Heat Capacity of CrBr₃ from 14 to 360°K*

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The heat capacity of CrBr₃ shows a lambda anomaly peaked at 32.55°K, a temperature somewhat lower than the reported Curie temperature of 37°K. Assuming the validity of the spin-wave dispersion relation of Davis and Narath, the entire magnetic heat capacity was derived. As is typical of a predominantly two-dimensional structure, this curve yields a large amount of entropy and energy of order $(S_\infty - S_c)/R = 0.62$ and $(E_\infty - E_c)/(E_\infty - E_0) = 0.72$.

A S part of a series of measurements[1-3] on the thermal and magnetic properties of the chromium (III) halides, we have measured the heat capacity of CrBr₃ over the temperature range 14 to 360°K. Publication of these measurements has been delayed for some years for lack of a suitable technique for interpreting the ordering entropy, but we have been encouraged by the present heavy interest[4,5] in this material to present our results at this time. In particular, Davis and Narath[6] have carried out a quite extensive spin-wave treatment of the magnetization in order to interpret their NMR data. Their treatment, which makes use of a renormalization procedure, is sufficiently complete that they are able to fit their NMR results up to 20°K, a temperature which is greater than half of the Curie temperature. Using methods which are detailed in the Appendix, we have computed the low-temperature magnetic heat capacity on the basis of the results of Davis and Narath. Assuming the validity of these results, we have been able to obtain a reasonable separation of the magnetic and lattice contributions to the heat capacity at all temperatures. The magnetic part of the heat capacity has the characteristic that a large fraction of the entropy of ordering is above the Curie temperature, as one might expect for a material such as CrBr₃ whose strong interactions are within a plane only.

We measured the heat capacity with a liquid-hydrogen-cooled adiabatic calorimeter.[1] The temperature scale was that established by the National Bureau of Stand-ards for platinum resistance thermometers, taking 273.16°K as the triple point of water. Above the lambda anomaly near 32.6°K, the precision of the measurements of $\Delta H/\Delta T$ is such that the smoothed heat capacity is determined within about 0.1%. Near the lambda anomaly, the large second derivative in the heat-capacity curve leads to reduced precision. Below 30°K, because of increasing difficulty in maintaining adiabatic conditions, the precision decreases to about

TABLE I. Thermodynamic functions of CrBr₃, J/mole deg.

T	C	$S°$	$(H° - H_0°)/T$
14	5.91	2.93	1.91
16	7.58	3.82	2.51
18	9.49	4.82	3.18
20	11.70	5.94	3.92
22	14.15	7.16	4.73
24	16.76	8.51	5.63
26	19.75	9.96	6.59
28	23.10	11.55	7.65
30	26.94	13.27	8.81
31	29.36	14.19	9.43
32.0	32.21	15.17	10.10
32.2	32.83	15.37	10.23
32.4	33.46	15.57	10.38
32.55	33.95	15.73	10.48
32.6	31.71	15.78	10.52
32.7	28.00	15.87	10.58
32.8	27.32	15.95	10.63
32.9	27.18	16.04	10.68
33	27.15	16.12	10.73
34	27.41	16.93	11.21
35	27.94	17.73	11.68
40	31.62	21.70	13.95
50	39.21	29.57	18.23
60	46.59	37.38	22.35
70	53.11	45.07	26.29
80	58.79	52.54	30.01
100	68.27	66.74	36.78
120	75.24	79.83	42.63
140	80.59	91.85	47.69
160	84.57	102.88	52.06
180	87.57	113.02	55.85
200	89.87	122.37	59.14
220	91.74	131.03	62.02
240	93.28	139.08	64.56
260	94.53	146.59	66.82
273.15	95.28	151.27	68.17
280	95.64	153.64	68.84
298.15	96.46	159.67	70.50
300	96.54	160.27	80.66
320	97.32	166.52	72.30
340	98.02	172.44	73.79
360	98.64	178.06	75.16

[1] W. N. Hansen and M. Griffel, J. Chem. Phys. 28, 902 (1958).

[2] W. N. Hansen and M. Griffel, J. Chem. Phys. 30, 913 (1959).

