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Identification of a phason heat capacity in the low-temperature specific heat of potassium

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The low-temperature specific heat of potassium has been remeasured in the temperature range 0.5 – 5 K. An anomaly located around 1 K is identified as a phason-heat-capacity contribution. The fraction of phonons converted to phasons is 2×10^{-5} and the Debye temperature of these phasons is 6 K. Two independent measurements of the same potassium sample show a difference of 2% in total specific heat but both sets show the same phason anomaly around 1 K.

I. INTRODUCTION

Does potassium have a charge-density wave? The answer to this question has been pursued by Overhauser[1] for the last two decades. He showed that a free-electron gas contained in a background of smeared-out positive ions (the jellium model) is inherently unstable and that charge-density waves (CDW's) can provide lower-energy states. The simple metals, like the alkalis, have an extremely weak Born-Mayer ion-ion interaction and consequently have difficulties in resisting lattice changes corresponding to a CDW, as shown by Overhauser.[2] With many collaborators Overhauser[1,3–6] worked out the consequences of this conjecture and found many (at least ten) experimental results indicating the existence of CDW's in potassium, e.g., linear magnetoresistence, anomalies in the optical absorption, residual resistivity, induced torque, etc. They succeeded in providing quantitative theoretical analysis for several of the anomalous properties observed in alkali metals, mostly in potassium. Two phenomena, however, Knight shift and de Haas – van Alphen effect, agree with the standard electron theory, without CDW's. Overhauser provides speculation why these phenomena show no evidence for CDW's. While this theory explains deviations from free-electron-gas behavior for alkali metals, the experimental results are sometimes irreproducible. This could be the result of domain structure induced by the CDW's. There are 24 equivalent directions[5] for the CDW's and so physical phenomena which depend on the charge-density-wave-vector direction will be irreproducible For the specific heat this difficulty was not expected to occur; however, we find that also for the specific heat of potassium the results are not reproducible, although still indicating the existence of CDW's.

When a CDW is incommensurate with the crystal lattice, translational symmetry is destroyed. This leads to collective modes of the phase of the CDW, known as "phasons." The phasons are a type of vibrational mode of the distorted charge distribution and are linear combinations of the original phonons. As compared to these original phonons half of the phasons are shifted downwards in frequency and will contribute additionally to the low-temperature specific heat of metals containing CDW's.

It became interesting to us when Overhauser, Boriack, and Giuliani[6,7] worked out the consequences of a CDW for the low-temperature specific heat. The predicted magnitude of the effect for potassium, which should occur around 1 K, is only about 1% of the low-temperature specific heat, which itself has a precision of the same order. We were, however, persuaded to measure the specific heat of potassium and to our surprise found an anomaly which is of the order of 4% of the total specific heat around 1 K and has the characteristics of the phason contribution.

We reported[8] our first measurements on potassium, they have been criticized as not convincing. When these criticisms were submitted we were in the process of recalibrating the thermometer and remeasuring the heat capacity of potassium and of copper. We present in this paper new data and the previous data, now based on a recently adjusted temperature scale of the thermometer. The previous conclusion remains the same.

II. EXPERIMENTAL

Two nearly identical, cylindrical calorimeters were made from 2-mil copper foil and with seams soldered with a low-melting-point silver solder. To enhance heat distribution five 50-mil annealed copper wires were placed in the center and soldered to the bottom. The mass of copper was approximately 12 g and that of the solder 1.5 g. One calorimeter was filled by the Callery Chemical Company with about 53 g of potassium under an argon atmosphere and sealed by them. The company supplied spectrographic analyses which are shown in Table I. All impurities with the exception of three nonmagnetic ones, were less than 10 ppm by weight and should have only a negligible contribution to the specific heat.

For this experiment we obtained a nitrogen-filled germanium thermometer which had been calibrated by the manufacturer between 0.1 and 6 K. This thermometer was compared with the National Bureau of Standards Fixed Point Device SMR767. We found some small deviations, less than 2 mK, which is within the accuracy of the superconductive transition temperature, and adjusted the temperature scale of the thermometer smoothly to agree with the fixed-point temperatures. The temperature range between 0.5 and 4 K was subdivided into three regions which are sufficiently overlapping. A computer fitted each region with a polynomial,

$$\frac{1}{T}=\sum_{i=0}^{7} A_i(\log_{10}R)^i$$

(where R is the resistance and the A's are constants). With eight coefficients this polynomial is capable of reproducing the temperatures to a precision of 0.1–0.2 mK. Recently we rechecked our thermometer after a six-month period with the Fixed Point Device and found no change from the previously obtained temperature scale. In addition we also compared the thermometer with the vapor pressures of ^{3}He and ^{4}He and found agreement within random errors of 3 mK, the accuracy of comparison. However, we readjusted the temperature scale below 0.6 K by one millidegree, which decreased the deviation of the copper specific heat from its least-squares fit. All the calculations done in this paper are based on this recently adjusted temperature scale.

