Measurement of the Equilibrium Net Vacancy Concentration in Sodium*†

George A. Sullivan‡ and John W. Weymouth

Physics Department, University of Nebraska, Lincoln, Nebraska

(Received 29 June 1964)

Simultaneous measurements of length and lattice thermal expansions have been made on two single-crystal rods of sodium, over a temperature range of −26°C to near the melting point of 97.8°C. The relative length changes were measured by means of two filar micrometer microscopes, and the lattice parameter changes were measured by a back-reflection, translated-sample method. The length and lattice expansions begin to diverge at approximately 10°C, with least-squares-fitted curves leading to a net atomic fraction of vacancies at the melting point of $(0.94\pm0.11)\times10^{-3}$ and $(0.66\pm0.15)\times10^{-3}$ for the two samples. These values are lower than some that exist in the literature but agree with one set of electrical resistivity measurements and with one set of specific-heat measurements. In the latter case, anharmonic contributions had been subtracted from the specific-heat data before arriving at a defect concentration. Proceeding on the assumption that only vacancy formation is present, energies of 0.157 ± 0.014 eV and 0.117 ± 0.023 eV have been obtained by fitting straight lines to semilog plots of the concentration versus reciprocal temperature. These values are lower than any existing in the literature with the possible exception of that of one set of electrical resistivity measurements. Entropies of formation have also been calculated by extrapolating the plots to infinite temperature. These appear to be negative well within the errors. It is quite possible that interstitial formation is present, thus lowering the semilog plots at the high-temperature end and giving erroneously low and negative entropies. Thus these values may be less meaningful than the values for melting-point concentrations. A value is given for the lattice parameter of sodium at 25°C, and the fitted thermal expansion coefficients are presented.

I. INTRODUCTION

IN a solid in thermal equilibrium the concentration n_i of point defects of type i in dilute solution will be governed by the equation

$$n_i = g_i \exp(S_i/k) \exp(-E_i/kT), \qquad (1)$$

where g_i is the number of possible orientations of the defect, S_i the vibrational entropy of formation, and E_i the energy of formation.

Such a concentration of defects can give rise to an excess resistivity and an excess specific heat. It has been known for some time that the electrical resistivity and specific heat of sodium departs from that to be expected on the basis of harmonic lattice dynamics near the melting point.[1-3] If these departures are assumed to be due to a concentration of point defects, then estimates of melting point concentrations and energies of formation can be made. Such estimates for sodium exist in the literature (see Table I), but there is disagreement among them. In addition, it is possible that the excesses in resistivity and specific heat are due to anharmonic force contributions in the lattice.[3,4] It would therefore be desirable to obtain a more direct measurement of the point-defect concentrations and energies of formation in order to separate these contributions from those due to anharmonic lattice dynamics.

We have measured the net vacancy concentrations in sodium metal over a temperature range from −26°C to near the melting point of 97.8°C and have obtained values for the energy of formation of vacancies.

II. PRINCIPLES OF MEASUREMENT

It can be shown[5] that the net vacancy concentration at temperature T is given by

$$n_v - n_i = \Delta N/N_0 = 3(\Delta l/l_0 - \Delta a/a_0), \qquad (2)$$

Table I. Net atomic fraction of sodium vacancies at the melting point and energies of formation as deduced by various methods.

Method	$\Delta N/N_0$ at melting point	Formation energy (eV)
Specific Heat		
Carpenter[a]	7.6×10^{-3}	0.26 ± 0.05
Machlup[b]	5×10^{-3}	
Martin[c]	1.0×10^{-3}	0.4
Electrical resistivity		
Bradshaw and Pearson[d]	0.7×10^{-3}	0.2
MacDonald,[e] Machlup[b]	2.5×10^{-3}	0.395 ± 0.004
Self-diffusion		
Bradshaw and Pearson[d]		0.2
Nachtreib et al.[f]		(0.45, total activation energy)
Theoretical		
Fumi[g]		0.53

[a] See Ref. 2.   [b] See Ref. 24.   [c] See Ref. 22.
[d] See Ref. 3.   [e] See Ref. 1.
[f] N. H. Nachtreib, E. Catalano, and J. A. Weil, J. Chem. Phys. 20, 1185 (1952).
[g] See Ref. 23.

