HEAT CAPACITY OF THE ANTIFERROMAGNET $CoCl_2 \cdot 6H_2O$ NEAR ITS NÉEL POINT*

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(Received 25 June 1964)

We wish to report measurements of the heat capacity C_p of the antiferromagnetic salt $CoCl_2 \cdot 6H_2O$ in the immediate neighborhood of its Néel point ($T_N \sim 2.3$°K for $H=0$). Earlier observations[1] on this salt and the isomorphous $NiCl_2 \cdot 6H_2O$ suggested a logarithmic rise in C_p as one approached to within ~0.07°K of T_N from either side. Such temperature dependence is obtained theoretically in the exact solution of the two-dimensional Ising problem[2] and has been suggested[3] as a property of three-dimensional Ising models for which only approximate descriptions are available. Experimentally, the λ anomaly in the heat capacity of liquid He^4 has been found,[4,5] within $\sim 10^{-6}$ °K of T_λ, to resemble a logarithmic singularity. Recent measurements of C_V for argon[6] and oxygen[7] at their critical points suggest similar behavior. As yet, however, no measurements with high temperature resolution have been reported for a coupled spin system at its ordering temperature, the situation to which existing theory is most directly applicable. We have felt it to be of interest, therefore, to examine the λ anomaly of a low-temperature antiferromagnet in detail and have chosen $CoCl_2 \cdot 6H_2O$ for study because of its convenient transition point.

These measurements were performed in a vacuum calorimeter of conventional design. Two speciments were studied. Specimen A consisted of 8.20 g of slices (~1 mm thick) cut from a large single crystal of the salt sandwiched between copper disks and sealed inside a cylindrical copper capsule together with He gas. Specimen B consisted of 54.51 g of small crystals of $CoCl_2 \cdot 6H_2O$ (average dimension ~3 mm) filling the interstices of an egg-box grid of sheet silver inside a cylindrical copper capsule. An electrical heater winding and a resistance thermometer consisting of a $\frac{1}{10}$-watt Allen-Bradley carbon resistor of 130-ohm nominal value were attached to each capsule. The thermometer resistance was measured with a specially constructed audiofrequency bridge circuit operating at 8 cps and employing synchronous detection. At $T_N \approx 2.289$°K, temperatures could be measured with an absolute accuracy estimated to be ±0.002°K while temperature intervals were determined to within $\pm 1.0 \times 10^{-6}$ °K. In order to permit the specimen to achieve thermal equilibrium at each point, heating was carried out discontinuously.

Data taken on specimens A and B were mutually consistent. Only those for specimen B are shown in plots of $C_p(H=0)$ versus T in Figs. 1(a) and 1(b). The data of Robinson and Friedberg[1] are also indicated in Fig. 1(a) and the agreement is seen to be quite satisfactory. The data near T_N are shown in greater detail in Fig. 1(b). Because of the rounding of the maximum evident under this resolution, the identification of T_N is not obvious. In Fig. 2, the data for $T > T_N$ and $T < T_N$ have been plotted versus $\ln|T-T_N|$ for a particular choice of T_N, namely, 2.2890°K. It will be seen that the curves so obtained for $(T-T_N) > 2 \times 10^{-3}$ °K and $(T_N-T) > 8 \times 10^{-3}$ °K are strikingly similar to those found for He^4 at its λ point. Over a significant interval they are essentially linear and parallel. This symmetry is lost for other choices of T_N leading us to conclude that the actual Néel point is quite close to 2.2890°K. A least-squares fitting of the data in the linear region of Fig. 2 for $T > T_N$ gives us the coefficient of the logarithmic term in C_p valid also for $T < T_N$ over a more restricted interval. The heat capacity near T_N is given by $(C_p/R) = -0.015 - 0.271 \ln|T-T_N| + \Delta$ where $\Delta = 0$ for $T > T_N$ and $\Delta = 0.574$ for $T < T_N$. This equation describes the dashed curves shown in Figs. 1(b) and 2.

