the $|-1\rangle$ state relative to the ground state, and, at the critical field at which they cross, a moment of $g\mu_B$ per hexagonal site would develop discontinuously. However, the value of the singlet-doublet separation deduced from neutron-scattering experiments,[7] together with molecular-field parameters which account for the easy-direction magnetization,[17] suggest that this crossing should not take place until about 50 T.[18] It seems more likely therefore, also in view of the size of the magnetization jump, which is $2.08\mu_B$ per hexagonal site, that the transition is due to the $2^{-1/2} \times (|3\rangle - |-3\rangle)$ level, which mixes with the $2^{-1/2} \times (|3\rangle + |-3\rangle)$ level and drops rapidly in energy on the application of an axial field. If this level lay about 50 K above the ground state, a transition would take place at the observed field, producing a moment increase of about $2.4\mu_B$ per hexagonal site ($g = \frac{4}{5}$). From the neutron-scattering results, the easy-axis magnetization, and the details of the magnetization in the hard direction, especially the transition field and the increase in the moment, we hope to be able to deduce the low-lying crystal-field levels on both the cubic and hexagonal sites, but this program is not yet complete.

The addition of Nd to Pr increases the tendency towards magnetic ordering, so that Pr–5.6% Nd orders antiferromagnetically on the hexagonal sites at 6.7 K and Pr–27% Nd at 12.2 K, in zero field. At the same time, the Nd causes a substantial decrease in the magnetic anisotropy, as illustrated in Fig. 2. The phase transition at high fields persists into the alloy system, however, indicating that the crystal fields at the Pr sites are not drastically altered by the addition of Nd. The transition broadens with Nd concentration, as would be expected for an inhomogeneous system, and the magnitude of the magnetization change decreases, reflecting the decrease in the number of Pr ions. The transition also moves to lower fields, which might reflect either a modification of the crystal fields or an increase in the molecular field, due to the presence of Nd.

The availability of large magnetic fields has thus allowed us to observe a number of interesting effects in the magnetization of the light rare-earth metals. In Eu and Sm the magnetic anisotropy may apparently de dominated by a large field, so that the configuration of the moments is principally determined by the combination of exchange and Zeeman energies. In Pr and Nd, the Zeeman energies are comparable to the crystal-field splittings, although the magnetization in our highest fields still falls substantially below that of the free ions. In Pr and Pr-Nd alloys, the crossing of crystal-field levels causes a first-order transition from a nonmagnetic to a magnetic phase on the hexagonal sites, and the magnetization curves give valuable information about

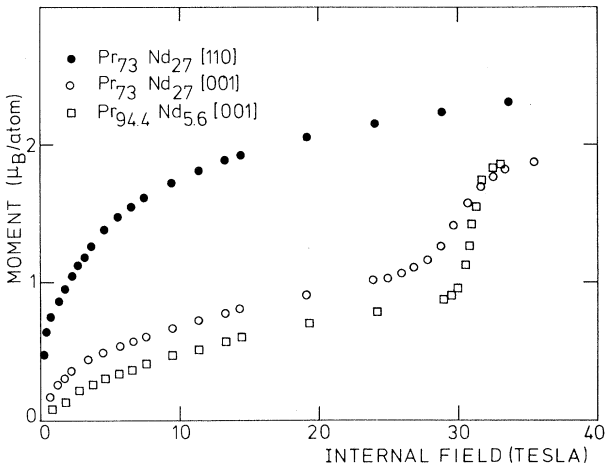


FIG. 2. Magnetization curves for Pr-Nd alloys.

the positions of these levels. In addition to those reported here, we have performed a variety of high-field measurements on single crystals of both light and heavy rare-earth metals, and a full account of these investigations will appear in due course.

We gratefully acknowledge fruitful discussions with F. A. Muller, G. de Vries, B. D. Rainford, R. J. Elliott, and M. Blume. P. Touborg and A. C. Moleman kindly assisted with the preparation and orientation of some of the crystals used in this study. This work is part of the research program of Stichting voor Fundamenteel Ondersoek der Materie which is financially supported by the Nederlandse Organisatie voor Zuiver Wetenschappelijk Ondersoek, and also benefitted from financial support through the NATO Research Grant Program.

[1]For a recent discussion of the magnetic properties of the light rare earths see A. R. Mackintosh, J. Phys. (Paris), Colloq. 32, C1-482 (1971).

