SPECIFIC-HEAT SINGULARITY IN MnF_2*

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The mathematical complexities associated with the theoretical study of critical point phenomena make experimental insight of primary importance.[1] Examples from the currently growing list of relevant experiments are the specific heat of helium and, more recently, argon, nuclear magnetic resonance near magnetic transitions, critical opalescence, critical scattering of neutrons and light, and a variety of new transport and relaxation experiments. In this Letter we report measurements of the specific heat of a classic magnetic system, MnF_2. The results demonstrate clearly the essential similarity between magnetic and gaseous systems and are in encouragingly good agreement with theoretical predictions, especially with respect to the strength of the singularity.

The experimental results are shown by the open and closed circles in Fig. 1. A logarithmic form of divergence is clearly indicated over about three decades from 10^{-4} to 10^{-1} T_N. The striking resemblance to the configurational specific-heat density of argon in the same region is shown by the closed squares which are taken from Fisher's analysis[2] of the results of Bagatskii, Voronel', and Guzak.[3] Our data cover almost an additional decade in $|\Delta T/T_N|$ and have a rather better signal-to-noise ratio than the argon results. The parameters that result from fitting the data with a logarithmic divergence of the form $C_\pm/R = A_\pm \log_{10}|\Delta T/T_N| + B_\pm$ are summarized in Table I. Comparison is made with the argon experimental results and with the theoretical estimates for a lattice gas. In reference 2 the results of various approximations are listed along with detailed references to their origins. We have tabulated here only rounded values. It is clear that while the present experiments reveal the character of the singularity, the signal-to-noise ratio is not good enough to warrant a discussion of the rather small effects of lattice structure.

It is important to consider the possibility of a stronger than logarithmic singularity, particularly on the high-temperature side. For purposes of comparison, a divergence of the form $C_+ = A|\Delta T/T_N|^{-\alpha}$ with $\alpha = 0.1$ is plotted as the dashed curve in Fig. 1. Deviation of the experimental points from the logarithmic straight line, i.e., $\alpha = 0$, is seen to be not inconsistent with a small positive α. Notice that shifting T_N down by 5 mdeg would improve the linear fit for $T < T_N$ but increase the upward trend of the points for $T > T_N$. The assignment of some definite value to α would place unjusti-

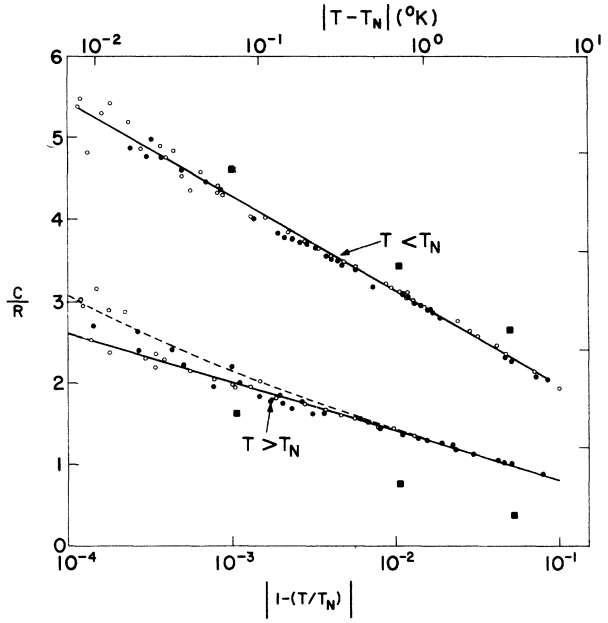

FIG. 1. Magnetic specific heat of MnF_2 near the Néel temperature. Open circles, IBM crystal; closed circles, Heller and Benedek crystal. The closed squares are the specific-heat density of argon. The dashed curve is for $\alpha = 0.1$.

Table I. Logarithmic parameters for magnetic and configurational specific heats in units of R.

