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John Van Curen, E.W. Hornung, J.C. Lasjaunias, and Norman E. Phillips

October 1982

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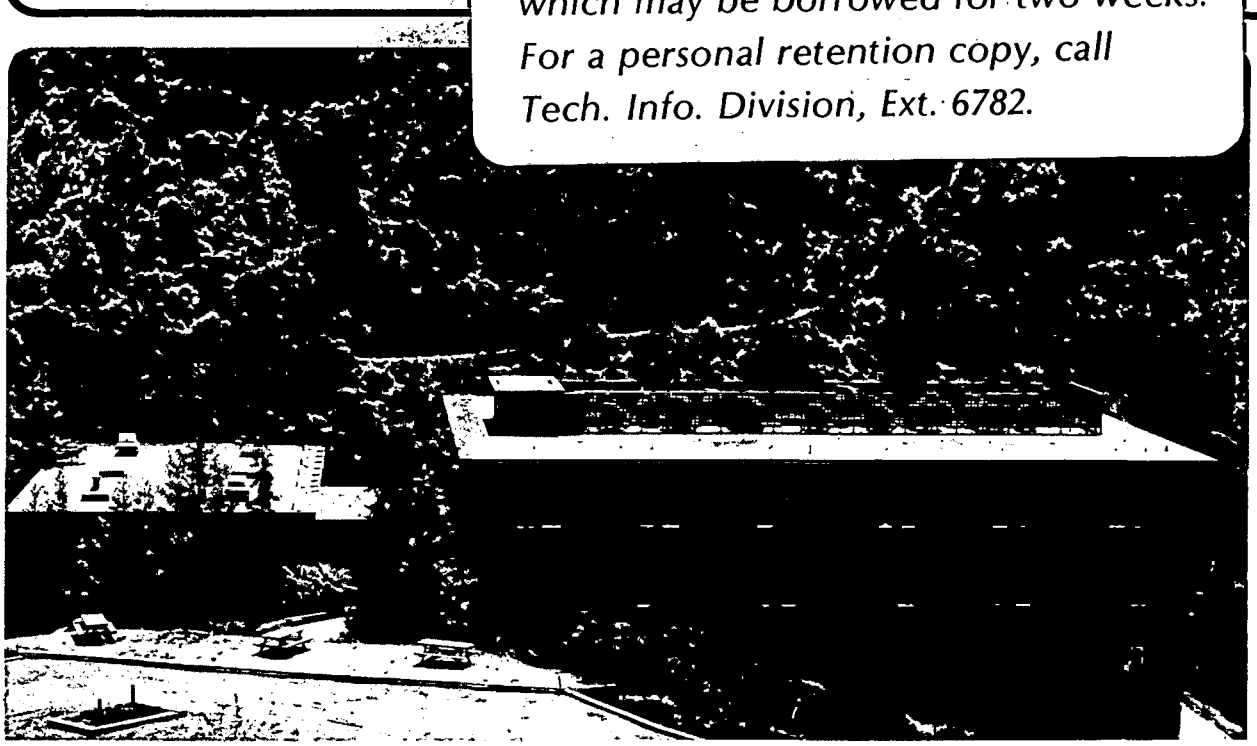

Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

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LBL 15126

Absence of Phason Contribution in the Specific Heat of Potassium

John Van Curen, E. W. Hornung, J. C. Lasjaunias,* and Norman E. Phillips

Department of Chemistry, University of California, and

Materials and Molecular Research Division, Lawrence Berkeley Laboratory,

Berkeley, California 94720

The specific heat of potassium has been measured between 0.33 and 20 K, on an accurate and well documented temperature scale. The results show no evidence of the previously reported phason contribution.

