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Use of Thermal Expansion Measurements to Detect Lattice Vacancies near the Melting Point of Pure Lead and Aluminum

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Dilatometric and x-ray measurements of the thermal expansion of pure lead and aluminum have been carried out between room temperature and the melting point. For lead, the results obtained by the two techniques agree within experimental error, which is interpreted to imply that the vacancy concentration at the melting point is (in mole fraction) less than or equal to 1.5×10^{-4}. For aluminum the dilatometric expansion appears to be slightly greater than the x-ray expansion. If this discrepancy is real, it corresponds to a vacancy concentration at the melting point of aluminum of about 3×10^{-4}. The corresponding estimate for the formation energy, ϵ_v, of a vacancy in lead is $\epsilon_v \geqq 0.53$ ev, and in aluminum, $\epsilon_v = 0.77$ ev.

INTRODUCTION

IT is well known[1] from elementary statistical mechanics that the mole fraction of vacancies, c, in a monatomic solid increases rapidly with increasing temperature, in accordance with the relation

$$c = e^{s_v/k} e^{-\epsilon_v/kT}, \tag{1}$$

where ϵ_v and s_v are the energy and excess entropy of formation of a vacancy, respectively, while k and T have their usual meanings. For the common cubic metals, the concentration of vacancies near the melting point, T_m (which depends primarily on the ratio ϵ_v/T_m), is still not established with certainty at present. Estimates based on indirect methods, such as the measurement of various physical properties up to the melting point and experiments on quenched specimens, are quite diverse. These estimates vary from a mole fraction of vacancies at the melting point in the range between 10^{-3} and 10^{-2} by Pochapsky[2] (for Pb and Al), MacDonald[3] (for the alkali metals), Meechan and Eggleston[4] (Cu and Au), Jongenburger[5] (Cu and Au), and Gertsricken[6] (Al, Ag, and Cu), down to values below 10^{-4}, based on the data of Kauffman and Koehler.[7] Other estimates fall in an intermediate range (see for example Bradshaw and Pearson's work[8] on Au and Al and the recent results of Bauerle *et al.*[9] on Au). Thus, the estimates that have been made on the basis of indirect methods cover a range of more than two orders of magnitude.

The most direct method of obtaining the equilibrium concentration of vacancies near the melting point is suggested by a theorem due to Eshelby,[10] which may be stated as follows: Consider a uniform distribution of point defects introduced into a crystal, and assume that the distortion about each defect may be calculated as if the defect were a center of dilatation in an isotropic elastic medium. Then, the fractional change in the average volume of a unit cell (as measured by x-rays) is equal to the fractional change in the macroscopic volume of a specimen, provided that the changes are calculated relative to the perfect crystal containing the *same number of lattice points* as the imperfect crystal. In order to apply this theorem to the case in which the defects are vacancies, the change in the number of lattice points due to the removal of extra atoms to the surface must also be taken into account. The increase in the macroscopic dimensions due to this factor is then responsible for a discrepancy between the thermal expansion as obtained from x-rays and that obtained dilatometrically. Since cubic crystals expand isotropically, length measurements may be used in place of volume measurements. Accordingly, if l is the length of a sample and a the lattice parameter at a temperature T while l_0 and a_0 are corresponding values at a standard temperature T_0, the mole fraction of vacancies, c, present at temperature T may be expressed as

$$c = 3(\delta l/l_0 - \delta a/a_0), \tag{2}$$

provided that T_0 is a low enough temperature that $c(T_0)$ is negligible. Here $\delta l = l - l_0$ and $\delta a = a - a_0$, and the factor 3 enters because changes in linear dimensions, rather than in the volume, are considered. Equation (2) is only valid exactly if the vacancy may be treated as an elastic center of dilatation, in accordance with Eshelby's theorem. However, since it is generally believed[11,12] that the relaxation of atoms about a

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[1] See, for example, H. Brooks' article in *Impurities and Imperfections* (American Society for Metals, Cleveland, 1955).

[2] T. E. Pochapsky, Acta Met. **1**, 747 (1953).

[3] D. K. C. MacDonald, *Report of a Conference on Defects in Crystalline Solids* (The Physical Society, London, 1955).

