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[1]For a review, see I. F. Silvera, in *Proceedings of the Fourteenth International Conference on Low Temperature Physics, Otaniemi, Finland, 1975,* edited by M. Krusius and M. Vourio (North-Holland, Amsterdam, 1975), Vol. 5, p. 123.

[2]J. F. Jarvis, H. Meyer, and D. Ramm, Phys. Rev. 178, 1461 (1969).

[3]A. F. Schuch, R. L. Mills, and D. A. Depatie, Phys. Rev. 165, 1032 (1968).

[4]N. S. Sullivan, M. Devoret, B. P. Cowan, and C. Urbina, Phys. Rev. B 17, 5016 (1978).

[5]W. N. Hardy, A. J. Berlinsky, and A. B.Harris, Can. J. Phys. 55, 1150 (1977).

[6]A. B. Harris, Phys. Rev. B 1, 1881 (1971).

[7]V. V. Goldman, unpublished.

[8]R. D. Etters, N. M. Kulkarni, and J. C. Raich, J. Low Temp. Phys. 10, 573 (1973); P. J. Berkhout and I. F. Silvera, Comm. Phys. 2, 109 (1977).

[9]We thank M. Sprik for pointing out that mixing can also effect $T_{\alpha d}$.

[10]A. B. Harris, A. J. Berlinsky, and H. Meyer, Phys. Rev. B 7, 4720 (1973).

[11]However, from Eq. (4) it appears that mixing can be considered as an effective, small change in the interaction.

[12]R. Jochemsen, A. J. Berlinsky, F. Verspaandonk, and I. F. Silvera, J. Low Temp. Phys. 32, 185 (1978).

[13]I. L. Spain and S. Segall, Cryogenics 11, 26 (1965).

[14]A. Driessen, J. A. de Waal, and I. F. Silvera, to be published.

[15]P. Pedroni, H. Meyer, F. Weinhaus, and D. Haase, Solid State Commun. 14, 279 (1974).

[16]L. Lassche, P. Zandveld, and I. F. Silvera, unpublished.

[17]S. A. Dickson and H. Meyer, Phys. Rev. 138, A1293 (1965).

[18]N. S. Sullivan, J. Phys. (Paris) 37, 981 (1976).

Nuclear Magnetic Ordering in $PrCu_6$

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We have observed in $PrCu_6$ a sharp peak in the heat capacity and rapid change in the magnetization at 2.5 mK consistent with the occurrence of nuclear magnetic ordering below that temperature. Applying magnetic fields greater than 100 G rounds the transition. The behavior observed is similar to ferromagnetism in electronic systems, but other structures showing weak "ferromagnetism" are not ruled out.

We have observed the transition from the paramagnetic to a nuclear ordered state in $PrCu_6$ at 2.45 ± 0.05 mK. We believe this to be the first observation of this ordered state in a metal in which the complete system (magnetic moments, conduction electrons, and lattice) is in thermal equilibrium. The heat capacity and magnetization and their dependence on temperature and applied magnetic field unambiguously display the characteristics of such a transition. Precursors to such ordering have previously been observed, but the transition itself had not been traversed.[1]

The praseodymium in $PrCu_6$ and many other compounds has a singlet electronic ground state, the other eight states in the $^3H_4$ manifold usually being raised above 10 K in energy by the crystalline field. Thus, at low temperatures the Pr ions exhibits temperature-independent Van Vleck paramagnetism. The exchange is apparently too small to induce moments and magnetic ordering in the electronic system, as shown possible by Trammell[2] and Bleaney.[3] Such a state was first observed in fcc Pr metal by Bucher and co-workers[4,5] with a Curie temperature of approximately 20 K. In the absence of nuclear moments hyperfine coupled to induced electronic moments, singlet ground-state systems do not order at any temperature if the ratio $2\mathcal{J}z/\Delta$ of exchange to crystal-field splitting (z being the number of nearest magnetic neighbors) is less than a critical value of order unity.