*On leave from Centre de Recherche sur les Très Basses Températures, C.N.R.S. BP166X, 38042 Grenoble-Cedex, France

A number of unexpected properties of the alkali metals, and particularly of potassium, can be understood on the basis of a charge-density-wave (CDW) ground state.[1] The relevant experimental evidence has been reviewed recently by Overhauser, who emphasized that CDW's are inconsistent with certain approximations commonly used in treating many electron effects in metals.[2] Experimental proof of the reality of CDW effects in potassium, one of the closest approximations to a free-electron metal, would thus have far-reaching implications for the theory of electrons in metals.

The broken translational symmetry associated with the CDW state gives rise to new collective excitations, "phasons," and a related anomaly[3] in the low-temperature specific heat, C, which is superimposed on the usual electronic and lattice contributions,

$$C = \gamma T + A_3 T^3 + A_5 T^5 + \cdots\cdots. \qquad (1)$$

Observation of the anomaly in potassium would constitute a persuasive proof of the reality of the phasons and of the CDW state more generally. Such an observation was reported recently: In measurements between 0.54 and 5 K, Amarasekara and Keesom[4] (AK) found an anomaly with an amplitude of 4% of C centered near 0.8 K, in reasonable agreement[2,4] with theoretical predictions. Their conclusion has been questioned on the grounds that the anomaly might be a manifestation of temperature-scale errors,[5,6] but AK have reported[7] that the anomaly was confirmed by additional measurements and have suggested[7] that evidence for it can also be found in other[8] data. The purpose of this Letter is to report new measurements between 0.33 and 20 K that are consistent with Eq. (1) to within the expected accuracy of ±0.2%. In particular, a feature in

the AK data that was crucial to their identification of a phason anomaly is not reproduced.

Because the phason contribution to C is small, the accuracy of the temperature scale is of primary importance. Between 1.5 and 4.2 K the scale used in the measurements described here is the $^4He/^3He$ vapor pressure scale[9], T_{58}/T_{62}. A CMN thermometer was used to interpolate between T_{58}/T_{62} at 1.5 K and nuclear-orientation thermometer data near 16 mK. The scale is in good agreement[10] with the NBS SRM 767 and 768 fixed point devices[11] at the eight fixed points between 99 mK and 7.2 K. (The differences[12] between T_{58}/T_{62} and the provisional scale T_{76} or the thermodynamic scale must be taken into account in these comparisons, but are not important for recognition of the phason anomaly as long as one scale or the other is used consistently.) The response of the CMN thermometer has a simple T dependence, very close to T^{-1} in the region of interest, and therefore gives a <u>smooth</u>[13] temperature scale. In this important respect it is quite possible that this scale is superior to the AK scale which was adjusted at the relatively widely spaced points of the NBS SRM 767. The specific heat of Cu was measured in the same temperature interval and with the same two Ge thermometers used in the potassium measurements, and to 0.1 K on another Ge thermometer that carries the scale to 60 mK. As verification of the temperature scale used in searching for a phason anomaly in potassium, the Cu data are of most interest in the region below 3.5 K. In that region the data are fitted by the first two terms of Eq. (1) with an rms deviation of ~0.1%, maximum deviations of ~0.2%, $\gamma = 0.694$ mJ/K^2 mole, and $A_3 = 0.0477$ mJ/K^4 mole. (On T_{76}, $\gamma = 0.691$ mJ/K^2 mole, and $A_3 = 0.0472$ mJ/K^4 mole.) These results are in excellent

agreement with a recent recommendation for the use of Cu as a calorimetric standard.[14] The deviations from the fit, shown in Fig. 1(a), are systematic, but a comparison with other fits, characterized by T_c, a cutoff temperature above which the data are omitted, and m, the exponent of the highest order term included, shows that they are associated with T-scale irregularities: For $m > 5$ and T_c varied in the range 2 to 10 K, the values of A_5 and higher order coefficients vary unsystematically in both magnitude and sign. Furthermore, the values of A_5 and A_7 determined for $T_c \geq 20$ K, which <u>are</u> relatively constant, would contribute only 0.04% to C at 3.5 K.