[4] C. J. Meechan and R. R. Eggleston, Acta Met. **2**, 680 (1954).

[5] P. Jongenburger, Phys. Rev. **106**, 66 (1957).

[6] S. D. Gertsricken, Doklady Akad. Nauk (U.S.S.R.) **98**, 211 (1954); Met. Abstr. **23**, 649 (1956).

[7] J. W. Kauffman and J. S. Koehler, Phys. Rev. **97**, 555 (1955); also see Table I in C. Y. Li and A. S. Nowick, Phys. Rev. **103**, 294 (1956).

[8] F. J. Bradshaw and S. Pearson, Phil. Mag. **2**, 379, 570 (1957).

[9] J. E. Bauerle and J. S. Koehler, Phys. Rev. **107**, 1493 (1957); Koehler, Seitz, and Bauerle, Phys. Rev. **107**, 1499 (1957).

[10] J. D. Eshelby, J. Appl. Phys. **25**, 255 (1954).

[11] H. B. Huntington and F. Seitz, Phys. Rev. **61**, 315 (1942).

[12] G. J. Dienes, Phys. Rev. **86**, 228 (1952).

vacancy is small in the common metals, the accuracy of this equation should be quite high.

If the higher range of estimates of $c(T_m)$ quoted above [i.e., $c(T_m) \gtrsim 10^{-3}$] were correct, there would be no difficulty in detecting the difference between $\delta l/l_0$ and $\delta a/a_0$ by standard dilatometric and x-ray techniques. On the other hand, if the lowest estimates quoted were valid, detection of the vacancy contribution would be much more difficult, if not impossible, using the most precise of present-day methods. Accordingly an attempt was made to detect the difference between $\delta l/l_0$ and $\delta a/a_0$ with the use of the best possible techniques. Lead and aluminum were selected because they are cubic metals of relatively low melting points and because of the fact that they do not oxidize to an extent that would interfere with the measurements, even in an air atmosphere. (Very recently, similar measurements on lead were reported by Van Duijn and Van Galen,[13] but the precision attained was not comparable to that of the present measurements, and the x-ray experiments covered a temperature range only up to 40°C below the melting point.)

EXPERIMENTAL PROCEDURE

The specimens were single crystals of pure lead (99.998%) and of pure aluminum (99.997%) grown by the Bridgman technique.

The length measurements were made by means of a quartz dilatometer based on that of Siegel and Quimby[14] but modified so as to use an optical lever in place of a microscope. The dilatometer was calibrated by means of a height vernier and a dial gauge sensitive to 0.0001 in. The lower part of the dilatometer containing the specimen was surrounded by a tubular furnace whose temperature was regulated to within 0.5°C by means of a temperature controller. The temperature was measured by means of a platinum platinum-rhodium thermocouple placed adjacent to the center of the specimen. For each reading taken, the furnace temperature was held steady for several minutes to insure that the specimen and thermocouple temperatures were the same. Most measurements were taken as part of a series of readings at successively higher temperatures, since results were somewhat more reproducible after the specimen had expanded than after contraction. It was consistently found that the specimen length remained unchanged when the temperature was held steady for a period of about 30 minutes, except for the anomalous behavior of aluminum just below the melting point, described in the following section. The precision of the dilatometric measurements was about one part in 10^5.

The x-ray measurements were carried out on the same single crystals used for the dilatometric measurements, by means of the high-angle oscillating crystal method developed by Murphy and Feder.[15] A high-temperature furnace for this camera was made by wrapping heating coils about the male section of a standard quartz taper joint. In addition, a quartz funnel-like tube about 5 cm long and containing aluminum foil across the opening was attached perpendicularly to the furnace for the entrance and exit of the x-ray beam. For the temperature measurements, a thermocouple was imbedded in a small hole drilled into the top of the specimen to a distance about 1 mm from the incident x-ray beam. The temperature was controlled to ±0.5°C. In all of the x-ray measurements on lead, Ni $K\alpha_1$ and Ni $K\alpha_2$ radiation was used; the 531 reflection was used from room temperature to 247°C (giving Bragg angles, θ from 80° to 82°), and the 442 reflection from 274°C to 323°C (giving θ in the range 86° to 88°). For the measurements on aluminum in the range 25°C to 97°C, Cu $K\alpha$ radiation and the 511 reflection were used (with θ near 82°), while from 246°C to 656°C Ni $K\alpha$ radiation and the 422 reflection gave Bragg angles decreasing from 88° down to 80°. In general the precision of the lattice parameter measurement increases with increasing Bragg angle; owing to the natural width of the characteristic radiation, however, the precision even at the highest Bragg angles was no better than one part in 10^5.