With a hyperfine coupling $A\vec{I}\cdot\vec{J}$ of the nuclear moments to the $4f$ electrons, two important effects occur. First, the ordering behavior is modified.[6] If $2\mathcal{J}z/\Delta$ is less than, but close to, the critical value, then the presence of a large hyperfine interaction may be enough to induce an ordered state at a temperature lower than would be observed for electronic ordering alone. The transition to such an intermediate or mixed electronic-nuclear state has been observed in $PrCu_2$ at 54 mK[7] and in $PrCu_5$ at 24 mK.[8-10] A broad (Schottky-like) heat-capacity peak with a maximum below the magnetic ordering temperature

was observed in $PrCu_5$.[8] This is the behavior expected from molecular-field models of this type of ordering.[6] If magnetic ordering occurs above 1 K in singlet ground-state systems, it is probably to a pure electronic state; if the critical temperature lies between 10 mK and 1 K, the state is probably a mixed one. Second, the effect of an applied magnetic field H_0 on the nucleus is enhanced, i.e., the net field at a Pr nucleus in the sample is

$$H_n = (1+K)H_0 = \eta H_0,$$

where K is the Knight shift and η the enhancement factor. For singlet ground-state Pr materials, η is typically between 5 and 20. This makes such materials excellent candidates for nuclear coolants.

If $2gz/\Delta$ is considerably below the critical value, then the system can best be described as a nuclear magnet with the nuclei coupled by an indirect exchange interaction. For Pr^{3+} ions for which $A/\Delta \approx 2\times10^{-3}$, this condition is expected to apply for transitions occurring below 10 mK. In this case, the magnetic nucleus in a Pr ion i can be thought of as inducing a $4f$ electronic moment in that ion. This moment then couples to the $4f$ electrons in a neighboring ion j by the Ruderman-Kittel-Kasuya-Yosida interaction and in turn to nucleus j through the hyperfine interaction. An indirect exchange energy of order 1 mK can be understood in this way.[11] The molecular-field models predict a sharp heat-capacity anomaly in this regime, distinguishing it experimentally from the mixed state.

Figure 1 shows the thermal and magnetic signatures of such a transition. Figure 2 contrasts the heat-capacity peak of $PrCu_6$ with that of $PrCu_5$. These results are in qualitative agreement with those of molecular-field theory. (See Andres, Ref. 6, Fig. 6.) Note that, unlike the thermal and magnetic anomalies in $PrCu_2$ and $PrCu_5$, the peak in the heat capacity and the rapid change in the magnetization coincide in $PrCu_6$. From our magnetization data we estimate that the peak in the susceptibility lies lower than 2.6 mK at low applied fields. The heat-capacity data were obtained with use of 100-sec heating pulses from a resistor. At this time we cannot definitely rule out a λ anomaly in the heat capacity, but a warm-up curve taken at a heat input rate of 13 ± 1 erg/min (the residual heat leak) shows no $dT/dt = 0$ portion (implying the heat capacity $C \neq \infty$). Thermal relaxation times of 5–10 min were observed near the transition, so that some thermal smearing may exist in the data. (Random errors in the heat capacity are estimated to be less