¹ D. K. C. MacDonald, J. Chem. Phys. 21, 177 (1953).
² L. G. Carpenter, J. Chem. Phys. 21, 2244 (1953).
³ F. J. Bradshaw and S. Pearson, Proc. Phys. Soc. (London) B69, 441 (1956).
⁴ J. S. Dugdale, D. Gugan and K. Okumura, Proc. Roy. Soc. (London) A263, 407 (1961).

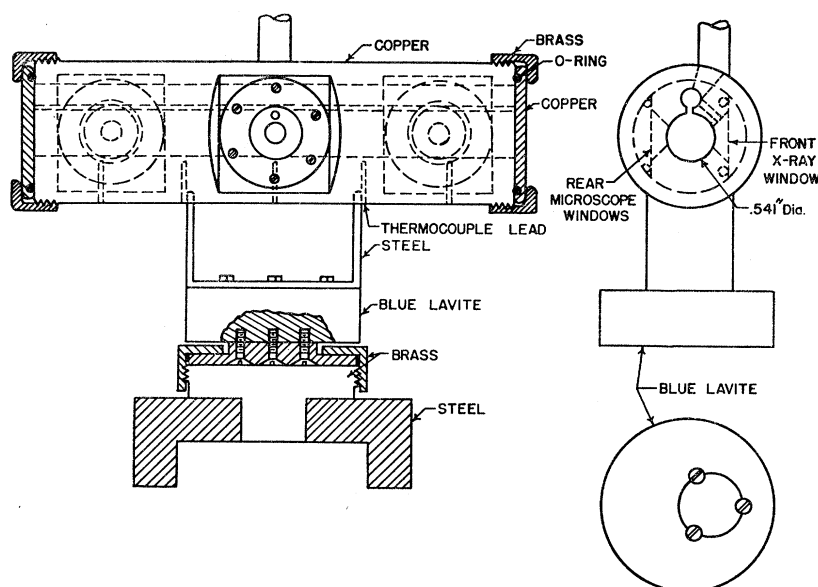⁵ R. W. Balluffi and R. O. Simmons, J. Appl. Phys. 31, 2284 (1960).

FIG. 1. The sample chamber. The channel along the axis of the copper cylinder accommodates the sodium rod.

where n_v and n_i are the vacancy and interstitial concentrations, and $\Delta l = (l(T) - l_0(T_0))$, $\Delta a = (a(T) - a_0(T_0))$ and $\Delta N = (N(T) - N_0(T_0))$ are the changes in length, lattice parameter and substitutional atomic sites, respectively. The reference temperature T_0 is taken to be low enough so that the defect concentration is negligible. This relation follows from the fact that the strain field resulting from uniformly distributed point defects has the same effect on both the length and the lattice parameter, whereas a change in the net vacancy concentration either creates or destroys atomic sites on the surface, making an additional contribution to the fractional change in length.

Feder and Nowick,[6] Simmons and Balluffi,[7–10] and d'Heurle, Feder, and Nowick[11] have carried out measurements on the length and lattice parameter thermal expansions in several face-centered cubic metals. Such measurements by Simmons and Balluffi on Al, Ag, Au, and Cu were done simultaneously on the same sample. Simultaneous measurements have the advantage that both l and a are obtained from the same sample, thus cancelling different expansions due to different impurity concentrations, physical treatment, etc., and that both measurements are made with the same temperature scale.