Both the dilatometric and x-ray measurements were carried out in air, but there was no evidence for any deterioration of the specimens due to oxidation.

RESULTS

The x-ray method employed in these experiments gives, for the absolute lattice constants of lead and aluminum at 25°C, the values 4.9509 A and 4.04948 A, respectively. The result for lead falls within about 1 part in 20 000, and that for Al within 1 part in 40 000, of the best values of these parameters determined previously by the powder method.[16]

The combined results of the dilatometric and x-ray expansion measurements on lead are presented in Fig. 1. The changes in the length and in the lattice parameter are reported relative to 0°C, although actual measurements were always started at room temperature. In making this adjustment to a reference temperature of 0°C, the value $\delta l/l_0 = 7.375\times10^{-4}$ at 25°C was used (taken from the data of Nix and McNair[17]). Figure 1 shows that, within the experimental error of the present measurements, there is no difference between $\delta l/l_0$ and $\delta a/a_0$ near the melting point of lead. It is therefore possible to estimate that the difference $\delta l/l_0 - \delta a/a_0$ is no greater than 5×10^{-5}. Applying Eq. (1), we may conclude that for lead, $c(T_m) \leqq 1.5\times10^{-4}$.

A comparison of the present results with earlier work

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[13] J. Van Duijn and J. Van Galen, Physica **23**, 622 (1957).

[14] S. Siegel and S. L. Quimby, Phys. Rev. **54**, 76 (1938).

[15] D. Murphy and R. Feder (to be published).

[16] H. E. Swanson and E. Tatge, National Bureau of Standards Circular No. 539 (U. S. Government Printing Office, Washington, D. C., 1953), Vol. 1.

[17] F. C. Nix and D. MacNair, Phys. Rev. **60**, 597 (1941); **61**, 74 (1942).