A heater, a 10-cm Pt-10 at. % W wire with 5-cm 40-gauge copper wire attached to each end, and the leads of the thermometer were wound on a calorimeter and fastened to it with a small amount of General Electric varnish no. 7031. In previous measurements we have had success with this kind of mounting. However, while our previous thermometers had copper lead wires, the leads of this thermometer are made of phosphorbronze and this gave us difficulty as the heat conduction by phosphorbronze wires is several orders of magnitude smaller than that of copper. As a consequence, the heat dissipation recommended by the manufacturers, which we had previously used successfully, heated this new thermometer significantly above the temperature of the sample. We found that after an increase of measuring current the subsequent data were about 10 to 20% too high and we had to discard the initial set of measurements.

The calorimeter was hung inside a vacuum chamber whose walls could be cooled down to 0.3 K with the use of ^{3}He liquid. When this vacuum chamber was evacuated the only path for heat to flow from the calorimeter to the surroundings was through eight 3-mil diameter niobium wires used for electrical connection to the thermometer and heater wire. At 0.5 K the heat leak to the potassium-filled calorimeter was 0.1 erg/sec and

TABLE I. Spectrographic analysis of impurities in potassium (in parts per million by weight). The amounts of metal impurities in K are calculated from the results of a spectrographic analysis of the chloride salt.

Element	ppm	Element	ppm	Element	ppm
Ag	<2	Cu	<2	Pb	<10
Al	<4	Fe	<10	Si	48
B	<19	K	Balance	Sn	<10
Ba	<6	Mg	4	Sr	<2
Be	<2	Mn	2	Ti	<10
Ca	15	Mo	<6	V	<2
Co	<10	Na	29	Zr	<19
Cr	<10	Ni	<10		

the drift rate was 5×10^{-6} K/sec. At this temperature we used heat pulses of 600 erg, producing a temperature jump of 0.03 K, so that the thermal insulation was more than adequate. To obtain the addenda correction we measured an empty calorimeter, on which were fastened the thermometer and heater with the same amount of varnish.

We found for the heat capacity of the addenda,

$$C_{\text{add}}=140T+19.9T^3\ , \tag{1}$$

in units of μJ/K, while we calculated for this addenda heat capacity from published values,

$$C_{\text{add}}=131T+19.9T^3\ , \tag{2}$$

in units of μJ/K. We assumed for the low-melting-point solder the specific heat of pure tin which probably is the reason for the difference in the linear term of these two equations. At 0.5 K the addenda heat capacity was 4% of the total, and decreased to 2 and 1% at 1 and 2 K, respectively.

As a check on the thermometer and the measuring system we measured twice, with an interval of half a year, the specific heat of a standard copper sample, designated *T*4.2, kindly given to us by Argonne National Laboratory.

A least-squares fit (up to 5 K) of the specific heat for this copper sample gave

$$C_{\text{LS}}=0.688T+0.048T^3\ , \tag{3}$$

in units of mJ/mole K, which is in good agreement with the copper reference of Osborne.[9] The coefficient of the linear term is 0.9% lower while that of the lattice term is 0.9% higher than that given by Osborne.[9] This is partially a consequence of the change from T_{62} to T_{76}. For example, just the change from T_{62} to T_{76} scale reduces the specific heat at 1 K by 0.6% and at 2 K by 0.4%. The relative deviation of the experimental points for copper from the least-squares fit is

$$\Delta C/C\equiv\frac{(C-C_{\text{LS}})}{C}\ ,$$

and is shown in Fig. 1.

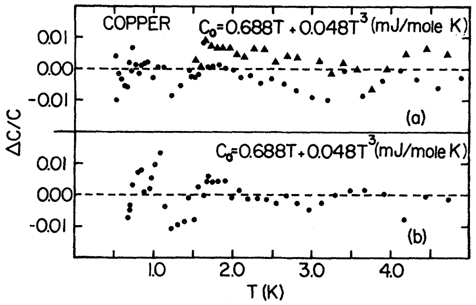

FIG. 1. Relative deviation of the specific heat of the standard copper sample *T*4.2, from least-squares fit; $C_{\text{LS}}=0.688T+0.048T^3$ mJ/mole K. (a) First set measured twice, distinguished by ● and ▲. (b) Second set measured after six months.