We present here our measurements on body-centered-cubic sodium metal. As far as we are aware, these measurements are the first such made on a nonclose-packed metal.[12]

[6] R. Feder and A. S. Nowick, Phys. Rev. 109, 1959 (1958).
[7] R. O. Simmons and R. W. Balluffi, Phys. Rev. 117, 52 (1960).
[8] R. O. Simmons and R. W. Balluffi, Phys. Rev. 119, 600 (1960).
[9] R. O. Simmons and R. W. Balluffi, Phys. Rev. 125, 862 (1962).
[10] R. O. Simmons and R. W. Balluffi, Phys. Rev. 129, 1533 (1963).
[11] F. M. d'Heurle, R. Feder, and A. S. Nowick, J. Phys. Soc. Japan 18, Suppl. II, 184 (1963).
[12] J. N. Eastabrook, Royal Aircraft Establishment, Farn-

III. EXPERIMENTAL METHOD

A. Outline of Method

The sample, purified sodium formed into a single-crystal rod 10 cm$\times$1 cm diam, was enclosed in an evacuated copper chamber and maintained at a constant temperature during the determination of a pair of values l and a. The chamber, mounted horizontally, had a Mylar window on one side for access of the x-ray beam to the sample and two Mylar windows on the other side for examination of the sample ends with 25 power microscopes. (See Fig. 1.)

Length changes of the sample were determined by using filar micrometer eyepieces on the microscopes. The lattice parameter values were obtained by an x-ray diffraction method using back-reflection, oscillation photographs in which the sample was translated a carefully measured distance between two exposures recorded on the same film. We shall now discuss the experimental methods in more detail.

B. Sample Preparation

The material for one of the two samples discussed in this paper, sample No. 7 R, was reagent grade sodium which was further purified by double distillation in glass at a pressure of about 10^{-5} mm Hg. This material was then zone-refined (10 passes) in a horizontal evacuated glass tube sealed off from the distillation system.[13]

For sample No. 9 the sodium was not distilled, but only zone-refined with 10 passes. To accomplish this, freshly cut lumps of sodium were introduced into the vacuum system, twice melted down through narrow

borough, England carried out nonsimultaneous measurements on sodium (private communication, May 1962).
[13] A commercial unit, Fisher Zone Refiner, designed for purification of organic chemicals, was used.

restrictions to remove the remaining oxide coat, collected in the zone-refining tube and sealed off. Analysis of another batch treated in this same manner showed the main impurities to be 50 ppm of K and 3 ppm of PO_4. There were no traces of B and Si at a level of 30 ppm and 10 ppm, respectively. These latter impurities were of concern because it is possible to pick these up from the glass.[14] The samples obtained by distillation might have had higher concentrations of B and Si. A residual resistivity measurement on sodium purified in the same manner as that used for sample 9 gave a ratio of 3870. A lower and not very accurate value (between 800 and 1300) was obtained for sodium which was processed in the same way as sample 7 R, supporting the belief that distillation in glass results in impurity pickup.

The formation of the crystals and the loading of the sample chamber were done in a nitrogen-(Sample 7 R) or helium-(sample 9) filled glove box. The gas was continually recycled through a system which removed H_2O (liquid N_2 traps) and O_2 (Cu turnings at 500°C).

The samples were grown by the Bridgman technique in a clean, smooth-walled steel crucible, lightly lubricated with petroleum oil to prevent sticking. (This was the only step in the procedure in which it was necessary to use oil.) The diameter of the crucible was 2% smaller than that of the sample chamber interior, to ensure that the sample be completely free of constraint at all temperatures. Etching the samples in isopropyl alcohol revealed that they were apparently both single crystals.

C. The Sample Chamber and Temperature Control

Copper was chosen as the material for the sample chamber for its high thermal conductivity, and its insolubility in sodium at temperatures below 500°C.[15] The chamber was a cylinder with a hole bored down the center to accommodate the sodium rod. No thermal gradients could be detected along a dummy sample of brass placed in the sample position. Rough calculations show that even at the higher temperatures differences in temperature between the portion of the sodium rod at the x-ray window and the bulk of the sample, arising from radiation losses, would be quite negligible. It was necessary to provide the windows with separate external heaters to prevent the formation of frost at low temperatures, and to prevent vacuum grease or condensed oil vapors from interfering with the microscope readings at temperatures above 60°C. The sample holder mounting bracket was designed to minimize heat conduction to the track, and the entire copper cylinder was insulated with fiberglass.

The chamber was evacuated with a mechanical pump for sample 7 R, and for sample 9, a mechanical pump

in combination with a diffusion pump and a liquid-nitrogen cold trap. The vacuum ranged from ~20 to ~0.1 μ Hg. The sodium samples in all cases would retain a very shiny surface for from several hours to a few days, and would then take on a dull metallic luster which was highly stable against further change. No diffraction pattern due to a contaminated layer was ever detected.