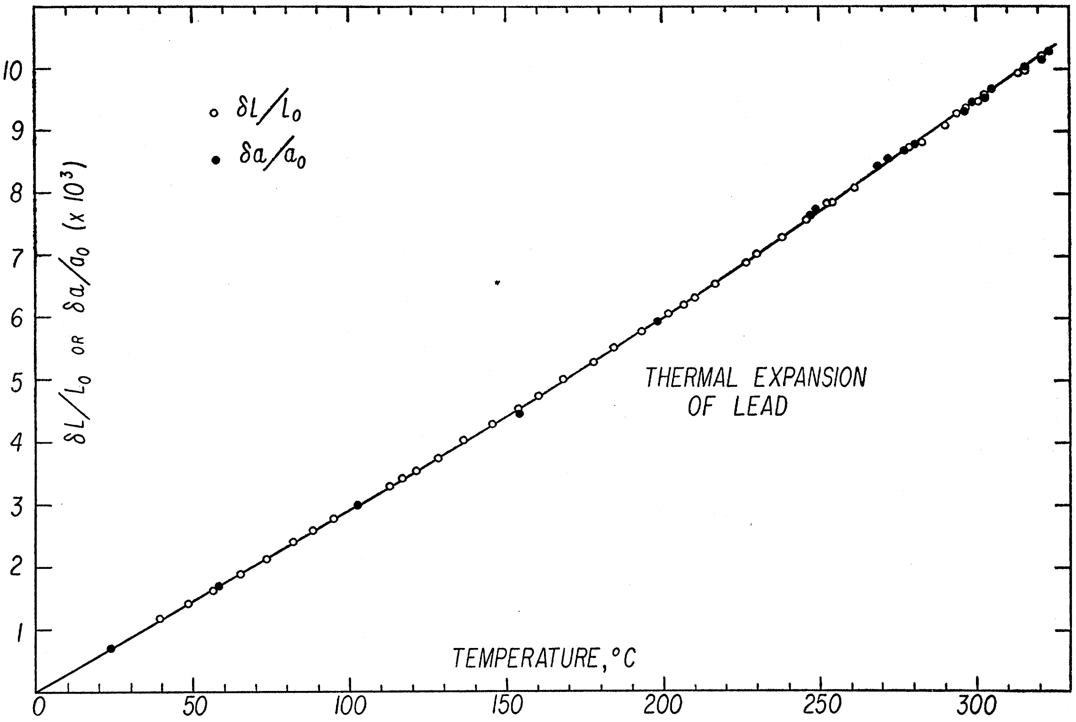

FIG. 1. Comparison of thermal expansion of lead as determined by dilatometer and x-ray methods.

is presented in Table I, where values of $\delta l/l_0$ and of $\delta a/a_0$ at 300°C obtained by previous workers are compared with the present data. It should be noted that the x-ray data of Stokes and Wilson[18] (from powdered samples) fall slightly above the present results while the dilatometric measurements of Hidnert and Sweeney[19] fall slightly below. Although the recent work of Van Duijn and Van Galen[13] also led to the conclusion that there is no discrepancy between dilatometric and x-ray expansion data, the equivalence of the two sets of measurements could not be established as closely as in the present experiments, because of poorer precision and cessation of the x-ray measurements further from the melting point. Although it is difficult to read a value for $\delta l/l_0$ at 300°C from the plot given by Van Duijn and Van Galen for comparison with Table I, it appears as if the value at 300°C obtained by these authors is somewhat lower than those given in Table I.

TABLE I. Comparison of thermal expansion of lead between 0°C and 300°C, as observed by various workers.

Author	$(\delta l/l_0)\times 10^3$	$(\delta a/a_0)\times 10^3$
Stokes and Wilson[a]	...	9.52
Hidnert and Sweeney[b]	9.36	...
Present work	9.47	9.47

[a] See reference 18.
[b] See reference 19.

The present dilatometric and x-ray data for aluminum are plotted in Fig. 2. Again changes are reported relative to 0°C to make the present results more directly comparable to the work of others. In view of some small discrepancies for different dilatometric runs in the range between room temperature and 200°C, it was found that the most reliable comparison of dilatometric and x-ray results near the melting point could be obtained by fixing all data to a value of $\delta l/l_0=\delta a/a_0=4.90\times 10^{-3}$ at 200°C. The present dilatometric results are in reasonably good agreement with earlier work[17,20] which did not go as high in temperature, and with the early data of Hidnert[21] who carried out measurements up to 600°C. Previous x-ray measurements of Wilson[22] on powdered aluminum samples also agree with the present results quite closely. A comparison of the present data with earlier work is given in Table II.

The data of Fig. 2 show a possible small difference between $\delta l/l_0$ and $\delta a/a_0$ at the higher temperatures. The smooth curve in this figure gives the best representation of the x-ray data. It may be seen, however, that the dilatometric data above 570°C consistently fall above this curve. The discrepancy corresponds to a

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[18] A. R. Stokes and A. J. C. Wilson, Proc. Phys. Soc. (London) **53**, 658 (1941).

[19] P. Hidnert and W. T. Sweeney, J. Research Natl. Bur. Standards **9**, 703 (1932).

[20] Taylor, Willey, Smith, and Edwards, Metals and Alloys **9**, 189 (1938).

[21] P. Hidnert, Sci. Papers Natl. Bur. Standards **19**, 697 (1924).

[22] A. J. C. Wilson, Proc. Phys. Soc. (London) **54**, 487 (1942).