III. ANALYSIS

The experimental specific heat of potassium for the first and second set of measurements between 0.5 and 3 K are listed in Tables II and III, respectively.

If we define C_0 as the specific heat of a pure metal, without CDW contributions, then at low temperatures it is expected that

$$C_0=\gamma T+\alpha T^3+\beta T^5\ . \tag{4}$$

The term linear in *T* is the electronic contribution

TABLE II. Specific heat of potassium in mJ/mole K; *T* in kelvin. First set.

T	*C*	*T*	*C*	*T*	*C*
0.540	1.442	1.179	6.771	1.937	24.43
0.573	1.596	1.224	7.394	2.005	26.86
0.648	1.968	1.276	8.151	2.077	29.77
0.691	2.217	1.332	9.059	2.160	33.16
0.760	2.658	1.395	10.14	2.246	37.31
0.798	2.943	1.460	11.36	2.337	41.60
0.840	3.275	1.514	12.51	2.435	47.05
0.885	3.632	1.578	13.92	2.538	53.38
0.936	4.060	1.642	15.47	2.649	60.85
0.991	4.587	1.705	17.19	2.767	69.25
1.052	5.216	1.765	18.86	2.890	79.61
1.113	5.947	1.824	20.67	3.020	91.59
1.142	6.290	1.880	22.39		

TABLE III. Specific heat of potassium in mJ/mole K; T in kelvin. Second set.

T	C	T	C	T	C
0.539	1.490	1.174	6.628	1.919	23.11
0.647	2.014	1.222	7.256	1.988	25.38
0.692	2.276	1.273	7.971	2.058	28.00
0.722	2.455	1.309	8.515	2.131	30.99
0.756	2.666	1.357	9.302	2.205	34.15
0.794	2.935	1.400	10.03	2.285	37.78
0.836	3.238	1.444	10.83	2.374	42.20
0.884	3.619	1.493	11.77	2.471	47.37
0.936	4.065	1.545	12.85	2.574	53.59
0.972	4.400	1.604	14.17	2.687	61.18
1.006	4.718	1.664	15.61	2.805	70.56
1.043	5.150	1.726	17.24	2.906	78.06
1.084	5.532	1.788	19.07	3.007	86.68
1.128	6.034	1.852	20.85	3.106	96.41

to the specific heat and the two following terms are the very-low-temperature lattice contributions. One of the difficulties in the interpretation is the following question: Up to what temperature is Eq. (4) a valid representation of the specific heat, as the lattice specific heat will show deviations at higher temperatures? This was the difficulty in the interpretation of the data of rubidium[6] for which Taylor *et al.*[10] showed that Eq. (4) can not be used above 0.25 K. But they also showed that for potassium Eq. (4) can be used up to 3 K. This conclusion was based on the results of a normal ground-state model which reproduces the experimental dispersion curves for the different alkali metals very well. Although their estimate of the coefficients are probably not more accurate than 10%, their main conclusion about the validity of Eq. (4) up to 3 K appears to be very well founded.

We analyzed the data as follows. We define

$$y \equiv \frac{(C-\gamma T-\beta T^5)}{T^3} .$$

This quantity y should be constant for the correct choice of γ and β and in the absence of other contributions. We applied this analysis first to copper. For Cu, $\beta=0$ and therefore we plotted y for several values of γ (see Fig. 2) and determined when y became constant. This way we found $\gamma=0.687$, $\alpha=0.048$. These values agree quite well with the least-squares fit given in Eq. (3).

For potassium we estimated from the data between 2 and 3 K that $\beta=0.051$ mJ/mole K^6, for both sets of measurements. This value was also found previously by Lien and Phillips.[11] With this β value y was calculated for different values of γ and then plotted versus T^2. In Fig. 3 are presented y for three different values of γ for the first set of

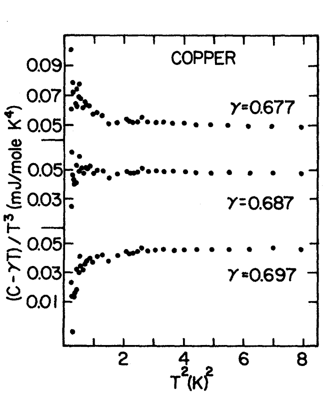

FIG. 2. Copper, first set of measurements. $(C-\gamma T)/T^3$ vs T^2 for three values of the constant γ in mJ/mole K^2.