[3] W. N. Hansen, J. Appl. Phys., Suppl. 30, 304S (1959).

[4] I. Tsubokawa, J. Phys. Soc. Japan 15, 1664 (1960).

[5] More than a score of papers dealing with the magnetic properties of CrBr₃ have appeared since the work of Refs. 3 and 4 showed that fields of a few kilo-oersteds were sufficient for saturation. Representative are H. Bizette and C. Terrier, J. Phys. Radium 23, 486 (1962); E. Legrand and R. Plumier, Phys. Status Solidi 2, K112 (1962); J. F. Dillon, Jr., H. Kamimura, and J. P. Remeika, Phys. Rev. Letters 9, 161 (1962); M. Yamada, J. Phys. Soc. Japan 18, 1696 (1963); A. C. Gossard, V. Jaccarino, E. D. Jones, J. P. Remeika, and R. Slusher, Phys. Rev. 135, A1051 (1964); and J. F. Dillon, Jr., J. Phys. Soc. Japan 19, 1662 (1964).

[6] H. L. Davis and A. Narath, Phys. Rev. 134, A433 (1964).

2% at 14°K. The sample of 146.5 g of CrBr₃ was prepared using the methods described previously.[2]

Selected values of the heat capacity, derived from our measurements, are given in Table I. Using considerations described below, we have extrapolated these values to absolute zero and have derived the usual thermodynamic functions, which are also given in Table I.

The primary interest in our work lies in its relation to the process of the development of the spontaneous magnetization. The ideas are summarized, for example, in the recent review of Domb and Miedema.[7] In order to investigate this relation, the straightforward way to proceed is to establish the part of the heat capacity associated with the lattice from independent considerations and then evaluate the magnetic heat capacity by difference. Unfortunately, there is not enough information available to evaluate the lattice heat capacity of CrBr₃ *a priori*. Instead we proceed with the following considerations.

We assume that the lattice and magnetic portions of the heat capacity are separable and that they represent the only contributions. We further assume that the magnetic heat capacity up to 20°K may be obtained from the dispersion relations of Davis and Narath[6] (with the results shown in Table II), that the magnetic heat capacity at high temperatures[8] drops slightly more rapidly than T^{-2}, and that the total entropy associated with the magnetic disordering is $R \ln(2S+1)$, where $S = \frac{3}{2}$ is the spin of the ground state $^4A_2$. This last assumption is extremely well justified inasmuch as the next higher level[9] is at $h\nu/k = 19\,300$°K. Our calculations do not depend heavily on the exact form of the high-temperature magnetic heat capacity and the T^{-2} dependence is almost surely adequate. On the other hand, our interpretation does depend heavily on the reliability of the Davis and Narath dispersion relation, which is verified so far only by their NMR results.

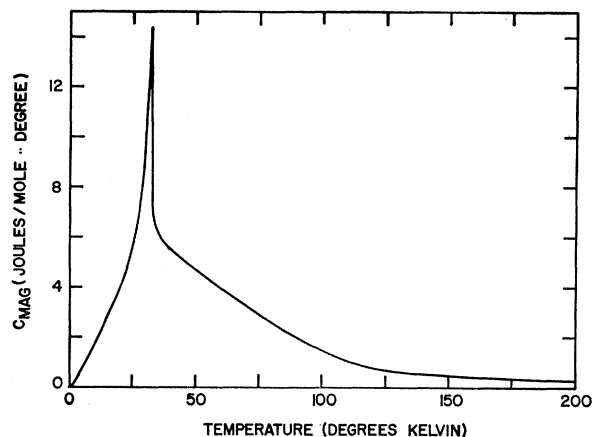Using these assumptions, the lattice heat capacity is determined in the range 14 to 20°K and both the heat

TABLE II. Thermodynamic functions arising from the magnetic part of the heat capacity of CrBr₃, calculated from the theory of Davis and Narath (see Ref. 6). Units are J/mole deg.