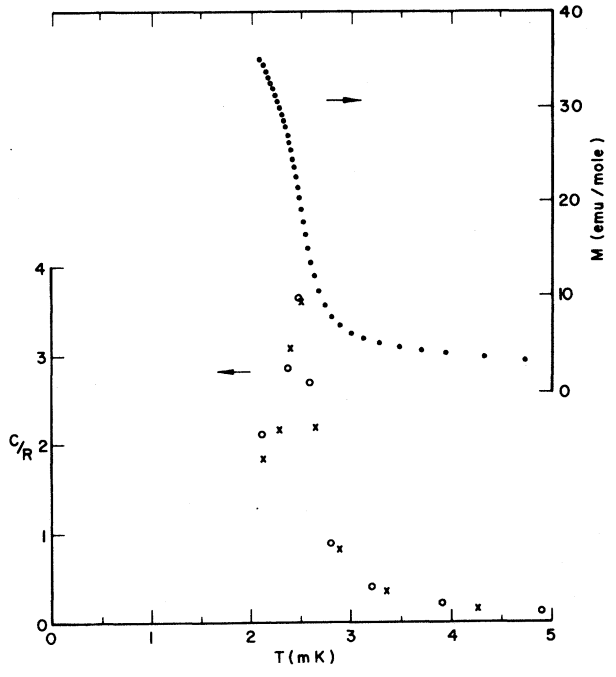

FIG. 1. Magnetization (dots) and specific heat (open circles and crosses) vs temperature, both at an applied field of 35 G. The two different symbols in the specific-heat curve represent two different data runs.

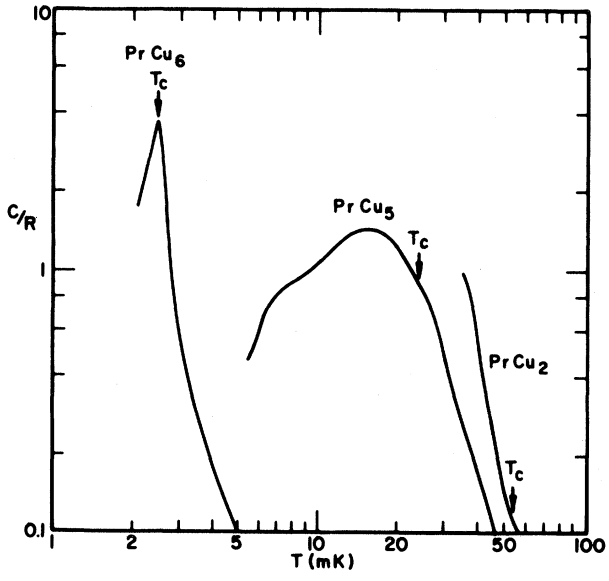

FIG. 2. Comparison of specific heats of $PrCu_6$ with mixed regime systems. The data for $PrCu_2$ and $PrCu_5$ are taken from Refs. 7–9. The arrows for $PrCu_2$ and $PrCu_3$ indicate the peaks in the magnetic susceptibility. For $PrCu_6$, see text.

than 5% at all temperatures. A systematic error, respectively raising and lowering the values below and above the peak by no more than 10%, could occur due to the long thermal relaxation time and the varying rate of increase of the temperature.)

The experiments were conducted using a metal Dewar and cryostat with a dilution-refrigerator unit. Initial temperatures of about 15 mK were achieved. A 40-kG superconducting magnet was used for demagnetizations and for applying a field to the sample and a 5.5-kG superconducting magnet for the nuclear-orientation thermometers (see below). The $PrCu_6$ sample was prepared for us at the Ames Laboratory of the Department of Energy at Iowa State University as a 1.7-cm-diam by 1.7-cm-long ingot weighing 28.6 g and examined there by x-ray diffraction and optical microscopy. The sample made thermal contact to the mixing chamber through a Pb heat switch operating in the fringing field of the 40-kG magnet.

The temperature of the $PrCu_6$ was measured with two nuclear orientation thermometers and a static nuclear susceptibility thermometer. The former thermometers provided a calibration of the absolute temperature; and the latter, fast response and high resolution. The orientation thermometers, ^{60}Co in Ni and ^{54}Mn in Ni, were attached to the end of a bus of high-purity silver strips 25 cm long and operated in a separate 5.5-kG magnet. The susceptibility of $\frac{1}{2}$ g of tin metal enriched to 85% ^{119}Sn was measured in a 400-G field trapped in a Nb cylinder with use of a flux transformer and superconducting quantum interference device (SQUID) magnetometer. The tin was independently attached to the $PrCu_6$ by high-purity Ag wires. Figure 3 shows the calibration of this thermometer against ^{60}Co in Ni. Because of deviations from T^{-1} above 20 mK, we have used only data between 2 and 20 mK in our analyses.