	MnF_2	Argon[a]	Lattice gas[a]
A_-	1.15	1.15	1.1
A_+	0.6	(0.5)	0.5
A_-/A_+	2.0	(2.3)	2.3
B_-	0.82	1.16	0.1
B_+	0.14	(−0.3)	−0.3

[a]See reference 2.

fied weight on the noisiest experimental points, those closest to T_N. We feel that these data can only be said to suggest that $0 \leq \alpha < 0.1$. A much better value of α is not inaccessible to experiment: Although rounding of the transition might be expected in the next decade closer to T_N, improved precision in the present range would allow us to set improved limits on α.

The experiments were performed on two single crystals. One crystal (0.02 mole, closed circles) of Bell Telephone origin was obtained from Heller and Benedek and is the same one used by them in their classic nmr experiments.[4] The other crystal (0.06 mole, open circles) was "on the shelf" at our laboratory and is of lost commercial pedigree. The character of the singularity is seen to be identical in both crystals, but we did find one important difference: The Heller and Benedek crystal had $T_N = (67.33 \pm 0.01)^\circ$K in agreement with their result, while the IBM crystal had $T_N = (67.23 \pm 0.02)^\circ$K. (The error limits represent confidence in the absolute calibration of the thermometers in each of the two runs.) The difference is well outside experimental error and also well outside combined uncertainties in locating T_N. The discovery of such a large difference between two high-quality crystals demonstrates the importance of single-crystal measurements. The transition in both crystals was sharper than our experimental resolution of about 10 mdeg K, and we are therefore unable to comment on the rounding or truncation of the singularity which Heller found to amount to about 15 mdeg.

The magnetic specific heat was separated from the lattice background by using the estimates given by Stout and Catalano,[5] and by Hofman, Paskin, Tauer, and Weiss.[6] Stout and Catalano use a corresponding state method to deduce the lattice heat capacity of MnF_2 from that of isomorphous ZnF_2. Hofman et al. use a method of matching two Debye entropy functions to the experimental entropy of MnF_2 at high temperatures, having first subtracted an amount $R \ln(2S+1)$. That is, they find that for two Debye temperatures, $\Theta = 220^\circ$K and $\Theta' = 575^\circ$K,

$$S_{MnF_2}(T) - R \ln 6 \cong S_D(\Theta/T) + 2S_D(\Theta'/T)$$

for temperatures above $\sim 2T_N$. This procedure when applied to ZnF_2 gives a two-parameter Debye curve that fits the observed specific heat to within $\frac{1}{2}\%$ in the temperature range 35 to 250°K. The results obtained by the two methods are in excellent agreement. The apparent character of the singularity depends only weakly on the slope of the lattice background; changing this slope by a factor of two produces only faintly perceptible kinks in the highest $|\Delta T|$ data shown in Fig. 1. The apparent magnitude of the magnetic specific heat, that is, the values of $B_\pm$, is more directly influenced by the lattice subtraction, but in view of the extensive work by the above authors it seems unlikely that an error larger than 10% is introduced by incorrect lattice subtraction.

We use the standard discontinuous heating method in these experiments. The sample is surrounded by a radiation shield, the temperature of which could be held constant to about 1 mdeg by referencing a platinum thermometer against a Mueller bridge. Sample and shield are inside a vacuum jacket surrounded by double Dewars of liquid nitrogen. The temperature of the sample is monitored by a thermister of the type used to sense the level of liquid nitrogen.[7] The thermister comprises one arm of a constant amplitude 100-cps resistance bridge stable to 1 part in 10^7. The over-all sensitivity was limited to about 30×10^{-6} °K by Johnson noise of the bridge detector. The thermister is calibrated against the platinum thermometer on the shield, equilibrium to within 5×10^{-4} °K being accomplished by condensing liquid nitrogen into the vacuum chamber. The platinum thermometer is calibrated against the vapor pressure of the condensed pure nitrogen, and the less than ideal arrangement for this part of the calibration is the cause of the relatively large systematic uncertainties quoted above. The function $Z_{63}^{77}(T)$ is used for interpolation.[8] Our apparatus records drift-rate and heating-interval data directly on punched cards, and all the data analysis including addendum corrections and lattice subtraction is done in a minute or two of computer time.[9]

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[1]A comprehensive review of both theory and experi-

ment may be found in the Proceedings of the Conference on Phenomena in the Neighborhood of Critical Points, Washington, D. C., 5-8 April 1965 (to be published).