We wish to emphasize two features of the experimental results. First of all, choosing T_N as has been done above, the heat capacity exhibits a logarithmic term whose coefficient, $0.27R$, is of the order of magnitude found in the exact theory of two-dimensional Ising antiferromagnets.[2] This is in contrast with corresponding coefficients observed for fluids[6,7] at their critical points which are larger by an order of magnitude. Secondly, the logarithmic rise of C_p appears not to continue without limit as T_N is approached. Rather, the experimental anomaly is rounded off over an interval of $\approx 15 \times 10^{-3}$ °K about T_N. Note that the temperature increments, ΔT, of the data points in this interval are $\leq 10^{-4}$ °K and that, following a heating period, the background temperature drift rate was re-established within ≈25 sec. Thus we are inclined to regard the observed rounding of the anomaly as an intrinsic property

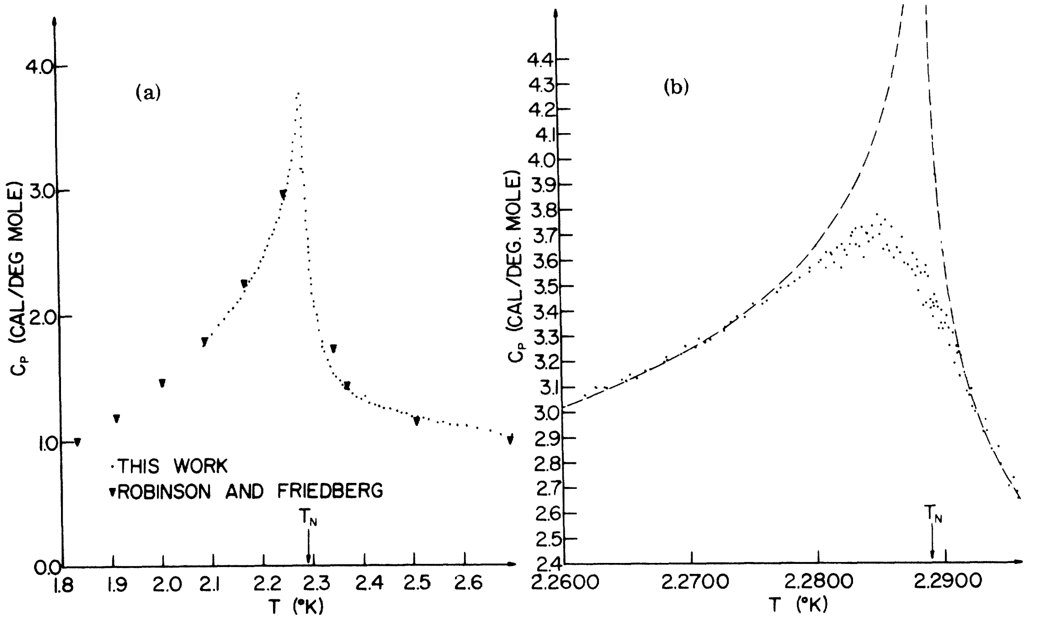

FIG. 1. The heat capacity, C_p, of $CoCl_2 \cdot 6H_2O$ as a function of temperature (a) with low temperature resolution and (b) on an expanded temperature scale.

of the specimen and not simply the result of experimental averaging or failure to achieve thermal equilibrium.

Interestingly enough Sawatzky and Bloom,[8] using proton resonance techniques, have found evidence of the coexistence of antiferromagnetic and paramagnetic phases over an interval of $\approx 10^{-2}$ °K about T_N in several specimens of $CoCl_2 \cdot 6H_2O$. These observations and our own suggest that crystals of $CoCl_2 \cdot 6H_2O$, at least those which have been studied, are probably inhomogeneous through imperfection and/or strain. These factors should affect the heat capacity anomaly in two ways. First of all, the specimen, already finite, is broken up further into smaller regions capable of sustaining long-range order. It is known, at least for two-dimensional Ising models, that the heat capacity of a finite crystal is finite