The impurity content of the potassium sample[15] was very similar to that of the AK sample--a total of 300 ppm with only B, Ca, Na, Si, and Zr present in excess of 10 ppm. The sample was sealed under vacuum in a thin-walled Cu container. The heat capacity of the container (measured after the potassium was removed) and the thermometer-heater assembly was at most 18% of the total measured heat capacity. AK found different specific heats (but the same phason anomaly) on different cooldowns, and speculated that the discrepancies might arise from different cooling rates. This possibility was tested to some degree in the present work by varying the cooling procedures on the three separate cooldowns from room temperature, and also by subjecting the sample to various temperature cycles between 0.3 and 20 K. No effect on C outside the precision of the data was observed. The results are in reasonable agreement with other data[4,8,16] except that they diverge from the AK results below approximately 0.8 K.

We present first an analysis of the data based on Eq. (1), i.e., on the assumption that there is no phason contribution: For potassium, terms

beyond the second are significant even at 1 K. An indication of the temperatures at which they become important can be obtained from Table I which gives the rms deviations from various least-square fits as a function of T_c and m (defined above). For a given T_c the rms deviations drop relatively rapidly with increasing m to a value near 0.07% and then more slowly with further increases in m. The fits just under the stepwise line in Table I are taken to be "reasonable" in the sense that the value of m is close to optimum for the T_c--for smaller m the number of terms is inadequate, and for much higher m the additional terms are to a greater degree fitting scatter in the data and the T-scale irregularities. The values of a given coefficient are reasonably consistent for all of the "reasonable" fits, but the uncertainty in the coefficient of course increases with the order of the term: For <u>all</u> fits below the line in Table I, γ = 2.081 or 2.082 mJ/K^2 mole, A_3 is between 2.60 and 2.61 mJ/K^4 mole, and A_5 is between 1.6×10^{-2} and 3.7×10^{-2} mJ/K^6 mole. For the "reasonable" fits the range of A_5 is reduced to 2.8×10^{-2} to 3.3×10^{-2} mJ/K^6 mole, and although A_7 and A_9 still vary by about 50%, they do remain constant in sign (respectively, positive and negative). Deviations from the T_c = 3.5 K, m = 5, 9 (3-, 5-term) fits are shown, as examples, in Figs. 1(b) and 1(c). For m = 5 the deviations are only ±.2%, but in this case they arise predominantly from the higher order terms omitted in the fit, as shown by several properties of the fits: (1) The temperature dependence of the deviations is not related to that of the Cu deviations [Fig. 1(a)] in the way expected for T-scale errors common to both. (2) The value of A_5 obtained for this fit is about 60% greater than that obtained by the "reasonable" fits. (3) The values of A_5, A_7, and A_9 obtained for the

T_c = 3.5, m = 9 fit <u>are</u> all very similar to the values obtained from the "reasonable" fits for all other T_c's.

As a basis for further discussion we take the T_c =3.5, m = 9 fit, for which

$$\begin{aligned} \gamma &= 2.082 \text{ mJ/K}^2 \text{ mole}, \\ A_3 &= 2.602 \text{ mJ/K}^4 \text{ mole}, \\ A_5 &= 3.185 \times 10^{-2} \text{ mJ/K}^6 \text{ mole}, \\ A_7 &= 3.116 \times 10^{-3} \text{ mJ/K}^8 \text{ mole}, \\ A_9 &= -1.652 \times 10^{-4} \text{ mJ/K}^{10} \text{ mole}. \end{aligned} \tag{2}$$

