A numerical estimate of the largest nontrivial eigenvalue for $l=0$ through $l=4$ was obtained using (5). Repeated applications on a trial function yield the eigenfunction with largest eigenvalue. The integrations were performed by the trapezoidal rule with a mesh spacing of $\Delta=0.1$ and integrating on $R=(u^2+2z^2-2\sqrt{2}\mu uz)^{1/2}$ from $|u-\sqrt{2}z|$ to $u+\sqrt{2}z$ and on u from 0 to 4.0.

For $l=0$ we obtained in this way $\lambda_{1s}=2.783$, $\gamma=1.354$. A comparison with the previous result $\lambda_{1s}=2.776$, $\gamma=1.357$ gives an estimate of the error involved in these numerical routines. Using the λ_{2s} eigenfunction obtained previously, Eq. (7) gives an estimate $\lambda_{2s}\sim 0.52$.

The other results obtained were $\lambda_{0p}=5.657$, $\lambda_{0d}=3.547$, $\lambda_{0f}=1.997$, and $\lambda_{0g}=0.9636$ (see Table I). Notice that $\log_2\lambda_{0p}=2.5=\frac{1}{2}d+1$. This result may also be obtained exactly from (3), and it offers an independent check on our results. From λ_{0d} and λ_{1s} one obtains the estimate $\phi=\nu\log_2\lambda_{0d}=1.237$, or, using the estimate $\nu=0.7$ obtained by Jasnow and Wortis, one finds $\phi=1.28$. These results for ϕ are in good agreement with estimates obtained by other means.[3,5,7]

*Work supported in part by the National Science Foundation.

†NSF Postdoctoral Fellow (1971–72).

‡Present address: Institute for Festkörperforschung of the Kernforschungsanlage, Jülich, Germany.

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PHYSICAL REVIEW B VOLUME 6, NUMBER 1 1 JULY 1972

Magnetic-Ground-State Properties in Praseodymium Single Crystals

K. Andres, E. Bucher, J. P. Maita, and L. D. Longinotti

Bell Telephone Laboratories, Murray Hill, New Jersey 07974

and

R. Flukiger

Université de Genève, Institut de Physique de la Matière Condensée, Switzerland

(Received 24 November 1971)

From hyperfine-specific-heat measurements at very low temperatures we conclude that the ground state in double hcp Pr single crystals must be a magnetically ordered state. Within experimental error the hyperfine specific heat in a single crystal is in agreement with data on polycrystalline material. This is surprising since recent neutron-scattering data in Pr single crystals do not indicate any magnetic order down to 1.7 °K, while neutron-scattering data on polycrystalline samples indicated antiferromagnetic order with a Néel temperature of 25 °K.

INTRODUCTION

The low-temperature form of Pr is known to exhibit the double hcp structure of the *ABAC* stacking type. Within the first-nearest-neighbor approximation there are 50% sites of cubic point symmetry (*A* layers) and 50% sites of hexagonal point symmetry (*B* and *C* layers). Correspondingly the $J=4$ ground state undergoes an entirely different crystal field splitting in the two sites. The ground state in both sites, however, is expected to be a singlet. Low-field susceptibility[1] as well as resistivity measurements[2] indicate a Néel temperature of 22–23 °K in polycrystalline material. In contrast, specific-heat results only show a very weak anomaly around 3.3 °K but no λ-type anomaly at 23 °K as characteristic of a cooperative magnetic-ordering effect.[3,4] Also, the specific-heat data of various authors differ by more than 30% below 4 °K. Neutron-diffraction studies in polycrystals by Cable *et al.*[5] showed a Néel temperature of 25 °K and indicate an average moment of $0.70\mu_B$ on the hexagonal sites only. Recent hyperfine-specific-heat measurements[6] as well as Mössbauer spectroscopy results[7] on a polycrystal of double hcp Pr are also consistent with this average moment. The fact that only the hexagonal sites order[5] is understandable since it takes a minimum ratio of exchange-interaction strength divided by the separation of the first two crystal field levels in order

