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EXPERIMENTAL EVIDENCE FOR SPONTANEOUS NUCLEAR ORDERING IN PARAMAGNETIC PrBi

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An unexpected ordered state among Pr nuclei in the Van Vleck paramagnet PrBi is inferred from a sharp increase in specific heat at 10 mK as well as from the onset of strong irreversible heating when sweeping the field at these temperatures. Several possible explanations are discussed, among which the coupling between the nuclei via hyperfine interaction (within the ions) and exchange interaction (between the ions) is likely to be the true ordering mechanism.

In the intermetallic compound PrBi which has the rocksalt structure, the $^3H_4$ state of the Pr ion is crystal-field split with a singlet Γ_1 as the lowest state, resulting in zero hyperfine field and therefore leaving the nuclei in the $(2I+1)$-fold degenerate ground state. ($I=\frac{5}{2}$ for Pr^{141}.) It has been shown in a previous Letter[1] how this degeneracy can be effectively lifted in an external magnetic field because of the large induced hyperfine interaction arising from admixing higher excited magnetic states into the nonmagnetic ground state, and how one can use this compound for nuclear adiabatic demagnetization starting from relatively high temperatures. We have performed such demagnetizations from different starting temperatures in the range 16-80 mK and find that the end temperature reached is never lower than 9 mK. Under the assumption of perfect reversibility, this would indicate the onset of some kind of order among the Pr nuclei. In order to demonstrate experimentally the expected decrease in entropy around 10 mK in zero field, we have performed a specific heat measurement from 10 to 150 mK in zero field following a nuclear adiabatic demagnetization.

The experimental arrangement is shown schematically in Fig. 1. Temperatures are measured with a cerium magnesium nitrate (CMN) thermometer consisting of 23 mg CMN powder mixed with Apiezon grease and 400 No. 42 copper wires. The relaxation time of this thermometer at 10 mK is about 4 min. The results are shown in Fig. 2, where heat content Q and specific heat C are plotted. The heat leak during the measurement is about 2 ergs/min and contributes a negligible error since the total heat content of the sample below 150 mK is 1400 ergs and the measurement is carried out in 60 min. We do indeed observe a large increase in specific heat around 10 mK which is consistent with the onset of nuclear ordering. The specific heat remains large to above 100 mK and actually has a shallow peak around 115 mK. This peak can be explained, however, as the contribution of a fraction of one percent of a rare-earth impurity which orders around that temperature. The entropy computed from these data is shown in Fig. 3. Also plotted in Fig. 3 is the entropy in 15.1 kOe, our magnetizing field, computed from the observed effec-

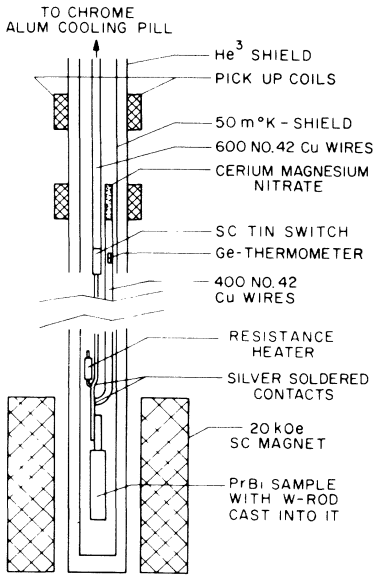

FIG. 1. Experimental arrangement for hyperfine-enhanced nuclear adiabatic cooling.

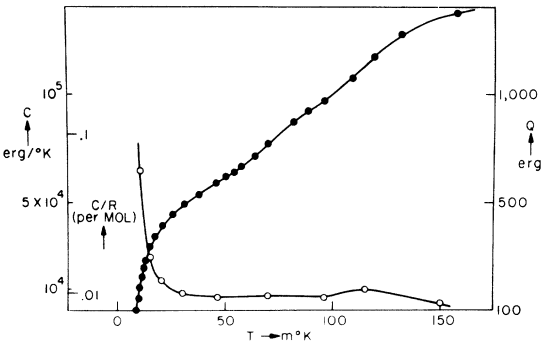

FIG. 2. Heat content Q and molar specific heat C/R of PrBi between 10 and 150 mK.