For this fit, and at 3 K, the T^5 term contributes 8.2% of C, and the T^7 and T^9 terms together, 4.6%. (For all the "reasonable" fits in Table I, the contribution of the T^5 and higher order terms is 12-13%, including 4-6% from the T^7 and higher terms.) The values of the phonon parameters can be compared with those derived[17] from inelastic neutron scattering data-- A_3 = 2.35 mJ/K^4 mole, and A_5 = 4.24 × 10^{-2} mJ/K^6 mole. The discrepancy in A_3, which corresponds to 3% in sound velocity, is reasonable in view of the uncertainty in the low energy neutron data. For the higher terms the agreement is actually much better than suggested by the reported calculated values, which are based on a linear approximation to the relation between C/T^3 and T^2. Fig. 1 of Ref. 17 clearly shows curvature in the calculated relation which corresponds to a lower value of A_5 and to non-zero values for the higher terms. That figure suggests that the calculated total contribution of the dispersion terms (T^5 and higher) is within a few percent of the experimental value at 3 K. The coefficient of the electronic term γ, corresponds to an effective mass ratio m^*/m = 1.25, in excellent agreement[6] with de Haas-van Alphen data and with the calculated band mass and phonon enhancement. Thus,

up to 3.5 K, C is in good agreement with other information on electronic structure and lattice dynamics.

It is also of interest to analyze our data by plotting $y \equiv (C-\gamma T-A_5T^5)/T^3$ against T^2, the method used by AK and which takes into account the expected T dependence of the phason contribution. If phasons are present and γ and A_5 correctly assigned, y would rise from a constant value in the temperature interval in which only terms through the T^5 term are important in Eq. (1) to a higher constant value in the low-T limit. Figure 2 reproduces AK's analysis of their data--with γ and A_5 chosen to give a roughly constant y for $2 \lesssim T^2 \lesssim 10\ K^2$ and below $T^2 \approx 0.7$. Since the sharp break at 0.8 K in the AK data does not occur in ours, the same criterion applied to our data leads to a much smaller and less precisely defined anomaly. One possibility is shown by the $\gamma = 2.082\ mJ/K^2$ mole points in Fig. 2. However, <u>even this anomaly</u> is a consequence of the arbitrary exclusion of the T^7 and T^9 terms from the analysis: the change in slope of y vs T^2 at $T^2 \sim 2.5\ K^2$ disappears if the observed T^7 and T^9 terms are also subtracted from C, and a change in A_5 then brings the points onto a horizontal straight line. [This was demonstrated in a different way in Fig. 1(c).] Fig. 2 also shows that an upturn in y comparable to that found by AK requires $\gamma = 1.88\ mJ/K^2$ mole for our data, but the behavior below 0.8 K then bears no resemblance to that expected for phasons.

In summary, the specific heat of potassium is consistent with other information about the electron and phonon densities of states, and not with the phason anomaly reported by AK. An anomaly that is smaller by about an order of magnitude is not completely ruled out, but the establishment of its existence would require accurate specific

information on the lattice heat capacity in the 1 to 3 K region. The principal reason for the difference between this conclusion and that drawn by AK is the discontinuity in slope in their data near 0.8 K, which is not reproduced in our data. Although this feature is small, only about 2% in C, it was critical to their conclusion. Because it occurs near the end of their temperature scale while our scale gives the expected values of the specific heat of Cu to 0.1 K, we conclude that the anomaly they report is a consequence of T-scale irregularities. Their assumption that the T^7 and T^9 terms in C were unimportant below 3 K also contributed, but to a much smaller degree, to the difference in the conclusions.

ACKNOWLEDGEMENTS

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

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Table 1. RMS deviations (percent) from least squares fits of Eq. (1) to the specific heat of potassium. See text for definition of T_c and m.

m	T_c(K)					
	2	3	3.5	4	5	6
5	.082	.116	.116	.170	.771	1.69
7	.070	.085	.112	.150	.239	.253
9	.069	.073	.073	.079	.131	.229
11	.069	.072	.071	.070	.071	.110
13	.065	.071	.071	.070	.067	.069

Figure Captions

Figure 1. Deviations from least squares fits to the Cu and potassium data below 3.5 K. C_o represents Eq. (1) with the specified number of terms.

Figure 2. The specific heat of potassium (see text for explanation).