T	C_{mag}	S_{mag}	H_{mag}/T
2	0.16	0.077	0.060
4	0.48	0.279	0.182
6	0.83	0.536	0.337
8	1.24	0.830	0.511
10	1.66	1.151	0.699
12	2.10	1.492	0.896
14	2.52	1.846	1.097
16	2.94	2.209	1.304
18	3.36	2.580	1.508
20	3.80	2.957	1.715

[7] C. Domb and A. R. Miedema, in *Progress in Low Temperature Physics*, edited by C. J. Gorter (North-Holland Publishing Company, Amsterdam, 1964), Vol. IV, Chap. VI.

[8] C. Domb and M. F. Sykes, Phys. Rev. **128**, 168 (1962).

[9] D. L. Wood, J. Ferguson, K. Knox, and J. F. Dillon, Jr., J. Chem. Phys. **39**, 890 (1963).

FIG. 1. The magnetic heat capacity of CrBr₃.

capacity and a preliminary value for the entropy in a high-temperature range, say above 150°K. One is then faced with the determination of the lattice heat capacity at other temperatures. It would be most helpful to use as a guide the heat capacity of a nonmagnetic material with a structure similar to the layered structure of CrBr₃. We were, however, unable to find any such heat capacities. We thus turned to a curve-fitting technique in which we were guided by the results of Hofmann *et al.*[10] who expressed the lattice heat capacity of a compound $R_n X_m$ in the form

$$C = [nf_D(\theta_1/T) + mf_D(\theta_2/T)][1 + \epsilon T], \qquad (1)$$

where f_D is the Debye specific-heat function and θ_1, θ_2, and ϵ are adjustable parameters. In agreement with the assertion of others[7] that Eq. (1) is not sufficiently general to fit the heat capacity of layered structures, we found that we were unable to meet our requirements for CrBr₃ with such a formula. However, by generalizing Eq. (1) with an additional parameter a, we were able to meet our requirements with a function

$$C = [af_D(\theta_1/T) + (n+m-a)f_D(\theta_2/T)][1 + \epsilon T]. \qquad (2)$$

Furthermore, we tested Eq. (2) by applying it to the case of a layered structure for which the lattice heat capacity has been evaluated,[11] MnCl₂, and found that we were able to reproduce the experimental values within $\frac{1}{4}$% over the entire range.

In actual fact, it is necessary to apply an iterative procedure: first one fits the experimental heat capacity data as well as possible in the range 14 to 20°K and above 150°K with a function of the form of Eq. (2) and uses the results to extrapolate the experiments to absolute zero. It is then possible to estimate more accurately the total entropy at, say, 150°K. Furthermore, an estimate may be made of C_{mag} at 150°K and the

[10] J. A. Hofmann, A. Paskin, K. J. Tauer, and R. J. Weiss, J. Phys. Chem. Solids **1**, 45 (1956).

[11] R. C. Chisholm and J. W. Stout, J. Chem. Phys. **36**, 972 (1962).

TABLE III. Values of some thermodynamic parameters derived from the magnetic heat capacity of $CrBr_3$.

Curie temperature	$T_c = 32.55°K$.
Total ordering energy	$(E_\infty - E_0)/R = 57°K$
Short-range ordering energy	$(E_\infty - E_c)/R = 41°K$
Total ordering entropy	$S_\infty/R \equiv \ln 4 = 1.39$
Short-range ordering entropy	$(S_\infty - S_c)/R = 0.62$

magnetic entropy above 150°K may be obtained by assuming that $C_{mag}/R = b/T^2$ as discussed above, and thus the lattice entropy from 150°K to, say, 250°K is determined. One may then make a more exact fit with Eq. (2) using both heat-capacity and entropy considerations in the range 14 to 20°K and 150 to 250°K. Our final fit is defined by $\theta_1 = 131.3°K$, $\theta_2 = 371°K$, $a = 1.28$, $\epsilon = 5 \times 10^{-5}$, and $b = 1100$. These parameters probably are not the "best" values, particularly with respect to ϵ and b, but we feel that they represent the data so well that there would be no advantage to improving them or in going to a formula even more general than Eq. (2). Our separated magnetic-specific-heat curve is shown in Fig. 1 and several interesting thermodynamic parameters derived from it are given in Table III.