After demagnetization it took about 20 min for the temperature indicated by the SQUID to stop decreasing. This time is consistent with the thermal response to heat pulses used in the heat-capacity measurements. It took 10 h or more for the sample to warm up from 2 to 3 mK.

The magnetization was measured with us of another niobium flux transformer. The sample was in one coil of an astatic pair. Twisted niobium wires connected this coil to another coil wound around a flux-gate probe. The output of this sensor should be linearly proportional to the

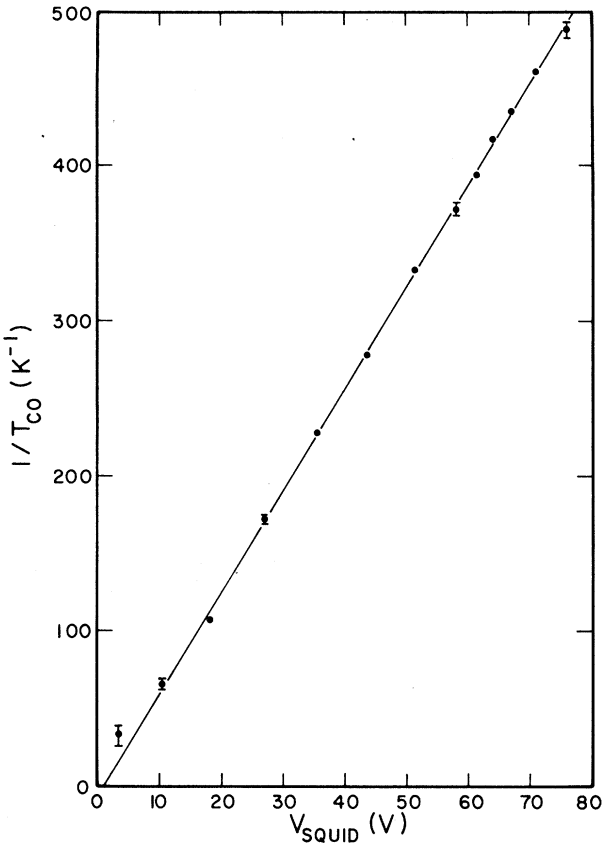

FIG. 3. Inverse temperature, as determined by ^{60}Co in Ni nuclear orientation thermometry, vs SQUID output voltage. This is the calibration of the SQUID thermometer for one of the heat-capacity data runs (the open circles) in Fig. 1.

sample magnetization. We have in a subsequent experiment measured the enhancement factor η to be 12.5 at 1 kG for this sample (viz. a range of 12 to 16.7 by other investigators[9,12]). From this separate experiment we have also obtained an absolute calibration of the magnetization. From this η we calculate the specific entropy ΔS removed at 40 kG and 16 mK, our initial conditions before demagnetization, to be $1.31R$ (73% of the Pr nuclear entropy). At both 35 and 1000 G, our measured C/T integrates to $(1.00\pm0.05)R$. An estimated eddy-current "loss" of $(0.10\pm0.01)R$ occurred during demagnetization. There is also the possibility of irreversibility on passing through the transition, particularly at low fields. In any case 75% of the calculated entropy is accounted for and no major discrepancies [e.g., $\int(C/T)dT > \Delta S$ or $\int(C/T)dT \ll \Delta S$] are observed.