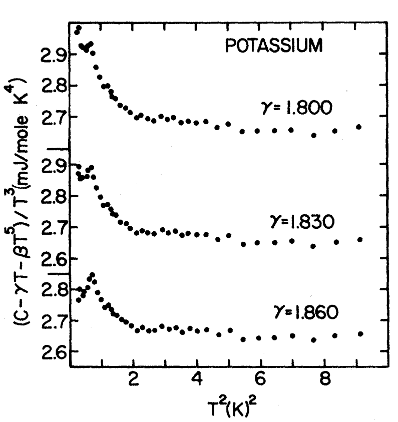

FIG. 3. Potassium, first set of measurements. $(C-\gamma T-\beta T^5)/T^3$ vs T^2 for three values of the constant γ in mJ/mole K^2; $\beta=0.051$ mJ/mole K^6.

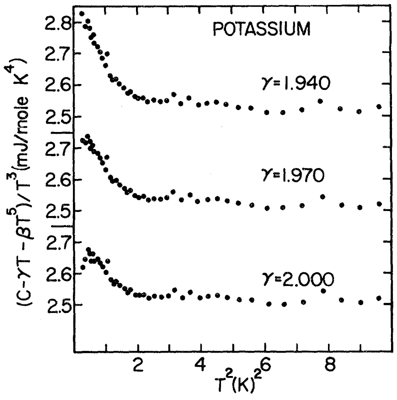

FIG. 4. Potassium, second set repeated after six months. $(C-\gamma T-\beta T^5)/T^3$ vs T^2 for three values of the constant γ in mJ/mole K^2; $\beta=0.051$ mJ/mole K^6.

measurements. In Fig. 4 we present the second set of measurements.

It appeared that the specific heat was anomalous as it was impossible with our data to find a value of γ that made y constant, so that we were forced to assume an additional low-temperature contribution to the specific heat. It also appeared unlikely that impurities could cause this anomaly.

We think that the logical explanation for this anomaly is the predicted CDW, and so we made use of the calculations of Giuliani and Overhauser[6] for this effect. The CDW introduces phasons and these have an additional contribution at low temperature that is proportional to T^3 and that will decrease rapidly at higher temperatures. As a consequence the CDW will manifest itself in y: y will be constant at very low temperatures but with a value higher than α, the coefficient of the cubic term in the specific heat. At higher temperatures y will decrease and become equal to α. And this is indeed what we observe. We can find a value for γ so that y is constant at the very lowest temperatures, then decreases and thereafter, up to 3 K, is constant again.

Accordingly, for the first set,

$$C_0=1.83T+2.66T^3+0.051T^5\ , \tag{5}$$

in units of mJ/mole K, and for the second set

$$C_0=1.97T+2.51T^3+0.051T^5\ , \tag{6}$$

in units of mJ/mole K.

In Fig. 5 we show $(C-C_0)/C_0$; a maxima is observed at $T=0.75$ K which leads to a maximum in ΔC vs T at 1.08 K, and a phason Debye temperature $\Theta_{\rm CDW}=6$ K. The maximum phason contribution is $(4\pm2)\%$, which corresponds to a fraction of the phonons converted to phasons of 2×10^{-5}.

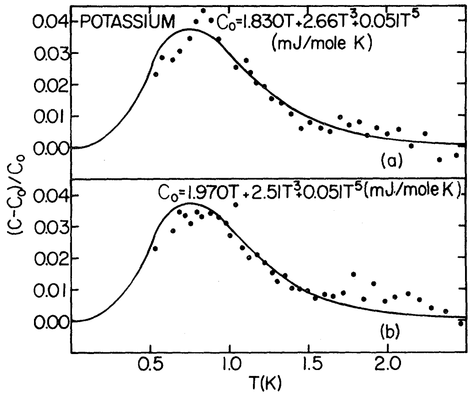

FIG. 5. Relative deviations of the experimental results from C_0: $(C-C_0)/C_0$. Smooth curve is the theoretical heat-capacity anomaly caused by the CDW structure, taken from Ref. 6 with the parameters $\Theta_{\rm CDW}=6$ K and the fraction of phonons converted to phasons of 2×10^{-5}. (a) First set of measurements reported previously but recalculated with a recently adjusted calibration for the thermometer. (b) Second set of measurements repeated after six months.