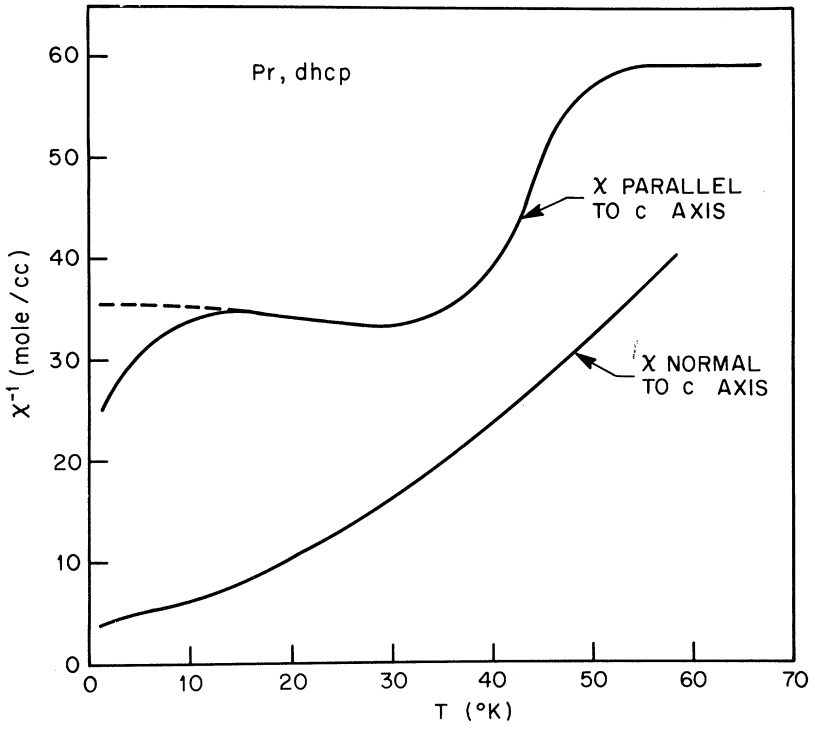

FIG. 1. Inverse molar susceptibility parallel ($\chi_{\parallel}^{-1}$) and normal ($\chi_{\perp}^{-1}$) to the c axis of a double hcp Pr single crystal plotted against temperature.

to induce a moment in a singlet ground state. This ratio seems to be overcritical only for the hexagonal sites.

Surprisingly, recent neutron-diffraction data in Pr single crystals showed no magnetic Bragg reflections down to 4.2 °K.[8,9] (The neutron-diffraction experiments have recently been extended to 1.7 °K. At this temperature there is still no evidence of magnetic order.[10]) Magnetic order in polycrystalline double hcp Pr was tentatively ascribed to strain due to strongly anisotropic thermal expansion and to the strain dependence of the exchange interactions.[8]

RESULTS

This situation prompted us to restudy the electronic properties of a high-purity double hcp Pr single crystal, particularly in view of the following two interesting possibilities: (i) If in Pr single crystals the Van Vleck paramagnetic state were indeed the ground state, there would be no hyperfine field at the Pr nuclei. Large hyperfine fields could then be induced in the direction of the largest Van Vleck susceptibility by a small external field and these fields could be used to generate very low temperatures by nuclear adiabatic cooling. This effect, originally proposed by Altshuler,[11] has been verified in a number of Van Vleck paramagnets.[12–14] (ii) If the exchange forces are very close to the critical ones, one may expect spontaneous nuclear ordering on the hexagonal sites, arising from the exchange coupling between hyperfine-induced electronic moments in the singlet ground states.[14] Such an effect might be expected in the 10^{-2} °K region.

High-purity Pr was kindly supplied by Henrie and Wong, Bureau of Mines, Reno. It was triply zone refined, the center section cut out, and etched. The very irregular rod contained only small single crystals. After casting it into a $\frac{1}{4}$-in. rod and mounting it strain free between two Ta clips, it was cycled five times through the double hcp-bcc transformation point between 750 and 830 °C at ≈4 °K/h. The largest of the three single crystals grown on the 3-in.-long sample was finally cut out strain free with a string saw and used for susceptibility and specific-heat measurements. The major impurities after zone refining were O, N, H, C in the 50–100-at. ppm level and Al, Cu, Fe, Mg, Si in the 5-at. ppm level.

Figure 1 shows the reciprocal susceptibility of the Pr single crystal vs temperature, taken at H = 100 Oe. It confirms earlier results[8,15] that at 1 °K the molar susceptibility $\chi_{\parallel}$ (parallel to the z axis) is about ten times smaller than $\chi_{\perp}$. Neutron-diffraction data in magnetic fields have shown that this anisotropy is mainly due to the hexagonal sites.[16] The low-temperature tail of $\chi_{\parallel}$ is probably due to other rare-earth impurities and/or slight misalignment of the crystal. An interesting feature is the fact that $\chi_{\parallel}$ actually decreases with decreasing tem-