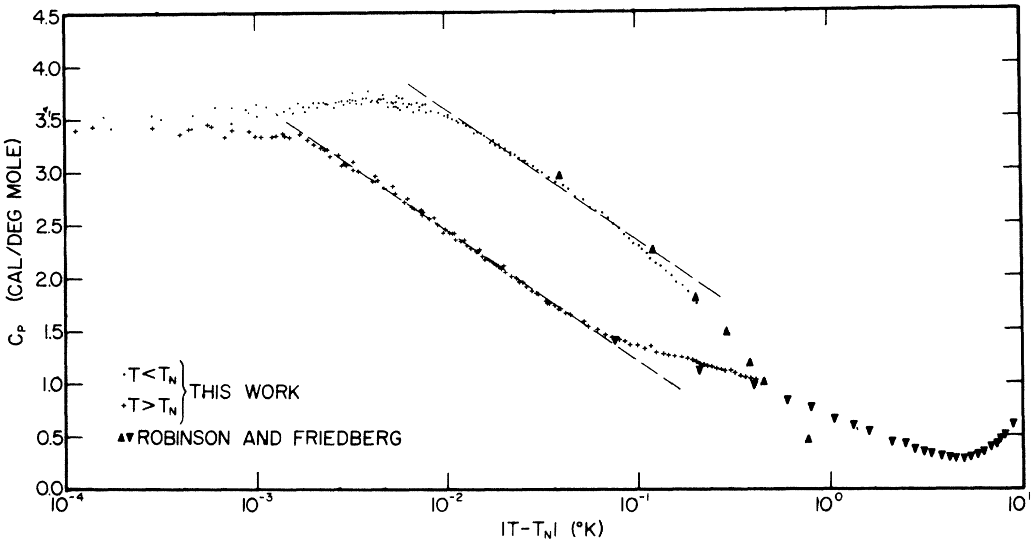

FIG. 2. The heat capacity, C_p, of $CoCl_2 \cdot 6H_2O$ as a function of $\ln|T-T_N|$ for $T_N = 2.2890$°K.

at T_N, becoming smaller as the specimen is reduced in size.[2] Secondly, strains, chemical impurities, and other lattice defects may be expected to cause local variations in the strengths of the interactions among magnetic ions. Different regions in the specimen would thus transform to the antiferromagnetic state at slightly different temperatures causing a broadening of the observed heat-capacity anomaly.

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*Work supported by the National Science Foundation and the Office of Naval Research. Based on a thesis submitted to the Carnegie Institute of Technology by John Skalyo, Jr., in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June 1964.

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ENERGY TRANSFER FROM 3*d* TO 4*f* ELECTRONS IN $LaAlO_3$:Cr, Nd

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(Received 25 June 1964)

We have observed transfer of energy between the 3*d* levels of Cr^{3+} and the 4*f* levels of Nd^{3+} in $LaAlO_3$. Evidence for transfer is the observation of Nd^{3+} fluorescence when the wavelength of the exciting light falls in a region where only Cr^{3+} absorbs. $LaAlO_3$ is an excellent host for studying cooperative effects between rare-earth and transition-metal ions since both types may be substitutionally incorporated over large ranges of concentrations. The absorption and fluorescence spectra of both Cr^{3+} and Nd^{3+} separately in single crystals of $LaAlO_3$ have been reported.[1,2]

The intensive investigation of the optical spectra of rare earths in ionic crystals has revealed the occurrence of energy transfer between the 4*f* electrons of ion pairs.[3-6] In this Letter we report the preliminary results on the resonance energy transfer between Cr^{3+} and Nd^{3+}. Transfer from Mn^{2+} to Nd^{3+} in glass has been reported by Melamed.[7] Very weak Nd fluorescence has been reported when pumping into the Cr absorption bands of mixed powders of ruby and Nd_2O_3.[8]

Powder samples of $La_{1-x}Nd_xAl_{1-y}Cr_yO_3$ were prepared by reacting the dried oxides,[9] La_2O_3, Al_2O_3, Nd_2O_3, and Cr_2O_3, intimately mixed in proper proportion, and firing at 1450 °C for 36 hours, with remixing after 18 hours. Examination of the product by x-ray powder diffraction techniques reveals single-phase $LaAlO_3$ within the limits of the sensitivity of the method. The values of x used were 0, 0.0005, 0.005, 0.01, 0.02, and 0.05, and those of y were 0, 0.0005, 0.001, 0.005, and 0.01.

Fluorescence spectra at 1Å resolution were obtained using a one-meter Jarrell-Ash Co. spectrometer and a cooled RCA 7102 photomultiplier, the samples being excited by an AH-6 mercury lamp with filtering by $CuSO_4$ solution. Excitation spectra at 100Å resolution were measured by exciting the sample with monochromatic light from a tungsten lamp filtered by a Farrand grating monochromator. In order to reduce the excitation spectra to the basis of constant incident quanta, the wavelength dependence of the quantal output of the Farrand monochromator was measured using a calibrated photomultiplier. In the excitation studies the fluorescence of Nd^{3+} was isolated using a Wratten No. 87C filter in front of the RCA 7102 photomultiplier, while Cr^{3+} fluorescence was isolated with a Wratten No. 88A filter in front of an RCA 7265 photomultiplier.

The room-temperature fluorescence spectrum, covering the region from 0.7 to 1.1 μ, of a powder