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AC MEASUREMENT OF THE HEAT CAPACITY OF NICKEL NEAR ITS CRITICAL POINT*

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Recent revival of interest in critical-point phenomena[1,2] creates a need for data giving the temperature dependence of the heat capacity, $C(T)$, at temperatures extremely close to the critical value, T_c. This Letter reports preliminary measurements of the specific heat of Ni near its Curie point (~625°K). The data were obtained using a simple but exceptionally sensitive ac calorimetric technique which permits measurement of the temperature variation of $C(T)$ over intervals less than 0.01°K (i.e., $\epsilon = (T-T_c)/T_c \approx 10^{-5}$).

The method of measurement is shown schematically in Fig. 1(a). The sample was a 0.025-mm thick nickel foil weighing about 0.4 mg, to which was spot-welded a Chromel-Alumel junction of mass much less than that of the foil. The "cold junction" of the thermocouple was also situated in the oven. The foil was periodically heated by chopped light (26 Hz) from a tungsten lamp with intensity constant to 0.5%. The temperature variation of the sample relative to the "cold junction" is converted by means of the Peltier effect into an ac voltage. The voltage is amplified and measured by means of lock-in detection referred to the phase of the chopped light.

A second thermocouple placed very close to the sample monitors the average temperature, T, of the oven. The output of the lock-in amplifier is proportional to $\Delta T = \Delta Q/C(T)$, where ΔT is the rms temperature rise, ΔQ is the energy absorbed by the Ni foil per cycle, and $C(T)$ is the heat capacity of the foil. An x-y recorder is used to plot ΔT vs T as the specimen temperature drifts slowly past the critical point. A typical chart record is shown in Fig. 1(b) on which the sharp minimum of ΔT corresponds to the cusplike singularity in $C(T)$ at the critical point. The rms temper-

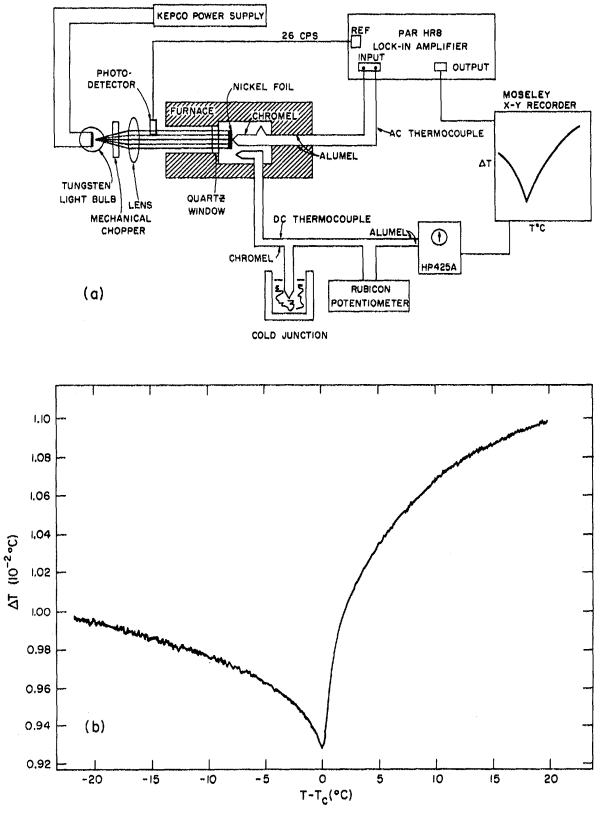

FIG. 1. (a) A schematic diagram of the experimental apparatus. (b) X-Y recorder trace of the experimental data. ΔT vs T over a range of 20°C on either side of the critical point.

ature variation of the foil, as estimated from the thermocouple voltage, was about 0.01°K in these measurements. The dc heating or cooling rate could be made as small as 2.3°K/h, although for the data of Fig. 1(b) it was 20°K/h.