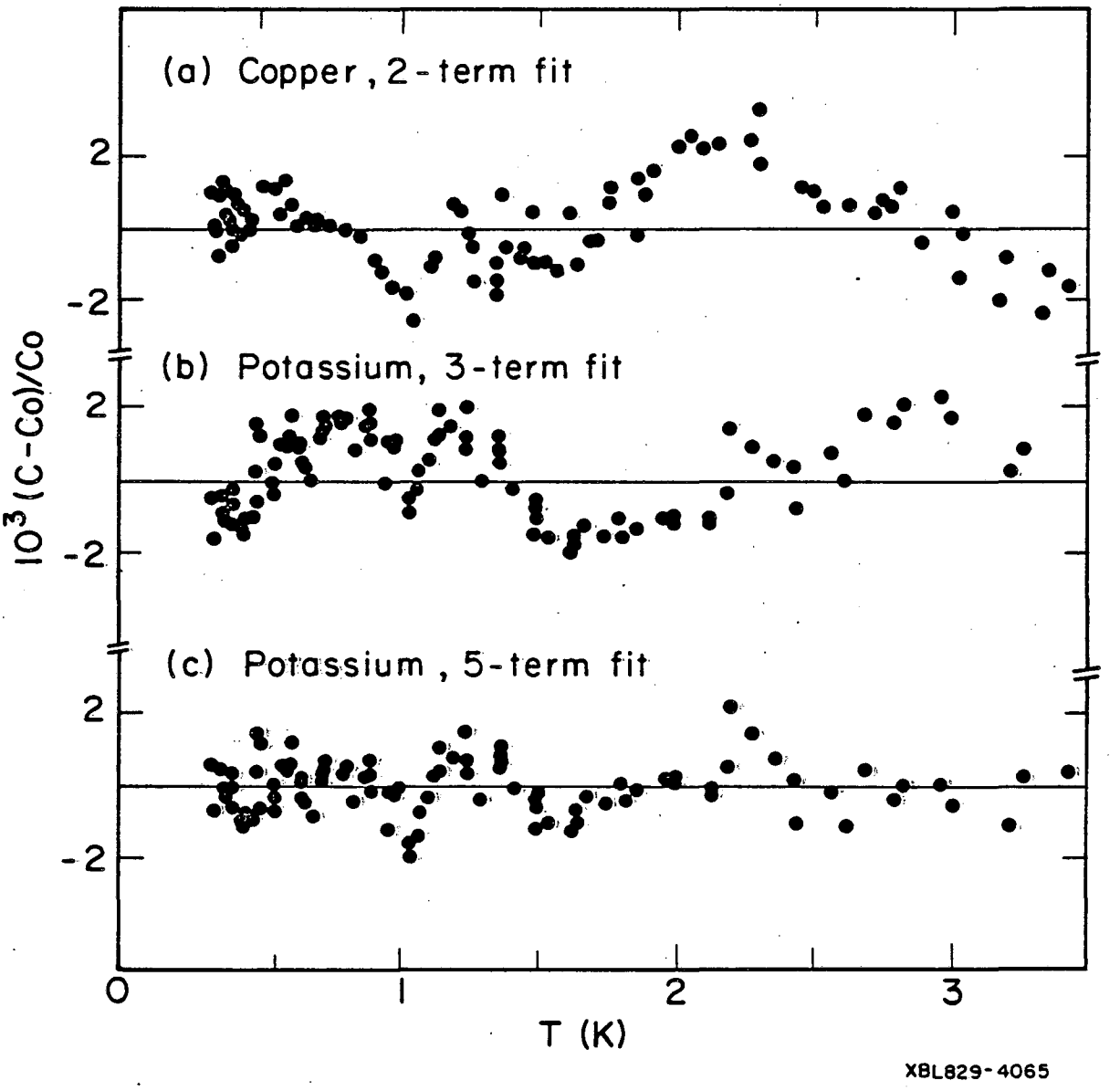

Figure 1. Deviations from least squares fits to the Cu and potassium data below 3.5 K. C_0 represents Eq. (1) with the specified number of terms.