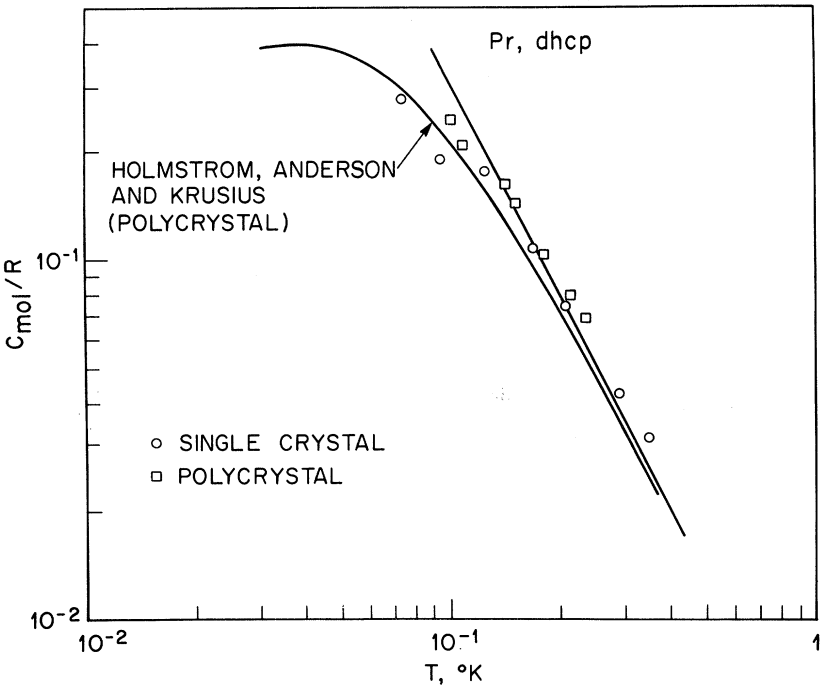

FIG. 2. Hyperfine molar specific heat of a double hcp Pr single crystal in a $\log_{10}C/R$-vs-$\log_{10}T$ plot (open circles). Also shown are our results on a polycrystalline sample of double hcp Pr (open squares) as well as the results by Holmström *et al.* on a polycrystalline sample of double hcp Pr.

perature below 30 °K. This can only be explained by the existence of anisotropic exchange interactions which are temperature dependent. From magnetic measurements down to 0.5 °K and from zero-field specific-heat measurements down to 1.5 °K (see Fig. 3), no evidence can be derived for a magnetic phase transition down to these temperatures. Therefore, the measurement of the hyperfine specific heat provides a crucial test whether Pr single crystals remain Van Vleck paramagnetic down to 0 °K. The results are shown in Fig. 2 on a $\log_{10}C_{mole}/R$-$\log_{10}T$ plot (open circles). For comparison we also show data taken on a polycrystalline sample of comparatively high purity (open squares, supplier, Lunex Co.), as well as recent results by Holmström *et al.*[6] The polycrystalline data were taken in an adiabatic demagnetization cryostat, whereas the present single-crystal results were obtained in a dilution refrigerator. The sample was in Apiezon grease contact with about 2000 No. 40 copper wires. Thermal contact between those wires and the mixing chamber was made with a superconducting thermal switch. Temperatures were measured with As-doped Ge resistors calibrated against cerium magnesium nitrate. We found it extremely difficult to take specific-heat data in the single crystal below 100 m °K because of unexpected long spin-lattice relaxation times of the order of hours below this temperature, a problem not occurring in polycrystalline material. The two lowest points therefore carry a larger error bar than those above 100 m °K.

It can be seen from Fig. 2 that there is virtually no difference in hyperfine specific heat between polycrystalline and single-crystalline material. This strongly suggests that the magnetic ground state in both materials is the same, namely, an antiferromagnetically ordered state. Assuming a uniform moment on the hexagonal sites only, we find $0.73\mu_B$ per site. In Fig. 3 we have plotted the specific heat in single-crystalline Pr above 1.5 °K in zero field as well as in a field of 9 kOe. Also plotted are some relevant specific data on polycrystalline material taken from the literature.[3,4] All these latter curves exhibit a specific-heat anomaly around 3.3 °K which we do not find in our single crystal. Instead, we observe a lowering of the specific heat in a field of 9 kOe below about 3.1 °K. This is in agreement with an antiferromagnetically ordered ground state and indicates the "freezing out" of spin waves due to the creation of an energy gap in the spin-wave spectrum by a magnetic field. We conclude that the anomaly around 3 °K observed by other authors must be due to impurities such as PrO_x or PrH_x. It should also be emphasized that the magnitude of the specific heat of our double hcp single crystal at 1.5 °K in zero field is a factor of 4 larger than that for double hcp La. Even if allowance is made for the evidently present hyperfine part, the remaining 200% excess specific heat must be associated with spin-wave entropy taken from $R\ln(2J+1)$. This again is consistent with an ordered ground state and a small gap in the spin-wave spectrum.