We comment on only two aspects of the information contained in Table III. Firstly, one notices that the entropy and energy associated with the short-range order region are larger than for any of the theoretical models discussed by Domb and Miedema. While this behavior is neither unusual nor unexpected for a material whose predominant interactions are two dimensional, the case of $CrBr_3$ has been extensively studied and it would be desirable to use the series expansion method coupled with the model of Davis and Narath to calculate the thermodynamic properties. In this connection, one may take note of the case of $CrCl_3$ for which $(S_\infty - S_c)/R = 0.87$ is perhaps the largest value yet measured. In this case, however, the heat capacity results[1] do not extend down to the region where the spin-wave calculation[12] is valid and so the separation of the lattice heat capacity is less reliable than in the case of $CrBr_3$.

Secondly, the temperature of the maximum in the heat capacity is 32.55°K, and the drop above this temperature is very rapid. It thus seems unlikely that there is appreciable long-range order above this temperature with zero applied magnetic field. This result is substantiated by recent measurements of Senturia et al. who have extended the temperature range of their published nuclear-resonance results[13] and find that the magnetization vanishes at some temperature in the range 32.45 to 32.60°K. On the other hand, Tsubokawa[4] concluded from his magnetization studies in applied fields of a few kilo-oersted that the Curie temperature is 37°K. This result points up the fact that fields of such

magnitude must be considered large in some cases even at such a comparatively high temperature.

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APPENDIX: CALCULATION OF THE SPIN-WAVE HEAT CAPACITY

Davis and Narath[6] chose a model for $CrBr_3$ comprised of $2N$ spins S, situated in N unit cells and interacting with each other through exchange expressed by parameters J_T and J_L and with the lattice through an effective anisotropy field expressed by a parameter $H_A(T)$. They find that when the excitations of this system are thought of as modes with wave vector λ, these modes are not independent. However, they may be approximately separated if the energy levels of each are taken as equally spaced, with the spacing $\epsilon(\lambda)$ dependent on the occupation numbers of the other modes. This dependence is expressed through renormalization constants $\xi_1(T)$ and $\xi_2(T)$, which must be determined by an iterative procedure. The final result is that, for $S = \frac{3}{2}$,

$$\epsilon^\pm(\lambda) = g\mu_B H_A(T) + 9J_T \xi_L(T)[1 \pm f_1(\lambda)] + 6J_L \xi_2(T)[1 - f_2(\lambda)], \quad (A1)$$

where the $\pm$ refers to the two branches arising from the two spins per unit cell and λ takes on the usual N allowed independent values. We took values for J_T, J_L, ξ_1, ξ_2, and H_A from the work of Davis and Narath and $f_1(\lambda)$ and $f_2(\lambda)$ are geometrical functions whose form depends on the coordinate system chosen for wave-vector space. They are given by

$$f_1 = \frac{1}{3}[3 + 2\cos(v-w) + 2\cos v + 2\cos w]^{1/2}, \quad (A2)$$

or

$$f_1 = \frac{1}{3}[3 + 4\cos(x/6)\cos(y/2) + 2\cos(x/3)]^{1/2} \quad (A3)$$

$$f_2 = \cos z, \quad (A4)$$

where Eq. (A2) is for our choice of coordinate system and Eq. (A3) is for that of Davis and Narath.

Using the results of thermodynamics applied to each quasi-independent mode and summing over all modes to give the total system energy, we have

$$E = \sum \epsilon^\pm(\lambda)/\{\exp[\epsilon^\pm(\lambda)/kT] - 1\}. \quad (A5)$$

Changing the sum over λ to an integration and explicitly separating the contributions of the two branches, we have

$$E = \frac{N}{2\pi^3} \int_{-\pi}^{\pi} dv \int_0^\pi dw \int_0^\pi dz$$
$$\times \left\{ \frac{\epsilon^+(v,w,z)}{\exp(\epsilon^+/kT)-1} + \frac{\epsilon^-(v,w,z)}{\exp(\epsilon^-/kT)-1} \right\} \quad (A6)$$

[12] A. Narath and H. L. Davis, Phys. Rev. 137, A163 (1965).
[13] S. D. Senturia, P. Heller, and G. B. Benedek, Bull. Am. Phys. Soc. 8, 592 (1963).