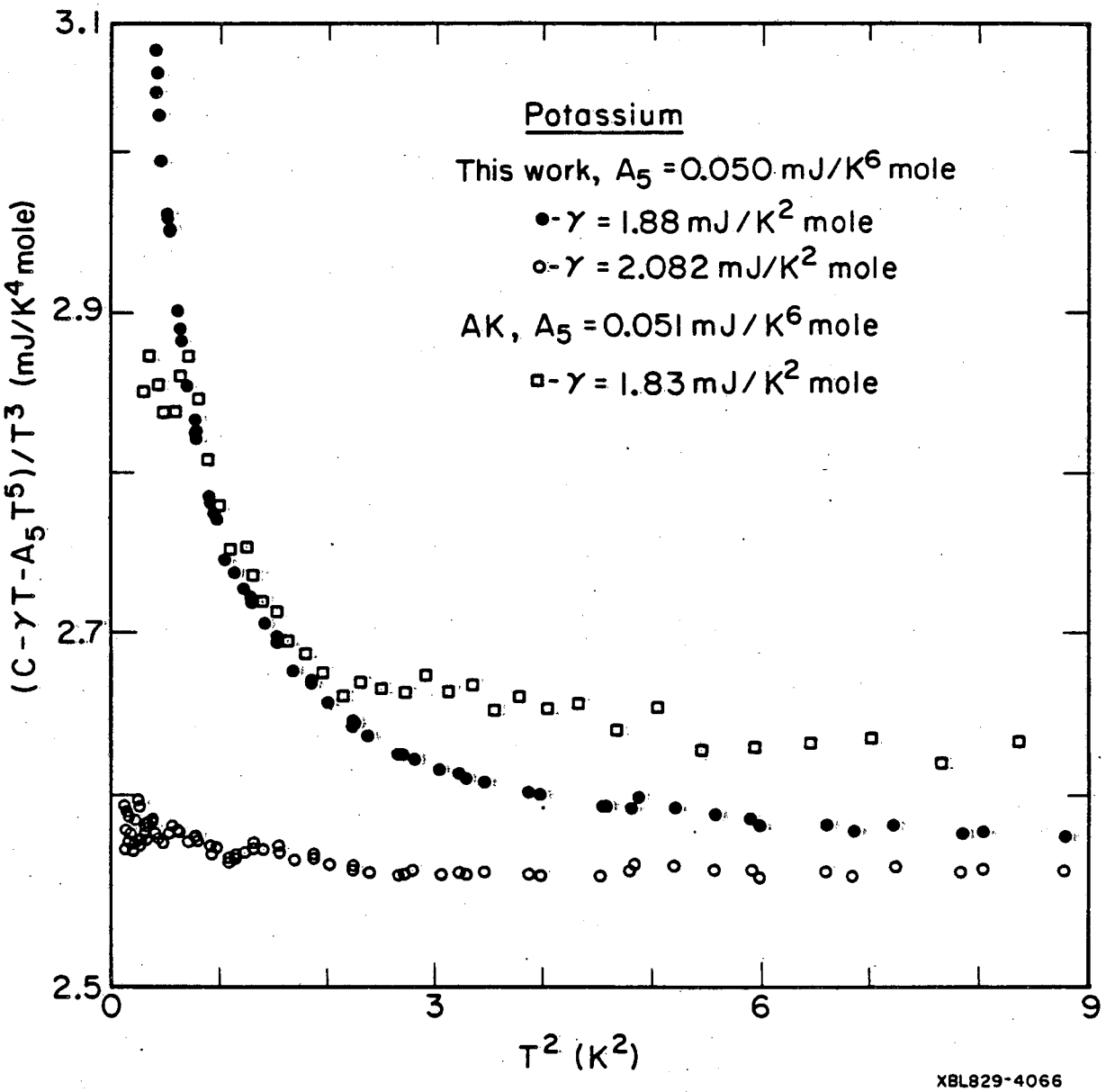

Figure 2. The specific heat of potassium (see text for explanation).

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