Experimental investigation and analysis of the temperature dependence of the specific heat of crystalline mercury in the vicinity of its melting point

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Measurements were made of the heat capacity $C_p(T)$ of high-purity mercury in the range 150.9–233.8 K in order to determine the dependence $C_p(T)$ in the vicinity of the melting point T_m. The published data were found to be insufficient for a detailed study. An analysis of the results showed that the temperature dependence $C_p(T)$ consisted of two intervals: far from and close to T_m. In the far interval the heat capacity $C_p(T)$ was described satisfactorily by an additive equation but without the term representing the contribution C_c of the disorientation of the crystalline clusters. An adequate description of the close interval was obtained by adding the contribution $C_c \propto F(\tau)^{-1/2}$. An analysis of the approximations used in the close interval led to the conclusion that a mobile and highly developed defect structure existed in mercury near T_m and its contribution was not described by the classical expression for vacancies $C_{\text{vac}} \propto (E_0^2/RT^2)\exp(-E_0/RT)$.

1. INTRODUCTION

A satisfactory description of such fundamental effects as melting is still lacking. The authors of many theoretical papers describing the melting processes start from certain model representations. It is not yet clear which of these models applies to the crystal lattice at high temperatures when the lattice is destroyed. In this situation an analysis of the temperature dependences of the thermodynamic properties in the vicinity of the melting point T_m may help in providing satisfactory model descriptions. This approach has been used successfully in studies of second-order phase transitions. However, since the anomalous component of the heat capacity $C_p(T)$ near T_m represents only a few percent of the total value, which is almost an order of magnitude less than the anomalous $C_p(T)$ near second-order phase transitions, experimental investigations near the melting point must be carried out on very pure samples, the precision of the measurements should be high, and the number of experimental values of $C_p(T)$ has to be large.

The singularities of the temperature dependences of the thermodynamic properties of crystals near T_m are usually attributed to:

a) an increase in the concentration of the equilibrium vacancies and other point defects on increase in temperature;

b) an increase in the amplitude of the ion vibrations, which enhances considerably the contribution of various anharmonic factors[1–4];

c) an increase in the mobility of the dislocations and the associated appearance of crystalline clusters.[5]

It follows that the specific heat $C_p(T)$ near T_m can be represented generally by the following sum of the contributions:

$$C_p = C_v^h + C_{\text{el}} + C_{\text{an}} + C_{\text{vac}} + C_c, \tag{1}$$

where C_v^h is the lattice component of the specific heat considered in the harmonic approximation. In an analysis of the experimental results the value of C_v^h is calculated by two methods:

a) in the Debye approximation, which gives

$$C_v^h = 3R[1 - {}^1/_{20}(\Theta_D/T)^2],$$

b) from the known phonon spectrum $g(\nu)$ (Ref. 6),

$$C_v^h = R\int_0^\infty g(\nu)\left(\frac{h\nu}{kT}\right)^2 \frac{\exp(-h\nu/kT)}{[1-\exp(-h\nu/kT)]^2},$$

where R is the universal gas constant; Θ_D is the characteristic Debye temperature; T is the absolute temperature; h is the Planck constant; k is the Boltzmann constant; ν is the frequency; $C_e = \gamma T$ is the electron component of the heat capacity (we shall ignore the electron-electron interaction effects).

The temperature dependence of the component C_{an} associated with the anharmonicity of the lattice vibrations is much more difficult to determine. In accordance with the theory of self-consistent phonons[3,4] and other theories of anharmonic melting, the value of $C_{\text{an}}(T)$ rises rapidly on approach to T_m. This rise should amount to hundreds of percent of C_v^h, but it has not been confirmed experimentally (particularly in the case of metals). Therefore, we have retained in C_{an} the usual anharmonic corrections in the form

$$C_{\text{an}} = BT + DT^2.$$

At high temperatures a considerable contribution to C_p of the crystalline phase may come from C_{vac} which is a component associated with the formation of equilibrium vacancies:

$$C_{\text{vac}} = \frac{LE_0^2}{RT^2}\exp\left(-\frac{E_0}{RT}\right).$$

It is assumed in this case that the vacancy formation energy E_0 is independent of temperature.

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Moreover, Eq. (1) includes a contribution C_c which is associated with disorientation of crystalline clusters. In accordance with the theory of quasicrystalline melting, we have

$$C_c=F\tau^{-1/2},$$

where $\tau=(T_c-T)/T_c$; T_c is the point of absolute instability of the crystal; L and F are constants.