or
$$E = \frac{N}{6\pi^3} \int_0^{2\pi} dy \int_0^{4\pi-y} dx \int_0^{\pi} dz$$
$$\times \left\{ \frac{\epsilon^+(x,y,z)}{\exp(\epsilon^+/kT)-1} + \frac{\epsilon^-(x,y,z)}{\exp(\epsilon^-/kT)-1} \right\}. \quad (A7)$$

We obtained E by numerically integrating Eq. (A6), with N set equal to one half of Avogadro's number, as is appropriate for one mole of CrBr₃. The magnetic heat capacity was then taken as the temperature derivative of E.

Longitudinal-Dielectric-Permittivity Criterion for Current Instability in a Polar Crystal*

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Electrodynamic phenomena in a spatially dispersive medium are governed by the dielectric permittivity tensor. It appears that this tensor is useful in describing small departures from a steady state as well as small departures from equilibrium. The existence of a simple relationship between the longitudinal parts of the permittivity tensor for certain systems in equilibrium and the same systems in a steady state is noted and then applied in a calculation of the longitudinal dielectric permittivity $\epsilon^L(q,\omega; v_D)$ of a polar crystal in which there is a stream of degenerate carriers with drift velocity v_D. Vanishing of $\epsilon^L(q,\omega; v_D)$ is associated with longitudinal electric waves in the system. Damping of these waves is governed by Im $\epsilon^L(q,\omega; v_D)$. It is argued that in some circumstances Im $\epsilon^L(q,\omega; v_D)$ can be made to vanish by adjusting v_D. This general argument is applied to the case of carriers drifting in GaAs, and it is found that the longitudinal electric waves (plasmons coupled to longitudinal optical phonons) become unstable for values of v_D not much larger than the value reported by Gunn as the threshold for the onset of current oscillations in GaAs. (It is assumed that $\omega\tau_{el} \gg 1$, where τ_{el} is the relaxation time for the distribution of electrons.) The significance of this result is discussed.

I. INTRODUCTION

ONE of the principal goals of the theory of solids is to elucidate as completely as possible the connections between the macroscopic electrodynamic phenomena observable in a medium and its microscopic constitution. A very useful tool in this work is the dielectric permittivity tensor, $\boldsymbol{\varepsilon}(\mathbf{r}, \mathbf{r}', t-t')$. In the next section this tensor is defined in the course of a review of the equations of the electromagnetic field and the description of plane electromagnetic waves in an infinite homogeneous medium. We allow the medium to be spatially as well as temporally dispersive and pay special attention to the longitudinal electric waves (plasma oscillation waves) which can exist when the longitudinal part of the permittivity tensor vanishes.

Most of this analysis applies not only to a medium in equilibrium but also to one in which constant currents are maintained. The problem of establishing relations between the permittivity of a current-carrying medium and that of the same medium in equilibrium is of considerable interest. A simple relation of this kind for the case of a translationally invariant medium is derived here (Sec. V). This relation is used in a brief investigation of longitudinal electric waves in current carrying media. The investigation begins with a calculation of

the longitudinal permittivity for a plasma of two components, each of which may have a drift velocity. This result and some results of Born and Huang[1] lead to an expression for the longitudinal permittivity of a polarizable medium carrying a current. Using the relation between the permittivities of the equilibrium and current-carrying medium, and exploiting a general symmetry property of the permittivity, we obtain information about the transfer of energy between the medium and a monochromatic longitudinal electric wave (for the system considered this wave is a collective mode of the lattice, the streaming electrons, and the electromagnetic field).

To illustrate the utility of these ideas we apply them to the case of a crystal of GaAs carrying a current. Gunn[2] has observed interesting current instabilities in this system. We calculate the longitudinal dielectric permittivity for one of Gunn's samples of GaAs and find that the smallest drift velocity for which the calculated permittivity vanishes approximates the drift velocity value reported by Gunn as the threshold for the appearance of instability. This result is interpreted and its significance is discussed.

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[2] J. B. Gunn, Solid State Commun. 1, 88 (1963); IBM J. Res. Develop. 8, 141 (1964).