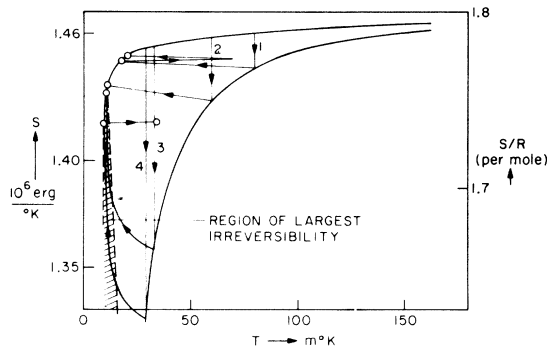

FIG. 3. Molar entropy of PrBi in 0- and 15.1-kG between 10 and 150 mK (with several magnetization and demagnetization runs starting from various temperatures included).

tive gyromagnetic ratio of 13 kHz/Oe,[2] neglecting any interaction between nuclei. We can now check our adiabatic demagnetizations for reversibility in this diagram. Shown are four actual demagnetizations. The heat of magnetization in run 4 (vertical arrow) has actually been measured by observing the corresponding temperature increase in the chrome alum salt. It amounts to 4800 ± 200 ergs in good agreement with the theoretically expected 4400 ergs (the sample contained 1.384 g Pr). As can be seen, runs 1 and 2 agree well with the measured zero-field entropy curve if we assume about 10% irreversible entropy production. Runs 3 and 4, however, show much more irreversible entropy production when approaching 10 mK. This suggests that one reaches an ordered state which shows hysteretic behavior. A fifth run (not shown in Fig. 3) with 0.364 g Pr actually started at 16 mK and ended at 17 mK, indicating that the irreversible entropy production exceeded the cooling entropy. Generally, the lower the starting temperature, the larger the irreversible effects. These heating effects are observed only when switching off the field, and they can therefore not be due to eddy currents or be of magnetostrictive origin. Theoretically one can think of various reasons for the onset of order among the Pr nuclei: (I) ordering due to zero-field splitting of the $2I+1$ nuclear levels; (II) ordering due to interactions with Pr neighbors, leading to a cooperative phenomenon, e.g., (i) enhanced nuclear dipole interaction, (ii) coupling between nuclei via hyperfine interaction and exchange interaction between Pr ions.

It is easy to show that in our case of crystal fields of cubic symmetry, case I is not expected to occur,[3] and besides, based on our observation of strong irreversibility at low temperatures, case I cannot be the explanation. Case II(i) can easily be evaluated:

$$E_{\mathrm{dip}} = \mu^2(1+K)^2/r^3, \tag{1}$$

where μ is the Pr^{141} nuclear moment ($4.28\mu_N$), $r = 4.57$ Å, and $K = (H_{\mathrm{eff}} - H_0)/H_0$ (H_{eff} = effective hyperfine field at the nucleus, H_0 = applied field) is the observed Knight shift ($K = 9$). E_{dip} comes out to be only 3.5×10^{-6} K, much too small to explain our effect. Case II(ii) on the other hand is likely to explain our observed ordering in PrBi, and we would like to present two different estimates to prove that case II(ii) gives the correct order of magnitude of nuclear ordering temperature.

The induced hyperfine field $H_{\mathrm{eff}} - H_0$ is due to the polarization of the singlet ground state in an external field. The resulting hyperfine splitting can formally be equated to the splitting of hyperfine-induced $4f$ moments ΔJ_f (which are proportional to the nuclear spin quantum number I) in the external field. The basic idea then is to consider the exchange coupling between those hyperfine-induced $4f$ moments to determine the ordering temperature. To find ΔJ_f we write

$$g_N\mu_N I(H_{\mathrm{eff}} - H_0) = g_J\mu_B \Delta J_f H_0, \tag{2}$$

or

$$\Delta J_f = IKg_N\mu_N/g_J\mu_B, \tag{3}$$

where K is the Knight shift already defined above. Since PrBi is metallic we first consider the indirect exchange interaction via conduction electrons. Using the Ruderman-Kittel expression[4] for the coupling energy between neighboring nuclei we replace