The present technique is the converse of a sensitive detection method used for many years in infrared spectroscopy.[3] Instead of detecting changes in radiation intensity, we hold the intensity constant and vary the temperature to observe the T dependence of the heat capacity of the detector. Advantages of this approach to calorimetry have been discussed recently by Sullivan and Seidel in connection with low-temperature measurements.[4]

The dynamic behavior of the system with oscillatory heat input involves two characteristic time constants: τ_1, the relaxation time which characterizes the thermal coupling between the specimen and its surroundings, and τ_2, the characteristic time for the sample to reach internal thermal equilibrium. The thermal diffusivity of the specimen determines τ_2 while, in the present work, τ_1 was determined by gas conduction through the surrounding air. If ω is the frequency of the chopped light, then it can be shown[3,4] that the optimum conditions for measurement occur when $\omega\tau_1 > 1$ and $\omega\tau_2 \ll 1$. Under these conditions, the observed ac temperature rise is inversely proportional to the heat capacity of the sample. The heat capacity of the attached thermocouple is quite small and varies slowly over the temperature range of these measurements. Therefore, corrections can be made satisfactorily.[3]

We have been able to record continuous curves of ΔT with a temperature resolution of about 0.25°K per in. The average sample temperature is changed slowly enough that reproducible data are obtained with a 3-sec time constant on the lock-in amplifier, resulting in signal-to-noise ratios of the order of 30 within ±1°K of T_c. The present technique is capable of providing heat-capacity data with a precision of $\simeq 0.3\%$ for temperature differences of less than 10^{-2} °K for any given temperature in the range of our measurements. Assuming that the sample quality warrants such precision, measurements to the value $\epsilon \simeq 10^{-6}$ appear possible.

The experimental results for a 99.8% pure annealed polycrystalline foil sample are shown in Fig. 2. To compare our data with the earlier work of Pawel and Stansbury[5] and Kraftmakher,[6] Fig. 2(a) shows a plot of log$C$ vs T.

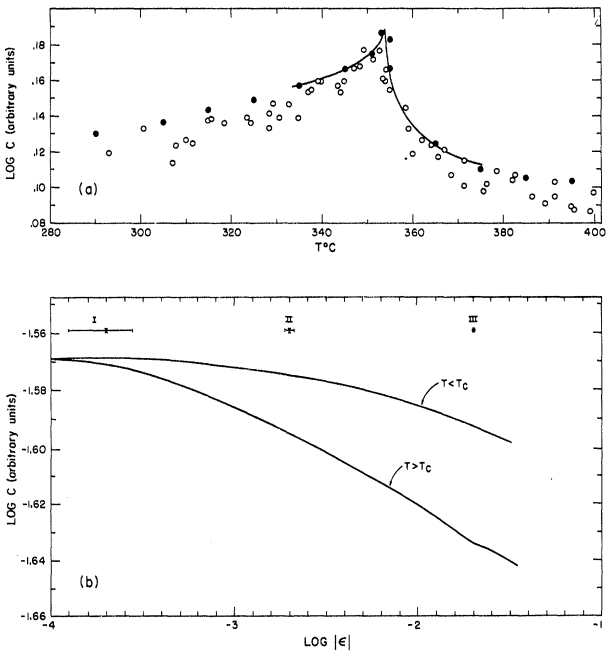

FIG. 2. (a) A comparison of the data of this work with previous results (log$C$ vs T). The open circles are the work of Ref. 6; the closed circles are the work of Ref. 5, to which our data have been normalized. The critical temperature found in this work was about 0.5% below the values quoted in Refs. 5 and 6. (b) Log$C$ vs logϵ. The error bars are discussed in the text.

The values of T_c and relative heat capacities for our work have been normalized to scale with the work of Pawel and Stansbury. Our data fall within the scatter of the other critical heat-capacity work. The precision of our data is roughly the width of the solid curve in Fig. 2(a). As a test of reproducibility, the same sample was heated or cooled through the critical point four times with no detectable change in the observed T-ΔT curve.