The sample chamber temperature was controlled with a thermistor probe and bridge circuit to ±0.1°C over a range of −26 to +96°C. The probes were in direct contact with the copper of the sample chamber. Below room temperature, cold air circulating through a copper tube soldered to the chamber was used in conjunction with the heating wire. Most of the temperature settings were reproducible to better than 0.1°C, as was demonstrated by observing the thermal expansion of the dummy brass sample. The temperatures were monitored by means of a Chromel-Alumel thermocouple junction inserted into the body of the sample holder.

D. The Length Change Measurements

The changes in the length of the sample were measured by directly viewing arbitrary reference marks at opposite ends of the sample with the measuring microscopes. The microscopes were clamped to a heavy Invar steel rod to minimize the thermal expansion of the microscope support. Several sets of marks were normally chosen, to reduce the chance of error due to changes in appearance of the reference marks. The microscopes were factory calibrated but were also checked against a micrometer. The sample and microscopes were lined up so that the motion of the ends of the sample during expansion would be parallel to the motion of the crosshairs of the microscopes.

The initial spacing between the reference marks at the ends of the rod were measured to approximately 0.1 mm or 1 part in 10^3 by comparing the microscope settings with a steel ruler. Since $[l(T=MP)-l(T_0)]/l(T_0)\approx 9.0\times10^{-3}$, this measurement was sufficiently precise to determine the relative linear expansion over the temperature range of the experiment with an absolute error of less than 2 parts in 10^5. Thermal equilibrium of the sample was assured prior to taking measurements by allowing several hours to pass at a given temperature setting after the reference marks had stopped changing position.

E. The Lattice Parameter Measurements

The x-ray diffraction method was a modification of one developed by Gurevich and Ormont.[16] A back reflection, oscillation picture was taken and one, or some-

[14] G. W. Horsley, Report No. AEREM/R 1152, Atomic Energy Research Establishment, Harwell, England, 1963 (unpublished).
[15] M. Sittig, *Sodium: Its Manufacture, Properties and Uses* (Reinhold Publishing Corporation, New York, 1956), p. 70.

[16] M. A. Gurevich and B. F. Ormont, Zh. Techn. Fiz. 26, 1106 (1956) [English transl.: Soviet Phys.—Tech. Phys. 1, 1081 (1957)].
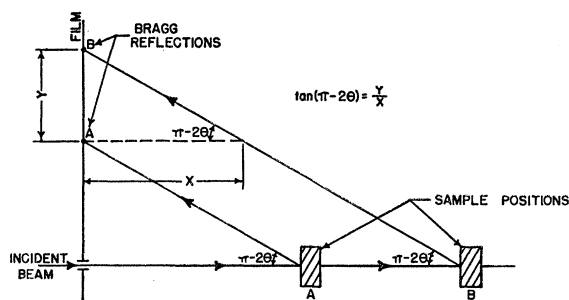
FIG. 2. Method of measuring lattice parameter. The sample is translated a carefully measured distance parallel to the x-ray beam.

times two, Bragg reflections were recorded on the film. The sample chamber was then translated a carefully measured distance and the process repeated, the picture being a double exposure. From the translation and spot shift, the Bragg angle of the reflection could be obtained (see Fig. 2). The main advantage of this method is that the crystal-to-film distance is not used. The translations were measured by a 5-cm micrometer having a least count of 0.001 cm. The precision in measuring the translation was greater than necessary for the experiment.
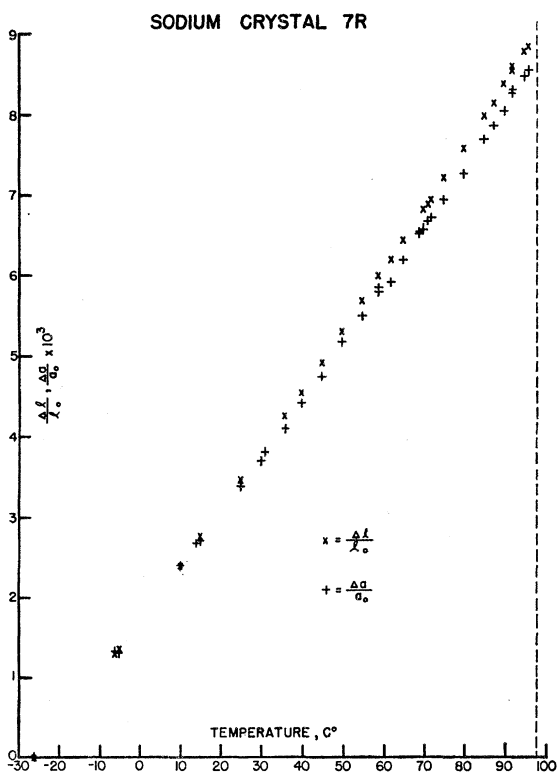