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[7]We are indebted to Dr. H. B. Sachse of the Keystone Carbon Company for samples of these thermisters and advice on their characteristics.

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[9]The computer program, expressly written to cover a wide range of laboratory circumstances, is available to interested experimenters.

INFLUENCE OF RADIATION TEMPERATURE ON THE STABILITY OF *F* CENTERS AND INTERSTITIALS*

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Creation of interstitial defects as well as *F* centers in alkali halides has been clearly established for irradiation below 50°K.[1] Recent indirect evidence adduced from measurements of the flow stress,[2,3] thermal conductivity,[4] and x-ray lattice expansion[5] indicate that interstitial-type defects are also produced at room temperature. Since flow-stress measurements are much more sensitive to interstitial defects than to *F* centers, they allow one to monitor changes in the amount of interstitial halide. We make use of flow-stress and optical-absorption measurements to examine the stability of interstitials and *F* centers, respectively. The results show that interstitials are produced together with *F* centers at all temperatures and, more important, that the stability of the defects remaining at 300°K depends on the radiation temperature.

In Fig. 1 are shown room-temperature spectra for crystals irradiated with 1.5-MeV electrons (current density 0.1 μA/cm^2): Fig. 1(a) after 37 min at 300°K, and Fig. 1(b) after 5½ hours at 80°K. It can be seen in Fig. 1(a) that, although many of the centers disappear after a three-hour bleach with white light, the total absorption throughout the remainder of the spectrum from 250 to 1500 mμ increases so that the total area of absorption for the bleached sample is comparable to that before bleaching. This reveals that the defects responsible for the initial absorption have been transformed but not annihilated. On the other hand, bleaching of the specimen irradiated at 80°K for only ½ hour almost completely removes the absorption even though the initial *F*-center concentration was higher than that of the sample irradiated at 300°K.

A clearer representation of the results is

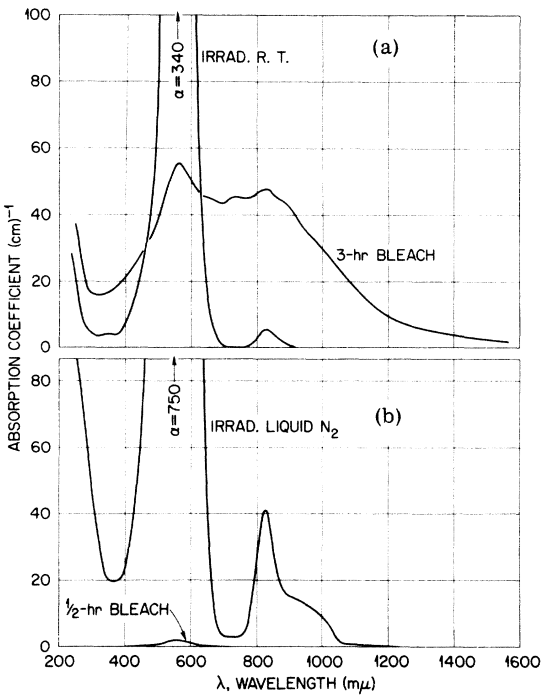

FIG. 1. Room-temperature spectra of KCl crystals. (a) Irradiation at room temperature; (b) irradiation at 80°K. In each case the spectrum with the large *F* band at 560 mμ was obtained before bleaching and the other spectrum was obtained after bleaching with white light.