Figure 2(b) shows results of one experimental run where log$C(T)$ is plotted versus log$|\epsilon|$. T_c was chosen as the temperature at which the heat capacity reached its maximum. Due to the rounding of the transition at small ϵ, there is an uncertainty (±0.1°K) in the choice of T_c used in calculating ϵ for our data. The uncertainty $\Delta T_c/T_c \simeq 2\times10^{-4}$ sets a lower bound on the values of ϵ for which our data can be considered significant. The error bars labeled I, II, and III in Fig. 2(b) show the effect of the uncertainty in T_c upon ϵ and limit the range in which functional fits can be made to our data. We expect such functions to be significant only for log$|\epsilon| \gtrsim -3$.

The principal interest in critical heat-capacity work is the determination of the indices α and α' in the function[1,2]

$$C(\epsilon)=(A/\alpha)(|\epsilon|^{-\alpha}-1)+B, \quad T>T_c, \qquad 1(a)$$

$$C(\epsilon)=A'/\alpha')(|\epsilon|^{-\alpha'}-1)+B', \quad T<T_c, \qquad 1(b)$$

where A, A', B, and B' are functions whose temperature variation is slow compared to $|\epsilon|^{-\alpha}$. One of the major problems encountered in the analysis of such data is that values of α and α' found from log-log plots like Fig. 2(b) can vary drastically[2] depending on the choice of B and B'.[7] Because of the smooth variation of $C(\epsilon)$ in the present work, this difficulty in the choice of B and B' can be avoided by differentiating the data curve. From Eq. 1(a), $dC/d\epsilon \simeq -A|\epsilon|^{-(\alpha+1)}$ and a plot of $\log dC/d\epsilon$ vs $\log|\epsilon|$ should yield a slope of $-(1+\alpha)$, independent of the value of B (provided B varies slowly with T). We have estimated the effect of the T dependence of B ($\simeq B'$) by assuming that it is due to the lattice and electronic contributions[5] to the heat capacity of Ni, the heat capacity of the ac thermocouple, and the air surrounding the Ni foil in the furnace. The respective contributions to $dB/dT(\simeq dB'/dT)$ are about 5×10^{-5}, 1×10^{-5}, and 1×10^{-5} cal/g (°K)^2 at $\epsilon\simeq-3\times10^{-2}$ and are approximately constant in the range of interest as ϵ changes. Since dC/dT varies from 3×10^{-4} cal/g (°K)^2 to about 4×10^{-2} cal/g (°K)^2 in the present work, the error in α or α' due to setting $dB/dT=dB'/dT=0$ is no larger than 2%. Our results for this sample for α and α' found by differentiating the curves in Fig. 2(b) are $\alpha=0.0\pm0.1$ and $\alpha'=-0.3\pm0.1$ for $-3.2\lesssim\log|\epsilon|\lesssim-1.5$ and represent the smallest uncertainty in these values yet observed.[2]

If the interest of the experimenter is limited to the determination of T_c or the effects of purity, cold working, and crystal perfection on the behavior of the heat capacity near T_c, the present method is especially advantageous. We are presently studying these effects on the rounding at the peak of the heat capacity in Ni and attempting to obtain more accurate values of α and α'.

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COLLISION ANNIHILATION OF SINGLET EXCITONS IN MOLECULAR CRYSTALS*

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A new theoretical analysis of the collision annihilation of the singlet excitons in molecular crystals and its application to the interpretation of experimental data reported in a recent Letter by Bergman, Levine, and Jortner[1] is presented in this Letter. In recent years, investigations have shown that the bimolecular collision annihilations of triplet and singlet excitons in some molecular crystals produce fluorescing singlet excitons and charge carriers, respectively.[1-12] So far, theoretical investigations on the singlet exciton-exciton collision annihilation has been limited to the collision ionization process in which an electron is promoted to a simple continuum, although a qualitative discussion of the role of an autoionized state in continuum was given in Ref. 10, and an attempt on the numerical analysis, although incorrect, has been made by Sharma.[13]

The theoretical and experimental investiga-