FIG. 3. Lattice and bulk thermal expansion data for sample No. 7R. Divergence of the curves, which begins at about 10°C, leads to a net vacancy concentration of $0.94\pm0.11\times10^{-3}$ at the melting point (dashed line).

The oscillations of the sample were achieved by means of a broad, reinforced pivot wheel at the bottom of the sample chamber base, which was driven by a one rpm motor, utilizing various off-center circular cams for varying oscillation angles. It was necessary to use small oscillations (1.2° near the melting point) at the higher temperatures, due to loss of intensity of the Bragg reflections.

A 0.05-cm-diam pinhole attachment was maintained at a distance of about 2 cm behind the film cassette. The closest film to crystal distance was 5 to 6 cm. In most cases copper $K\alpha_1$ radiation was used, together with the sodium (521) crystal planes. The Bragg angle varied from 78° near the melting point to 81° at the lowest temperatures.

Film shrinkage corrections were made by placing a carefully measured steel template with pinholes partially open to the light in contact with the film during x-ray exposure. This method was also capable of compensating for changes in the size of the film due to fluctuations in temperature and humidity, and was a reasonably good way of determining whether the film was in equilibrium throughout the x-ray measurement. No significant changes in the film temperature could be detected due to a change in distance to the sample chamber.

It was necessary to align the x-ray beam carefully so that the translation of the sample was exactly in the beam direction. Departures from this alignment could cause a systematic error in the absolute value of the lattice parameter which, due to the nonlinearity of the trigonometric functions involved in obtaining the lattice parameter, would also result in a systematic error in the value of $\Delta a/a_0$. However, the standard deviation from the mean (4.28865 Å) of the 25°C lattice parameter values of three different samples, each sample with an independent beam alignment and a different position of the Bragg reflection, was only ±0.00026 Å (Table V). If the value of a_0 at -26°C were too large by this amount, or about 6 parts in 10^5, then the same misalignment would cause $a(T=MP)$ to be too large by 0.00031 Å, or about 7 parts in 10^5. Consequently, the absolute error in $[a(T=MP)-a_0(T_0)]/a_0(T_0)$, due to the beam misalignment, would only be about 1×10^{-5}.

It was also necessary to make certain that the reciprocal lattice point always completely passed through the sphere of reflection, i.e., that no part of the reflection was cut off. Care was also taken to see that the results were not biased by overemphasis of one edge of the spectral x-ray line at the expense of the other edge. Both of these requirements were met by choosing the angular position of the sample in such a manner that the reflections did not occur near either extreme position of the sample oscillation.

One further experimental difficulty should be discussed before we examine the results. It was observed that small irreversible increases occurred in the length of the sodium rods upon thermal cycling, amounting to from