We first tried to analyze the available published data on the temperature dependence of $C_p(T)$ in the vicinity of the melting point T_m of mercury,[7] argon and krypton.[8] With this in mind we approximated the results by two possible expressions that follow from Eq. (1):

$$C_p(T)=C_v^h+BT+C_{\text{vac}}, \tag{2}$$

$$C_p(T)=C_v^h+BT+C_c. \tag{3}$$

This approximation was carried out by the method of least squares. The adequacy of the description of the experimental data was tested in the same way as in Ref. 9.

It follows from our analysis that a satisfactory description can be provided for all three elements by using Eq. (2) or Eq. (3). In the case of mercury the parameters of the approximation of E_0 by using Eq. (2), and T_c and F by using Eq. (3) are in full agreement with those predicted theoretically.[5-10] In the case of krypton and argon these parameters are different from the theoretical predictions.

We can therefore see that the published experimental data do not allow us to separate the various mechanisms of the premelting anomalies of $C_p(T)$. This conclusion is also confirmed by an analysis we made of Zn, Al, Pb, In, and Sn (Ref. 11).

We carried out a computer experiment to determine what experimental data near T_m are needed in order to carry out the proposed analysis. A set of values of $C_p(T)$ at N points in the temperature interval $(T_m-T)\approx 20$ K was calculated from Eq. (2). Use was made of the parameters obtained by approximation to the data of Ref. 7. The computer introduced a Gaussian random scatter of the results, with an rms deviation $\sigma=0.05\%$. The values of $C_p(T)$ obtained in this way were approximated by Eq. (3). The number of points N was gradually increased until a saisfactory description of the set of data on $C_p(T)$ was obtained using Eq. (3). It was found that the number N should not be less than 100–150. Since we were not aware of any experimental results which would satisfy such conditions, it was necessary to carry out a new experiment.

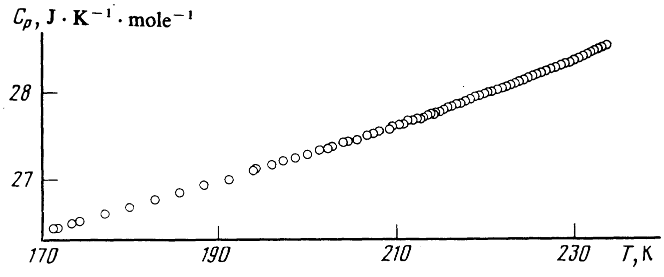

FIG. 1. Temperature dependence of the heat capacity of mercury.

2. SAMPLE AND EXPERIMENTAL METHOD

We determined experimentally the values of $C_p(T)$ for crystalline mercury at high temperatures in the vicinity of T_m. The sample was subjected to a comprehensive purification procedure and was doubly distilled. The total number of impurities was estimated from the depression of the melting point and was less than the sensitivity of the method (2×10^{-4} wt.%). Moreover, a special chemical analysis was made in order to detect the following 23 trace elements: Cu, Zn, Ca, Al, Bi, Li, Fe, Pb, Cr, Mg, Mn, Co, In, As, Ba, V, Be, Ga, Ho, Sb, Te, Tl, and Pt. The sensitivity of this chemical analysis was 10^{-6}–10^{-7}%. It was found that out of all these elements only Cr (8×10^{-7}%) and Fe (5×10^{-6}%) were present.

Measurements of $C_p(T)$ were made in the range 150–234 K using a nickel adiabatic calorimeter[7] in which we placed 288.385 g of mercury. The rms deviations from the smoothed values amounted to 0.025% in the interval 170–210 K and 0.03% above 210 K. The mercury sample remained solid throughout the series of imvestigations (~2 months). During these measurements there were no changes in the properties of the sample since the initial and final points coincided within the limits of the experimental error. Hence, we concluded that there was no gradual contamination of the sample in the calorimeter and, moreover, during the measurements (kept near T_m) the sample was undoubtedly annealed and became recrystallized, so that the initial number of defects and the polycrystalline structure changed in the course of the measurements without affecting significantly the thermodynamic properties.

We made 257 measurements in the range 150.9–233.9 K (Fig. 1). An analysis of the temperature dependence $C_p(T)$ was made employing 250 values of the heat capacity in the range 170–234 K.

