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Evidence for Antiferromagnetism in $CoBr_2\cdot 6H_2O$†

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An antiferromagnetic-paramagnetic transition has been observed in a single crystal of $CoBr_2\cdot 6H_2O$ by by using the proton resonance technique and by measuring the heat capacity in the temperature range 1.65–5.05°K. The Néel temperature, obtained by the magnetic measurement is 3.08°K while the heat capacity measurement gave 3.07°K. The entropy change associated with the transition was calculated from the heat capacity data and yielded 1.42 cal/mole deg. The contribution to the entropy change above the Néel temperature was approximately 38% of the total entropy change, which indicates a rather slow diminution of the short-range ordering of the Co^{++} spins.

A PRELIMINARY study of the magnetic properties of $CoBr_2\cdot 6H_2O$ by the proton resonance technique has indicated that it possesses an antiferromagnetic state below 3.08°K. In conjunction with this study, heat capacity measurements have also been made in order to determine whether the λ-type anomaly, characteristic of the antiferromagnetic-paramagnetic transition, could be observed.

The heat capacity measurements were made in the temperature range of 1.65–5.05°K using a vacuum calorimeter described elsewhere.[1] The crystals were grown from an aqueous solution at room temperature and are monoclinic.[2] These crystals are similar in external appearance to the crystals of $NiBr_2\cdot 6H_2O$. Their point group is $2/m$ but their space group is apparently not known. The crystal used in the heat capacity experiments was approximately 3 cm long and 1 cm wide, and weighed 3.191 g.

The results are shown in Fig. 1. The heat capacity appears to rise very rapidly in a temperature interval of 0.06°K to a value of approximately 3.3 cal/mole deg, at the Néel temperature of 3.07°K, and then decreases continuously due primarily to the reduction in the short-range ordering of the Co^{++} spins. To estimate the entropy change associated with this transition, it is convenient to separate the total magnetic entropy into contributions above and below the Néel temperature. Friedberg[3] and Kapadnis and Hartmans[4] have suggested a method for doing this. In the paramagnetic state, the magnetic specific heat will be inversely proportional to the square of the temperature. This is based on work by Van Vleck[5] which describes the behavior of a system of paramagnetic ions with magnetic dipole-dipole and exchange coupling. It is believed that $CoBr_2\cdot 6H_2O$ does represent such a system. The lattice contribution will be proportional to the cube of the temperature, as well, so that the total heat capacity will be the sum of these two terms. By plotting CT^2 *versus* T^5 for those measurements above the Néel temperature, a straight line was obtained and the intercept gave the constant of proportionality for the the magnetic contribution. This value is 11.0 cal deg mole^{-1}. Consequently, the magnetic contribution to the entropy was obtained by evaluating the integral

$$\int_{3.20}^{\infty} \frac{11.0}{T^3} dT.$$

This was 0.54 cal/mole deg. To obtain the magnetic entropy below the Néel temperature, a plot of C/T *versus* T was made. The area under this curve extrapolated to 0°K was graphically determined. The value obtained in this way, 0.88 cal/mole deg, therefore, represents the entorpy change below the Néel temperature. The total entropy change is 1.42 cal/mole deg. The entropy change expected from $R\ln(2S+1)$ is 1.38 cal/mole deg where $S=\frac{1}{2}$ for the ground state of Co^{++}. This seems to be a fair agreement.

It is interesting to note that approximately 38% of the total entropy seems to be gained above the Néel temperature. This large contribution would indicate that a substantial amount of short-range ordering still persists above the critical temperature. Such large contributions have also been observed by Friedberg,[3]

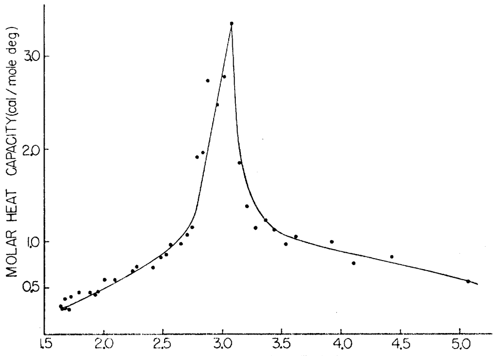

FIG. 1. The molar heat capacity of $CoBr_2\cdot 6H_2O$ from 1.65–5.05°K.

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[2] The authors wish to thank Mr. W. J. Hoopfer for growing the crystals.

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[4] D. G. Kapadnis and R. Hartmans, Physica **22**, 181 (1956).

[5] J. H. Van Vleck, J. Chem. Phys. **5**, 320 (1937).