[2]T. Johansson, B. Lebech, M. Nielsen, H. Bjerrum Möller, and A. R. Mackintosh, Phys. Rev. Lett. 25, 524 (1970); B. Lebech and B. D. Rainford, J. Phys. (Paris), Colloq. 32, C1-370 (1971).

[3]W. C. Koehler, R. M. Moon, J. W. Cable, and H. R. Child, in *Magnetism and Magnetic Materials—1971*, AIP Conference Proceedings No. 5 (American Institute of Physics, New York, 1972), p. 1434.

[4]A. H. Millhouse and K. A. McEwen, to be published.

[5]T. Johansson, K. A. McEwen, and P. Touborg, J. Phys. (Paris), Colloq. 32, C1-372 (1971); M. Schieber, S. Foner, R. Doclo, and E. J. McNiff, J. Appl. Phys. 39, 885 (1968).

[6]S. Foner, C. Voigt, and E. J. Alexander, in *Magnetism and Magnetic Materials—1971*, AIP Conference Proceedings No. 5 (American Institute of Physics, New York, 1972), p. 1435; K. A. McEwen and G. J. Cock, to be published.

[7]B. D. Rainford and J. C. G. Houmann, Phys. Rev. Lett. 26, 1254 (1971), and 27, 223(E) (1971).

[8]R. J. Birgenau, J. Als-Nielsen, and E. Bucher, Phys. Rev. Lett. 27, 1530 (1971).

[9]K. A. McEwen and P. Touborg, to be published.

[10]L. W. Roeland, F. A. Muller, and R. Gersdorf, Colloq. Int. Cent. Nat. Rech. Sci. No. 166, 175 (1967).

[11]L. W. Roeland, F. A. Muller, and R. Gersdorf, Colloq. Int. Cent. Nat. Rech. Sci. No. 166, 185 (1967).

[12]F. A. Muller, R. Gersdorf, and L. W. Roeland, Phys. Lett. 31A, 424 (1970).

[13]T. Nagamiya, in *Solid State Physics*, edited by F. Seitz, D. Turnbull, and H. Ehrenreich (Academic, New York, 1967), Vol. 20.

[14]R. M. Moon, J. W. Cable, and W. C. Koehler, J. Appl. Phys. 35, 1041 (1964).

[15]K. Andres, E. Bucher, J. P. Maita, L. D. Longinotti, and R. Flukiger, Phys. Rev. B 6, 313 (1972).

[16]T. Tsuneto and T. Murao, Physica (Utrecht) 51, 186 (1971); Y. L. Wang and M. R. H. Khajehpour, Phys. Rev. B 6, 1778 (1972).

[17]B. D. Rainford, in *Magnetism and Magnetic Materials—1971*, AIP Conference Proceedings No. 5 (American Institute of Physics, New York, 1972), p. 591

[18]P. A. Bak, G. J. Cock, and B. D. Rainford, private communication.

# Resistive Anomalies at the Critical Point of Isotropic Ferromagnets*

T. G. Richard and D. J. W. Geldart
*Department of Physics, Dalhousie University, Halifax, Nova Scotia, Canada*
(Received 30 November 1972)

The effect of spin fluctuations on electrical resistivity $\rho(T)$ is studied in a single-band model. It is shown that $d\rho(T)/dT$ varies as the magnetic specific heat for $T<T_c$ as well as $T>T_c$ and that both short-range and long-range correlations yield $d\rho(T)/dT>0$ for $T>T_c$.

The study of the effect of critical spin fluctuations on the electrical resistivity of metallic ferromagnets has attracted much attention. Recent reviews, to which the reader is referred for a survey of the literature, have been given by Kawatra and Budnick[1] and by Parks.[2] Theoretical discussion of resistive anomalies [i.e., singularities of $d\rho/dT=\rho'(T)$ at $T_c$] have been based on the $s$-$d$ (or $s$-$f$) exchange model used by de Gennes and Friedel,[3] in which conduction electrons are coupled by exchange interactions to localized spins $\vec{S}_{\vec{R}}$ located at lattice sites $\vec{R}$. Assuming the electrons to be weakly and quasielastically scattered by long-lived spin fluctuations, the spin contribution to the total resistivity of an isotropic system can be written in terms of the high-temperature (spin disorder) limit $\rho_0$ as

$$\rho(T)/\rho_0=\sum_{\vec{R}}\Gamma(\vec{R},T)\Phi(\vec{R}), \quad (1)$$