2 parts in 10^5 over each cycle for sample 7R, to 7 to 8 parts in 10^5 for sample 9. Careful examination of the experimental conditions ruled out measuring errors or temperature errors as a cause of this behavior. Also ruled out were constricting of the sample by the chamber, flow under gravity, and impurities diffusing into the sample while in the evacuated chamber. These irreversible changes did not appear to influence the results significantly, as long as the measurements were all taken with increasing temperatures. The close agreement in the $\Delta l/l_0$ curves for samples 7R and 9 substantiates this argument. The $\Delta l/l_0$ values were all completely reproducible, as long as the initial length was cor-
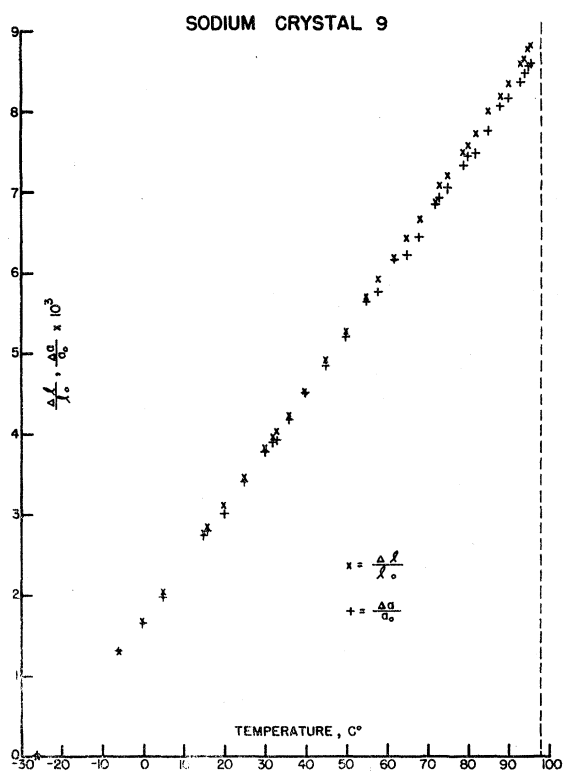

FIG. 4. Lattice and bulk thermal expansion data for sample No. 9. Divergence leads to a net melting point vacancy concentration of $0.66\pm0.15\times10^{-3}$.

rected for its new value at the start of each run. Also, the lattice parameter measurements were completely reproducible. Although we do not know the reason for this behavior, we suspect it to be related to impurity precipitation, occurring primarily during the cooling process.

IV. RESULTS

Values of $(\Delta l/l_0-\Delta a/a_0)$ taken directly from pairs of simultaneous measurements for each sample are plotted in Figs. 3 and 4, and the melting point net vacancy concentrations for each sample are given in Table II. These latter data were obtained by extrapo-

TABLE II. Melting point $\Delta l/l_0$ and $\Delta a/a_0$ values from fitted curves (referred to $T_0 = -26°C$), and the net vacancy concentrations.

Sample No.	$\Delta l/l_0$	$\Delta a/a_0$	$\Delta N/N_0$
7R	$9.004\pm0.016\times10^{-3}$	$8.690\pm0.031\times10^{-3}$	$0.94\pm0.11\times10^{-3}$
9	$8.983\pm0.023\times10^{-3}$	$8.764\pm0.043\times10^{-3}$	$0.66\pm0.15\times10^{-3}$

lating equations of the form $\Delta l/l_0=\sum C_n t^n$ and $\Delta a/a_0 = \sum D_n t^n$ to $n=3$, fitted to the expansion curves by weighted least squares. The estimation of the random error in the final result for the values of $\Delta N/N_0$ was taken to be $3[S_l^2+S_a^2]^{\frac{1}{2}}$, where S_l^2 and S_a^2 are the variances of the $\Delta l/l_0$ and $\Delta a/a_0$ curves calculated by the least-squares fitting program.