$$I \rightarrow IKg_N\mu_N/g_J\mu_B, \tag{4}$$

and

$$\mathcal{J}_{sn} - \mathcal{J}_{sf}, \tag{5}$$

and obtain the following expression for the exchange energy between two nearest neighbors:

$$E_{\text{exch}} = (IK)^2 \left(\frac{g_N \mu_N}{g_J \mu_B}\right)^2 N(0) \mathcal{J}_{sf}^2 \left(\frac{V_a}{V_e}\right)^2 \times 3\pi \frac{x\cos x - \sin x}{x^4} \tag{6}$$

with

$$x = 2k_F r.$$

We derive $N(0)$, k_F, and V_e, the density of states per conduction electron, the Fermi wave vector, and the volume per conduction electron, respectively, from the observed electronic-specific-heat coefficient $\gamma = 0.8$ mJ/K^2 mole Pr assuming that $m^* = m_e$. This might appear to be a crude approximation. It is noteworthy, however, that in LaSb, in which we found the same γ value,[5] an electron carrier concentration of 2.5×10^{21} cm^{-3} was derived from transport and galvanomagnetic properties[6] compared with 1.83×10^{21} cm^{-3} as calculated from our specific-heat data. For $\mathcal{J}_{sf}$ we take 0.7 eV, a value found by Jones[7] from Knight-shift measurements in PrP. V_a is the volume per Pr atom and r again the nearest Pr-Pr distance. Equation (6) then leads to an ordering temperature of 17 mK which is about the observed order of magnitude.

Now the true nature of exchange in PrBi is not known, and it is therefore worthwhile to estimate this interaction alternatively from the ordering temperatures of the two neighboring compounds CeBi and NdBi in which the rare-earth ions have a magnetic ground state. We can write

$$T_c/T_N = (\Delta J_f/J_{\text{eff}})^2, \tag{7}$$

where T_N is the ordering temperature and J_{eff} the effective angular momentum in the ground state of either CeBi or NdBi. For CeBi $T_N = 25$ K and[8] $J_{\text{eff}} = \frac{5}{6}$, for Nd $T_N = 24.5$ K[5] and $J_{\text{eff}} = 11/6$. These numbers lead to values of T_c of 21 and 4.3 mK again in reasonable agreement with our observation. A third estimate of the exchange interaction can be obtained from crystal-field parameters (computed from the observed Stark-type specific-heat anomaly between 1.5 and 30 K) and the observed Van Vleck susceptibility $\chi(T=0)$ in PrBi (0.0604 cm^3/mole Pr[5]). Using the molecular field approach we can write

$$\chi = \chi_c/(1-\bar{\mathcal{J}}\chi_c). \tag{8}$$

χ_c, the crystal field susceptibility, was determined experimentally in the dilute limit of PrBi in LaBi to be 0.047 cm^3/mole Pr.[5] The splitting between the ground state Γ_1 and the next higher magnetic state Γ_4 was found to be[5] 62 ± 2 K leading to χ_c of 0.051 cm^3/mole Pr (neglecting sixth-order crystal-field-potential terms). The exchange derived from (8) yields an ordering temperature of only $T_c = 0.29$ mK, as computed from

$$kT_c = \tfrac{1}{3}(g_J \mu_B)^2 \bar{\mathcal{J}} (\Delta J_f)^2. \tag{9}$$

This is about an order of magnitude less than observed. A very possible explanation of this discrepancy may be the complex nature of the exchange interaction which we may have in PrBi, and which does not enter the molecular field approximation, since here one considers only the $q = 0$ component of the Fourier-transformed exchange interaction. The importance of $\bar{\mathcal{J}}(q)$ is especially suggested from the complicated ordering in CeBi[8] and NdBi.[5] $\bar{\mathcal{J}}(q)$ may exhibit strong peaks for certain q values leading to a much stronger coupling between the nuclei than estimated by (9).