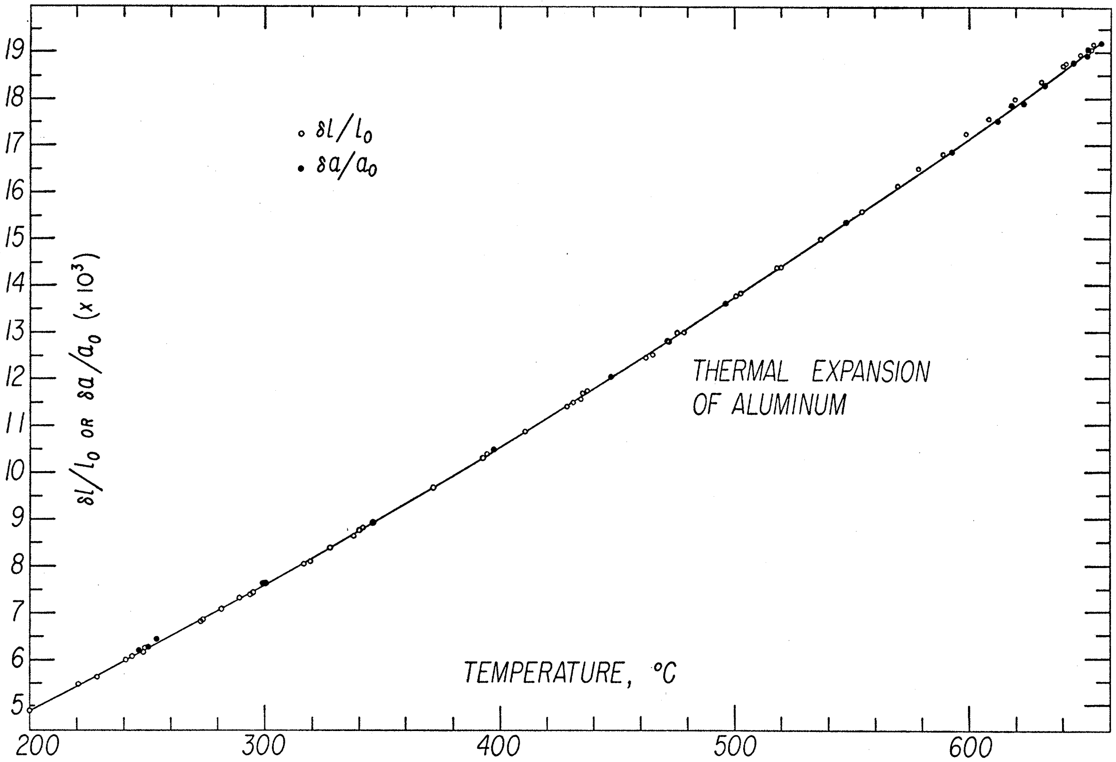

FIG. 2. Comparison of thermal expansion of aluminum as determined by dilatometer and x-ray methods.

difference $\delta l/l_0 - \delta a/a_0 = 1.0 \times 10^{-4}$ near the melting point. If this effect is real, it corresponds to a vacancy concentration $c(T_m) \cong 3 \times 10^{-4}$, obtained from Eq. (2). The discrepancy between the dilatometric and x-ray curves of Fig. 2, expressed as a horizontal shift, is only 2°C. In spite of the fact that the nominal temperature is believed reliable to within 0.5°C, it is certainly conceivable that part or all of this 2°C shift between the dilatometric and x-ray data may represent experimental error in the temperature measurement, i.e., that $c(T_m)$ is actually less than the value quoted above.

It is important to note that in the case of all dilatometric measurements carried out at temperatures more than 5°C below the melting point, there was no evidence for creep of the specimens when the temperature was held constant over a period of the order of 30 minutes. In the case of aluminum, some measurements were made within 3°C of the melting point. In this range, the length first approached a definite value as soon as the temperature achieved stability. This value was found to fit very well on the extrapolation of the curve through the dilatometric data at lower temperatures. However, in a time of the order of ten minutes, the specimen showed an additional expansion (corresponding to a fractional change in length of the order of 10^{-3}) followed by a contraction which increased in rate with increasing time. This contraction was permanent, i.e., it represents a creep phenomenon. The origin of the initial expansion is not clear, however. One possible explanation, that the true specimen temperature had exceeded the melting point in the range where the anomalous behavior took place, seemed to be ruled out by the initial expansion as well as by the calibration of the thermocouple.

TABLE II. Comparison of thermal expansion of aluminum for the ranges 0°–500°C and 0°–600°C, as observed by various workers.