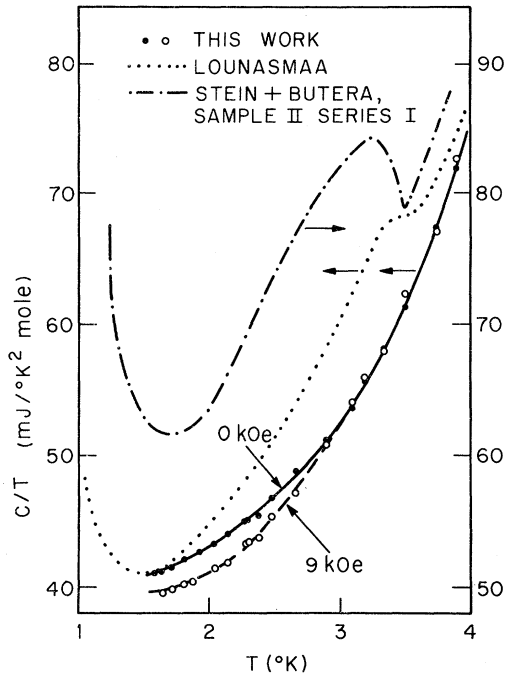

FIG. 3. Molar specific heat C/T vs T of a double hcp Pr single crystal between 1.5 and 4 °K with typical reference curves on polycrystalline material.

CONCLUSIONS

We propose to explain the observed properties of single-crystalline and polycrystalline double hcp Pr as follows: In both materials, anisotropic exchange interactions are strong enough to produce an induced-moment state below about 25 °K. This is close to the temperature below which $\chi_{\parallel}$ is decreasing. The induced moment is located on the hexagonal sites and oriented normal to the c axis, the type of order being antiferromagnetic. In polycrystalline material, there is enough strain in the crystallites to produce magnetic anisotropy also in the planes normal to the c axis. Hence in each crystallite a preferred orientation exists and the moment can be seen by Bragg reflections in neutron scattering. The transition is also visible in the magnetic susceptibility, since some of the domains will be oriented such that one measures their longitudinal susceptibility, which decreases below the ordering temperature. In a single crystal, however, there is almost no magnetic anisotropy in the planes normal to the c axis: The antiferromagnetically aligned moments have no preferred orientation in the planes. Magnetic-susceptibility measurements normal to the c axis will then always measure the transverse susceptibility in the antiferromagnetic state. The transverse susceptibility, however, is not expected to change much with temperature and is actually hard to distinguish from the susceptibility of a Van Vleck paramagnet. This would explain why the ordering temperature cannot easily be determined by susceptibility measurements, and also why the neutron-scattering data show strong antiferromagnetic correlations but no Bragg reflections. This model is also not inconsistent with the assumption of a small gap in the spin-wave spectrum of the ordered state. We can expect two transverse and one longitudinal spin-wave branch to exist in the induced-moment ground state, and we would require that one of the transverse branches has almost no energy gap above the ground state. This is compatible with the assumption that there is almost no magnetic anisotropy in the plane normal to the c axis. It is still surprising that no ordered moments in zero field have been seen by neutron scattering even at 1.7 °K. The anisotropy energy of the ordered domains in the plane normal to the c axis is apparently so small that cooling to below 1 °K is necessary to "freeze" the moments and obtain Bragg reflections.

As far as nuclear-cooling experiments in single crystals are concerned, the success of those would depend on the nuclear spin-lattice relaxation rates of the cubic sites. If those are substantially smaller than the long relaxation rates of the hexagonal sites, a nuclear-cooling experiment in a Pr single crystal is still possible at low enough temperatures, say, below 60 m °K. The nuclear spin system of the hexagonal sites would then be thermally decoupled from the cubic sites and remain at some arbitrary temperature, and one would cool only the nuclei on the cubic sites. Such experiments are being planned. Nuclear-cooling experiments on a polycrystalline sample of Pr have already been carried out by Gregers-Hansen *et al.*[17] Working with the Van Vleck paramagnetic cubic sites, cooling from 30 to 12 m°K has been observed.

ACKNOWLEDGMENTS

We would like to thank Dr. T. H. Henrie and Dr. M. M. Wong, U. S. Bureau of Mines, Reno, for supplying high-purity Pr metal.

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