We would like to mention in this connection the work by Grover,[9] Cooper,[10] and Wang and Cooper[11] who used many-body techniques to treat the problem of a system of ions in a singlet ground state which are exchange-coupled together. These authors find spin-wavelike excitations in the system at $T = 0$ which consist of admixtures of excited and ground states varying from ion to ion in a wavelike manner. Due to these excitations being bosons, they are still populated at $T = 0$ with their zero-point energy and can (via hyperfine coupling) mediate an interaction between nuclei in a manner similar to the one considered by Suhl[12] and Nakamura.[13] No reliable quantitative calculations along these lines exist so far. We would, however, expect the magnitude of the nuclear coupling in this model to be between the limits estimated above, since the underlying physics is essentially the same.

It thus seems that a coupling between nuclei mediated by the hyperfine and exchange interactions is the most likely explanation of our observed ordering phenomenon which, to our knowledge, is the first of its kind. A determination of the true nature of the ordered state must await more detailed information on specific heat, mag-

netization, and eventually Mössbauer-effect measurements down to below 10 mK.

We are very much indebted to W. F. Brinkman for many suggestions and his help in deriving Eq. (6), and we would like to thank A. M. Clogston, A. C. Gossard, C. C. Grimes, and W. M. Walsh, Jr., for many stimulating discussions and critical reviews of our manuscript.

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MAGNETIC EQUATION OF STATE OF $CrBr_3$ NEAR THE CRITICAL POINT*

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We present the results of analysis of our measurements of the magnetic properties of the insulating ferromagnet $CrBr_3$ near its critical temperature. From this analysis we obtain a mathematical representation of an equation of state valid over the entire critical region.

We have used the Faraday effect to measure the magnetization M of the insulating ferromagnet $CrBr_3$ as a function of field along 30 isotherms in the temperature range $T_C - 0.9°K < T < T_C + 6.7°K$, where the critical temperature is $T_C = 32.844°K$. In this Letter we present the results of an analysis of our measurements and report the first determination of a mathematical representation for the equation of state of a ferromagnet which is valid over the entire critical region. Our measurements[1] provided the first verification of the scaling hypothesis[2-4] for an insulating or localized-spin ferromagnet. Experiments to test the scaling hypothesis in metallic ferromagnets have been done by more conventional methods.[5-7]

We define the reduced magnetization $\sigma = M/M(0°K)$ and the scaled magnetization $m = \sigma|1-T/T_C|^{-\beta}$, where β gives the shape of the coexistence curve. Our data cover the range $0.01 \lesssim m \lesssim 6.5$ plus the critical isotherm where m is infinite. Scaling has been verified[5] in CrO_2 for $0.12 \lesssim m \lesssim 2.3$ but only for $T > T_C$. The experimental results of Kouvel and Comly[6] ($0.42 \lesssim m \lesssim 2.8$) and of Arrott and Noakes[7] ($0.23 \lesssim m \lesssim 4.6$) for nickel are consistent with scaling laws for both $T > T_C$ and $T < T_C$. A scaling law equation of state has been shown to hold for a number of fluids in the critical region.[8]

We first analyzed data near the critical isochore, the coexistence curve, and along the critical isotherm to determine the values $\gamma = 1.215 \pm 0.015$, $\beta = 0.368 \pm 0.005$, and $\delta = 4.28 \pm 0.1$. These exponents were used to compute the scaled magnetic field $h = H|t|^{-\beta\delta}$ and the scaled magnetization $m = \sigma|t|^{-\beta}$, where $t = (T-T_C)/T_C$.

The scaling laws predict that h is a function of m only, viz.,

$$h = h(m).$$

This is equivalent to the homogeneity argument of Widom[2] or the equation of state proposed by Griffiths.[4] Our measurements enable an experimental determination of the scaling function $h(m)$. The accuracy of our magnetization measurements is comparable to that of nuclear magnetic resonance and our data are sufficiently precise that we may use the experimental scaling function to establish the mathematical form of $h(m)$. This mathematical representation constitutes an equation of state valid over the entire critical