Robinson and Friedberg,[6] Kapadnis and Hartmans,[4] and Spence *et al.*[7]

It is of further interest to observe that the Néel temperature for the present compound is higher than the corresponding $CoCl_2\cdot 6H_2O$, whose Néel temperature is 2.29°K. This difference in transition temperature for the bromine and chlorine salts has also been observed by others[4,6,7] in the case of manganese and nickel, in each case the bromine salt having the higher Néel temperature.

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[7] Spence, Forstat, Khan, and Taylor, J. Chem. Phys. **31**, 555 (1959).

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Spin Alignment in the Superconducting State

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It is argued that spin alignment can and will occur for ion-core spins in superconductors, but that the alignment is in the form of extremely small domains. Central to the argument is the concept of the nonlocal susceptibility $\chi(r-r')$, which leads to a positive short-range Kittel-Ruderman-Yosida interaction of ion-core spins, but a negative long-range interaction of range ξ_0.

Very general arguments suggest that purely ferromagnetic alignment should not be observed in preference to this domain-like "cryptoferromagnetic" alignment.

Specific heat data on a 0.7% Gd in La sample[1] indicate an alignment of Gd spins in the superconducting state. An almost equally convincing demonstration of such alignment is the observation in (Ce-Gd)Ru_2 that the superconducting transition can occur below a ferromagnetic one,[2] although the ferromagnetic energy per atom, $\sim kT_c(N_I/N)\ln(2S+1)$, must be ~ 100 times the superconducting energy $\sim kT_c(kT_c/\epsilon_F)$ (since the entropy in the ferromagnetic transition is far larger); some alignment must lower the energy of the superconducting state correspondingly.

It is here suggested that this alignment occurs and is ferromagnetic, but only in extremely small domains, certainly smaller than the coherence length ξ_0 and probably of the order $(r_s{}^2\xi_0)$—about $(50\text{ A})^3$. The domains may even be so small that density fluctuations (or the absence of true long-range order) account for the transition breadth. The net polarization averaged over the coherence length must, by very general arguments, be nearly zero.

To see these facts, we start by understanding the general phenomenon of spin-coupling via polarization of conduction electrons. We write the exchange interaction of rare earth ion spins $\mathbf{S}_j$ and conduction-electron spin density $\mathbf{s}(\mathbf{r})$[3]:

$$H'=\Omega_0\sum_j\int d\tau\, J(|\mathbf{r}-\mathbf{R}_j|)\mathbf{s}(\mathbf{r})\cdot\mathbf{S}_j, \qquad (1)$$

J being the exchange integral, the r-dependence of which will serve only as a short-wave cutoff; Ω_0 is the cell volume.

The conduction-electron spin polarization resulting from this interaction is given by a position-dependent susceptibility $\chi(r)$:

$$\mathbf{s}(\mathbf{r})=J\sum_j\chi(|\mathbf{r}-\mathbf{R}_j|)\mathbf{S}_j, \qquad (2)$$

resulting from the action of the "effective field" $J\mathbf{S}_j$ on the electron gas, which responds according to its susceptibility. This spin density reacts back on the ion cores, resulting in the spin polarization energy

$$U=-\tfrac{1}{2}J^2\sum_{j,j'}\chi(|\mathbf{R}_j-\mathbf{R}_{j'}|)\mathbf{S}_j\cdot\mathbf{S}_{j'} \qquad (3)$$

$$=-\tfrac{1}{2}J^2\sum_{\mathbf{q}}\chi(q)|\mathbf{S}(\mathbf{q})|^2, \qquad (4)$$

where

$$\mathbf{S}(\mathbf{q})=(1/\sqrt{N})\sum_j e^{i\mathbf{q}\cdot\mathbf{R}_j}\mathbf{S}_j,$$

$$\chi(q)=(1/\Omega)\int d\tau\,\chi(R)e^{-i\mathbf{q}\cdot\mathbf{R}}. \qquad (5)$$

We have introduced here the wave-number-dependent susceptibility, $\chi(q)$, which determines the interaction with a spin density of wave number q. $\chi(q=0)$ is the usual Pauli spin susceptibility. The difference from the normal state of the integral of (3) or (4) for a paramagnetic arrangement of $\mathbf{S}_j$'s was the result found in Suhl and Matthias,[3] giving the loss in energy of the superconducting state.

In the normal metal, $\chi(|\mathbf{r}-\mathbf{r}'|)$ is like the Ruderman-

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[2] Matthias, Suhl, and Corenzwit, Phys. Rev. Letters **1**, 449 (1958).

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