Author	$(\delta l/l_0) \times 10^3$ at 500°C	$(\delta l/l_0) \times 10^3$ at 600°C	$(\delta a/a_0) \times 10^3$ at 600°C
Taylor *et al.*[a]	13.76	...	...
Hidnert[b]	13.82	17.22	...
Wilson[c]	...	...	17.23
Present work	13.75	17.25	17.15

[a] See reference 20.
[b] See reference 21.
[c] See reference 22.

DISCUSSION

The failure of the present experiments to detect a difference in the thermal expansion of lead as measured by dilatometric and by x-ray methods has led to the conclusion that, for this metal, $c(T_m) \lesssim 1.5 \times 10^{-4}$.[23]

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[23] Although the experiments of Van Duijn and Van Galen[13] also showed no discrepancy between dilatometric and x-ray data for lead, these authors concluded, however, that the results of their experiments did not rule out the possibility of a high value for $c(T_m)$. This conclusion apparently stemmed from their misinterpretation of Eshelby's work.

This upper limit disagrees with the much higher estimate that Pochapsky[2] considered as a possible explanation for the anomalous specific heat increase in lead near the melting point. It therefore appears that this anomalous specific heat increase should be related to anharmonic vibrations rather than to vacancies. The present estimate for $c(T_m)$ in lead is lower than most of the various estimates based on indirect methods which were quoted in the Introduction for various pure metals. On the other hand, since lead has one of the highest ratios of diffusion activation energy to melting point among the various pure metals,[24] it seems likely that ϵ_v/T_m is also relatively high for lead and therefore [from Eq. (1)] that $c(T_m)$ is low. Thus, the results for lead may not be typical of other metals.

In the case of aluminum the value $c(T_m)\sim 3\times 10^{-4}$, indicated by Fig. 2, is low compared to the estimate of 6×10^{-4} of Bradshaw and Pearson.[8] The latter estimate, however, was made quite indirectly, by extrapolation of the results of experiments on the quenching of aluminum from below 470°C. Accordingly, the agreement may be regarded as reasonably good. On the other hand, the much higher values suggested by Pochapsky[2] and by Gertsricken[6] appear to be ruled out.

Finally, it seems appropriate to attempt to estimate lower limits for the vacancy formation energy, ϵ_v, with the help of Eq. (1). Such estimates can be made reasonably well because the entropy factor, $\exp(s_v/k)$, appears to be known within reasonably narrow limits from theoretical considerations. The best theoretical estimate of s_v/k is probably that of Huntington *et al.*[25] for the case of vacancies in copper, for which $s_v/k=1.5$ is obtained. If it is assumed that this same estimate is valid for lead and aluminum,[26] one obtains from the upper limit on $c(T_m)$ of lead quoted above, a lower limit on ϵ_v, *viz.*, $\epsilon_v \geqq 0.53$ ev. Similarly, a value $c(T_m) = 3\times 10^{-4}$ for aluminum corresponds to a formation energy $\epsilon_v = 0.77$ ev. The latter value compares favorably with the estimate of 0.76 ev by Bradshaw and Pearson.[8]

In summary, it may be stated that the present results show no evidence for vacancies near the melting point in the case of lead, and some evidence for a possible vacancy concentration of about 3×10^{-4} for aluminum. These results are in striking disagreement with estimates in the vicinity of 0.1% and higher which some authors have deduced from various indirect measurements. It must therefore be concluded that, in the case of Pb and Al, an unexpected increase in a physical property at high temperatures must be explained in terms of the anharmonicity of lattice vibrations, rather than in terms of large vacancy concentrations.

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[24] A. H. Cottrell, *Theoretical Structural Metallurgy* (St. Martin's Press, New York, 1955), Chap. 12.

[25] Huntington, Shirn, and Wajda, Phys. Rev. **99**, 1085 (1955).

[26] The error in ϵ_v resulting from an incorrect choice of s_v is relatively small. For example, for both lead and aluminum, if the estimate $s_v/k=1.5$ is incorrect by as much as 0.5, the corresponding estimate of ϵ_v is in error by only 5%.