The theoretical heat-capacity anomaly caused by the CDW structure[6] with the above parameters fits the experimental points very well as shown by the solid curves.

IV. DISCUSSION

We measured twice the same potassium sample in the same calorimeter with the same thermometer and addenda. After each potassium measurement we measured our standard copper sample and also recalibrated the thermometer. The thermometer was stable in this time span of a half-year and we found excellent agreement between the two sets of copper data. However, the two sets of potassium measurements show systematic differences. As compared to the first set of measurements, the second set is higher by 2% at 0.6 K, low by 2% at 3 K, and no difference around 1 K. After all the different checks, we conclude that the differences of 2% are real. This leaves us with the following puzzle: Why does the heat capacity of potassium not reproduce, which is the normal behavior for most materials? We have no answer for this enigma.

It is unlikely that the original filling and handling of the calorimeter would have left a significant amount of defects as potassium is self-annealing at room temperature. The possible cause for the difference between the two results may arise from the rate of cooling of the sample. In the first experiment the cooling was twice as fast

TABLE IV. Comparison of experimental specific-heat data of potassium with prior measurements.

	C (mJ/mole K)				
Reference	1.0 K	1.5 K	2.0 K	2.5 K	3.0 K
This work (first set)	4.65	12.2	26.5	50.1	88.5
This work (second set)	4.65	11.9	25.9	48.9	86.7
Lien and Phillips (Ref. 11)	4.7	12.2	26.3	50.2	87.8
Filby and Martin (Ref. 12)	4.65	12.3			88.3
Roberts (Ref. 13)		12.7	26.4	50.2	86.6

as for the second one. In the latter it took two weeks to cool from 300 to 4 K and two days from 4 K to the lowest temperature. On cooling potassium shrinks faster than copper and this can cause stresses, an effect already discussed previously by Filby and Martin,[12] in their analysis of the specific heats of rubidium and cesium.

As a consequence of the difference between the two sets, the values of γ and α in C_0 are different [see Eqs. (5) and (6)]. The theoretical values[10] for α and β are both substantially lower than the experimental values. Although the theory reproduces the neutron scattering data very well, it apparently does not reproduce the acoustic range accurately. Both sets, however, show the same anomaly which led us to conclude in favor of the existence of phasons. Although Lien and Phillips[11] indicate difficulties between 0.7 and 1.1 K, their results also point to the existence of phasons. The relative deviations of their experimental results from C_0, using their values for γ, α, and β in Eq. (4) are displayed in Fig. 6, and show the same maximum around 0.8 K, although less pronounced.

In Table IV we compared our two sets of heat-capacity measurements with prior measurements.[11–13] Both our first and second set of measurements agree very well with all the previous results around 1 K. Above 1 K our first set is in good agreement with all the prior measurements except with Roberts.[13] While the difference between the first and second set is about 2% as we discussed before.

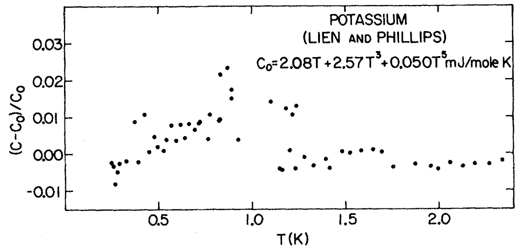

FIG. 6. Relative deviations of the experimental results for potassium taken from Lien and Phillips (Ref. 11).

The effective-mass ratio for potassium calculated for the first and second set of results are 1.10 and 1.18, respectively. These values are lower than the value 1.23 which follows from the de Haas–van Alphen measurements.[14] However, because of electron-electron interactions[15] the effective-mass ratios deduced from the two different types of measurement can differ by several percent.

The value of the phason Debye temperature, 3.25 K, estimated from the low-temperature resistivity[16] is lower than the value of that reported in this work. This is not unexpected since the resistivity caused by phason scattering involves the matrix element for electron-phason scattering, which is expected to decrease at higher phason frequencies. The fraction of phonon modes converted to phasons was estimated by comparison with the theoretical curve (Fig. 1) of Ref. 6. We obtained a value 2×10^{-5}, which is approximately the same fraction needed to fit the low-temperature resistivity.[16]

In conclusion this work on specific heat of potassium provides experimental evidence for the existence of phasons and thereby charge-density waves in potassium. In addition the electron and phonon contribution to the specific heat of potassium can differ by 2% for different measurements on the same sample. This observation is not understood.

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