3. ANALYSIS AND DISCUSSION OF RESULTS

It should be pointed out that the use of two approximation variants in the determination of the lattice component C_v^h altered only slightly the fitting parameters and had no effect at all on the accuracy of the description, which was likewise affected by variation of the Debye temperature between 71.9 and 115 K.

The general expression (1) with seven fitting parameters failed to provide a satisfactory description of the experimental results throughout the investigated range $0.721<T/T_m<0.997$. It was natural to assume that the characteristic features of $C_p(T)$ could change on approach to T_m. We tried, by varying the limits of the temperature intervals of the approximation and by using different combinations of the approximating functions, to select temperature regions in which a satisfactory description of the experimental data could be made. We began from the assumption that far from T_m the $C_p(T)$ dependence should be described by a function of the type

$$C_p=C_v^h+C_{\text{an}}+C_{\text{el}}+C_{\text{vac}}=C_v^h+BT+C_{\text{vac}} \tag{4}$$

or

$$C_p=C_v^h+BT+DT^2+C_{\text{vac}}, \tag{5}$$

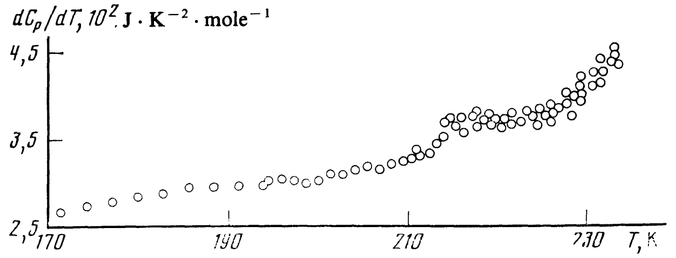

FIG. 2. Temperature dependence of the derivative of the heat capacity with respect to temperature.

whereas close to the melting point it should be described by an even more general expression

$$C_p=C_v^h+BT+DT^2+C_c+C_{\text{vac}}.$$

In fact, misorientation of crystalline clusters in the lattice, manifested by the component C_c, may contribute significantly only in the temperature intervals sufficiently close to T_m. Numerous variations have shown that two temperature intervals relative to T_m can be identified: far from the melting point and corresponding to $0.73 < T/T_m < 0.91$ and close to the melting point where $0.91 < T/T_m < 0.997$. The search for a stable description of the experimental results led us to the conclusion that the boundary between these intervals should occur at $T = 210$–216 K (i.e., at $T/T_m \approx 0.91$). Figure 2 shows the $dC_p(T)/dT$ dependence determined by two methods: direct differentiation at isolated experimental points and differentiation of the smoothed curve at $C_p(T)$. The results were independent of the calculation method. Clearly, the $dC_p(T)/dT$ dependence has a point of inflection which occurs at the same temperature as the boundary of two temperature intervals already considered. The derivative of the approximating general function and of various combinations of its components fails to predict an inflection point in this temperature range if reasonable values of the fitting parameters are used.

We might assume that the observed anomaly of $dC_p(T)/dT$ and, consequently, the appearance of two temperature intervals in $C_p(T)$ are associated with the influence of impurities. The plot with an inflection point may be the result of differentiation of a broad maximum of the $C_p(T)$ curve. Such maxima may be due to impurities that form a eutectic with mercury. By determining from the experimental data the quantity

$$\int_{210}^{230} \Delta C_p(T)\,dT$$

and assuming that the enthalpy ΔH_m of the melting of such eutectics is close to ΔH_m of mercury, we can easily show that singularities of this type may be due to the presence of $\approx 10^{-2}\%$ of eutectic impurities in mercury. The most appropriate for this temperature interval is the thallium-mercury eutectic. The total concentration of thallium should then be $8\times 10^{-4}\%$ (Ref. 12). However, our chemical analysis showed that there was no thallium to within $10^{-7}\%$. Similar estimates were also obtained for other known eutectics. The necessary amount of the impurity was found to be $\sim 10^{-3}$–$10^{-4}\%$, which was several orders of magnitude higher than the real concentration of the impurities in the sample. Hence, we concluded that the observed inflection point is not due to impurity effects but is related to the properties of mercury itself. An analysis of various approximations to the $C_p(T)$ dependence in the close interval 210–234 K supports this conclusion. In fact, we carried out approximations in which the dependence $C_p(T)$ was described well by the same function as the temperature interval near T_m was gradually made narrower. We used a computer to select practically the same parameters of the approximating function, which implied stability of the approximation. It is difficult to see how such approximations could account for a broad $C_p(T)$ extremum associated with the presence of impurities.