The effect of an applied magnetic field on the transition has been studied up to 2.5 kG. Fields

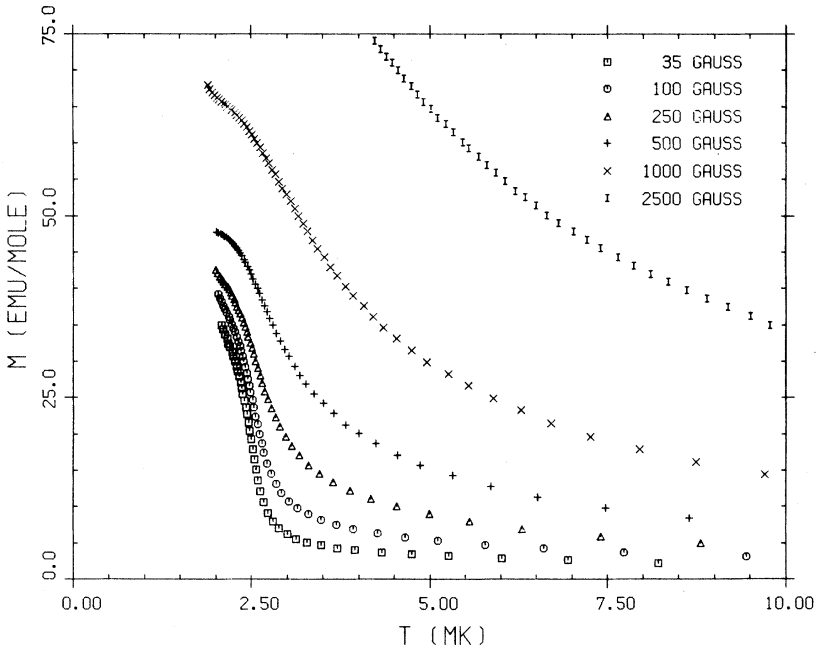

FIG. 4. Magnetization vs temperature for different applied magnetic fields. (Temperature-independent magnetization not included.)

greater than 100 G broaden the sharp heat-capacity peak, as expected. The broadening of the transition is shown in the magnetization curves in Fig. 4. The qualitative features are those of regular ferromagnetic transitions. The magnetization data between 5 and 15 mK were fitted with the simple equation

$$M(T) = M_0 + A/(T-\theta),$$

where M_0, A, and θ were varied for each value of field. The Weiss constant θ varied between -1.5 and $+0.6$ mK for different values of applied field and A was not linearly proportional to the field. These deviations are possibly because of nuclear quadrupole interactions in the orthorhombic $PrCu_6$, but more investigation is required to establish this. It is also possible that $PrCu_6$ is antiferromagnetic in zero applied field and that we are observing a canted or spin-flop state. The large magnetization observed would require a relatively large canting angle. The data are consistent with a ferromagnetic state with large anisotropy.

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[1]K. Andres and E. Bucher, Phys. Rev. Lett. 22, 600 (1969), and J. Appl. Phys. 42, 1522 (1971).

[2]G. T. Trammell, Phys. Rev. 131, 932 (1963).

[3]B. Bleaney, Proc. Roy. Soc. London, Ser. A 276, 19 (1963).

[4]E. Bucher, C. W. Chu, J. P. Maita, K. Andres, A. S. Cooper, E. Buehler, and K. Nassau, Phys. Rev. Lett. 22, 1260 (1969).

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

[6]See, for example, T. Murao, J. Phys. Soc. Jpn. 33, 33 (1972); K. Andres, Phys. Rev. B 7, 4295 (1973); B. B. Triplett and R. M. White, Phys. Rev. B 7, 4938 (1973).

[7]K. Andres, E. Bucher, J. P. Maita, and A. S. Cooper, Phys. Rev. Lett. 28, 1652 (1972).

[8]K. Andres, E. Bucher, P. H. Schmidt, J. P. Maita, and S. Darack, Phys. Rev. B 11, 4364 (1975).

[9]J. L. Genicon, thesis, University of Grenoble, 1978 (unpublished).

[10]J. L. Genicon, J. L. Tholence, and R. Tournier, J. Phys. (Paris), Colloq. 40, C6-798 (1978).

[11]K. Andres and E. Bucher, Phys. Rev. Lett. 22, 600 (1969), and 24, 1181 (1970).

[12]K. Andres and E. Bucher, J. Low Temp. Phys. 9, 267 (1972).