Plots of $\log(\Delta l/l_0-\Delta a/a_0)$ versus $(T°K)^{-1}$ for the determination of energies and entropies of formation [see Eq. (1)] are presented in Figs. 5 and 6. Assuming only monovacancy formation is present, straight lines were fitted by weighted least squares. The slope in each case yields the formation energy, and the limiting value as $T \to \infty$ yields the entropy of formation. These values, with standard deviations obtained by the fitting program, are presented in Table III.
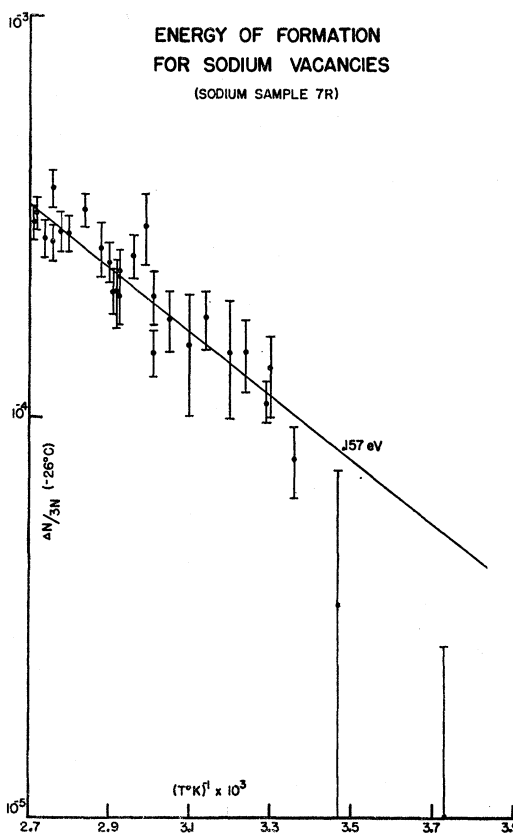

FIG. 5. Semilogarithmic plot of the differences in the bulk and lattice expansions versus reciprocal absolute temperature for sample No. 7R. A straight line fitted to the data leads to a vacancy formation energy of 0.157 ± 0.014 eV, assuming only one process is present.

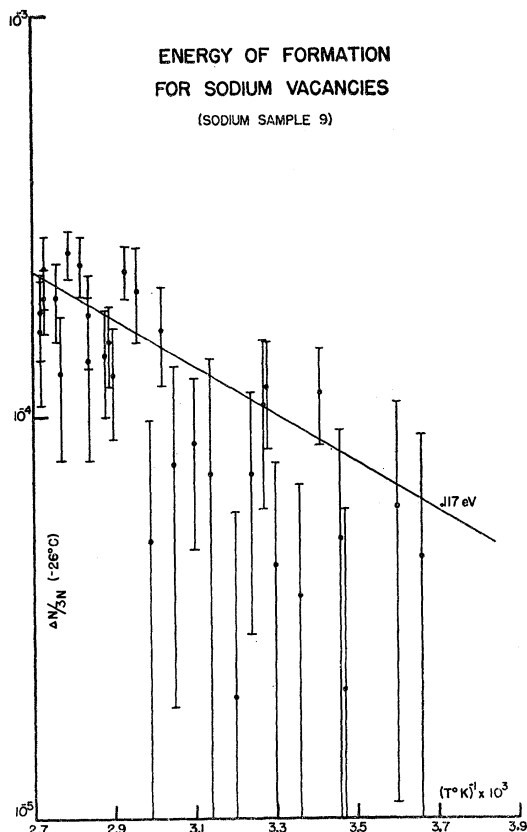ENERGY OF FORMATION
FOR SODIUM VACANCIES
(SODIUM SAMPLE 9)

FIG. 6. Energy plot for sample No. 9, leading to a vacancy
formation energy of 0.117±0.023 eV.

The expansion coefficients of the several samples are listed in Table IV. For purposes of comparison, coefficients derived from an expression for the density of sodium taken from Sittig[17] are also listed.

Table V gives the absolute values of the lattice parameter at 25°C for samples 7R, 8,[18] and 9. The mean and the standard deviation are 4.28865±0.00026 Å.

The values of $\Delta N/N_0$ for samples 7R and 9 agree within 2σ. The values for the energy of formation almost agree within the overlapping errors, but these errors are quite large. The entropy of formation of sample 9 is lower than that for 7R by approximately 3σ. Both

TABLE III. Formation energies and entropies for sodium vacancies.

Sample No.	Formation energy (eV)	Vibrational entropy, S/k
7R	0.157±0.014	−2.0±0.5
9	0.117±0.023	−3.8±1.0

[17] M. Sittig, Sodium: Its Manufacture, Properties and Uses (Reinhold Publishing Corporation, New York, 1956), p. 448.
[18] The vacancy data for sample 8 are not included in these results because of an unusually large irreversible length increase (>10⁻⁴ relative, per cycle), in addition to a failure in the vacuum system before the data were complete.