Our estimates and analyses thus show convincingly that either an unknown process which makes an additional contribution to $C_p(T)$ acts in the interval in question or the experimental $C_p(T)$ dependence has different asymptotes in different temperature intervals. The observed singularity of the temperature dependence of $C_p(T)$ is directly related to the properties of mercury itself.

In the far interval we can identify the temperature range ($0.82 < T/T_m < 0.92$) where the function (4) describes satisfactorily the experimental data and the fitting parameters ($E_0 = 12\,000$ J/mole, $B = 7.9\times 10^{-3}$ J · K^{-2} · mole^{-1}, $L = 2.6$; the confidence intervals and the significance level of 95% are 50–100% and agree satisfactorily with the values predicted by the theory: $BT \propto (C_p - C_v)$ on the assumption that $(C_p - C_v) > C_{v.\text{an}}$ (Ref. 13) and $E_0 \approx (0.2 - 0.3)\,Q_{\text{ev}}$, where Q_{ev} is the heat of evaporation.[10] However, in the close interval $0.91 < T/T_m < 0.997$, when the approximating function is (4) or (5), a satisfactory description of the experimental data cannot be obtained. Nevertheless, the results obtained at these temperatures can be described if the approximating expression (4) is supplemented by a component with a square-root singularity:

$$C_p=C_v^h+BT+C_{\text{vac}}+C_c. \tag{6}$$

The computer-selected values of the parameters are then $F = 1.9\times 10^{-2}$ J · K^{-1} · mole^{-1} and $T_c = 236.35$ K, in satisfactory agreement with the values predicted theoretically.[5] However, the energy of formation of vacancies E_0 then differs considerably from the values obtained in the approximation used for the far interval, and also from estimates. The coefficient B becomes negative. It is unlikely that the sum of the anharmonic components and of the electron heat capacity could make a negative contribution to $C_p(T)$. Moreover, the quality of the approximation is not improved if Eq. (6) is supplemented by a term DT^2 with a quadratic temperature dependence. If we select the values of B and E_0 to be the same as those found for the far interval, the description becomes unsatisfactory. We can improve the agreement between the parameters by allowing for a possible weak temperature dependence of the vacancy formation energy E_0. With this in mind, we substitute in the expression for the thermodynamic potential G_{vac} the value $E_0(T)$ in the form

$$E_0(T)=E_0(0)+aT+bT^2. \tag{7}$$

It is assumed that $bT^2 \ll at \ll E_0(0)$. The expression for C_{vac} deduced from G_{vac} is then used in the approximating function (1). However, the computer-selected parameters a and b become so large that the expression (7) becomes meaningless. If we assume that E_0 exhibits a more complex and fairly strong temperature dependence, this means that $C_{\text{vac}}(T)$ can no longer be described by the classical expression. It should be pointed out that the term C_c in Eq. (6) was found in Ref. 5 by using the Landau approximation. This approximation may not describe the real situation and it may be necessary to use the theory of scaling invariance in calculations of this kind. We can then expect

$$C_\iota'=F\tau^{-\alpha}, \qquad \alpha\approx 0.1-0.2.$$

In view of this situation we approximated the experimental data in the close temperature interval by

$$C_p=C_v^h+BT+C_{\text{vac}}+C_c', \tag{8}$$

where α was varied within the range 0–0.5. It was found that the optimal value of the critical exponent corresponding to the minimum of the sum of the squares of the deviations is $\alpha\approx 0.5$.

The presence in the dependence $C_p(T)$ of a component with a square-root singularity shows that the disordering processes occurring in the premelting region can be described by the Landau theory. Effects of this kind are dealt with theoretically by Mitus' and and Patashinskiĭ[5] who postulated the existence near T_m of locally ordered crystalline clusters undergoing a misorientation. The possibility of misorientation of such clusters is due to the presence of very mobile and highly developed defect structure. Clearly, a description of the behavior of such a system does not fit the framework of the existing theory of vacancies. We shall assume that this is the reason for the disagreement between the experimental and predicted values of the parameters of the components C_{vac} and C_{an} when the approximation is carried out on the basis of Eq. (6). It is not known which components should in reality enter in Eq. (6) in order to describe such a defect structure. However, even the replacement of the approximating expression (6) with

$$C_p=C_v^h+A+B'T+C_c \tag{9}$$

provides a satisfactory description of the experimental results in the close temperature interval.

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