TABLE IV. Thermal expansion coefficients of sodium fitted to
$$\Delta l/l_0 = \Sigma \, C_n T^n (°C),$$
$$\Delta a/a_0 = \Sigma \, D_n T^n (°C),$$
where l_0 and a_0 were measured at −26°C.

	Sample No. 7R	Sample No. 9	Sittig[a]
$10^3 \times C_0$	1.718±0.006	1.719±0.008	0.0
$10^5 \times C_1$	6.828±0.030	6.828±0.029	6.89
$10^8 \times C_2$	7.5 ±1.0	7.7 ±1.1	5.14
$10^{10} \times C_3$	−1.2 ±0.8	−1.6 ±1.0	
$10^3 \times D_0$	1.711±0.009	1.697±0.017	
$10^5 \times D_1$	6.655±0.041	6.703±0.066	
$10^8 \times D_2$	3.9 ±1.5	6.0 ±2.2	
$10^{10} \times D_3$	1.0 ±1.3	−0.6 ±2.0	

[a] See Ref. 17.

entropy values are negative by a significant amount. This point will be discussed below.

Measurements were also carried out for another distilled, zone-refined sample, sample No. 7. This was a preliminary run and was lacking in the quantity of data, and also in many of the refinements of experimental technique such as were used for samples 7R and 9. However, the net melting point vacancy concentration was $(0.97±0.17)\times 10^{-3}$, in very close agreement with sample 7R (sample 7 recast).

V. DISCUSSION

In comparing our results with those listed in Table I, it is desirable to reexamine the previous data. The energies from specific-heat data are obtained by fitting a semilog plot to a relation of the form

$$\Delta C = A E^2 \exp(-E/kT),$$

where ΔC is the excess specific heat, A is a constant, and E is the energy of formation of the defect. We are dealing here with C_v, whereas the data used are for C_p. Because of the experimental errors involved, the difference will be neglected. Carpenter used his data, originally published in 1938,[19] plus some older data from the literature. Martin used much more recent data of his own (1960), up to 300°K,[20] and those of

TABLE V. Absolute values of the lattice parameter of sodium at 25.0±0.1°C.[a] The errors for each sample are standard deviations. The data were not pooled. The error in the average is the standard deviation of the three sample values.

Sample No.	a_0 (CuKα_1) = 1.54051 Å	No. of films
7R	4.28840±0.00021	11
8	4.28892±0.00014	8
9	4.28864±0.00017	11
Average	4.28865±0.00026	

[a] Corrected from 24.5°C for a systematic error of 0.5°C.

[19] L. G. Carpenter, T. F. Harle, and C. J. Steward, Nature 141, 1015 (1938).
[20] D. L. Martin, Proc. Roy. Soc. (London) A254, 433 (1960).

Ginnings, Douglas, and Ball (1950).[21] The latter are from an interpolation formula fitted to four points at four temperatures between 30.6 and 94.0°C, each point being the average of 3 or 4 separate determinations. Depending on how he related the extrapolation of his data to those of Ginnings *et al.*, Martin obtained values of formation energy of 0.31 to 0.43 eV.[22] As in all the work to be discussed, the defects were assumed to be vacancies. We are inclined to put most weight on the energy as determined by Martin. This, however, disagrees with our results to the greatest extent, but is in fair agreement with a calculation by Fumi.[23] In comparing these results with ours, it should be noted that Carpenter's "normal" specific heat from which excesses were determined is apparently constant in temperature. Thus, the excess would contain defect as well as anharmonic and electron specific-heat contributions. Martin, on the other hand, took as "normal" a linear extrapolation which increased with temperature. The excess over this, interpreted as only a defect contribution, rose markedly above the linear extrapolation, starting at about 270 to 300°K.

The melting point concentrations were determined from the specific-heat data in two ways. Carpenter used his energy value and

$$\Delta N/N_0 = \left(\int_{T_0}^{T_m} \Delta C dT \right) \bigg/ E N_0$$

to obtain 7×10^{-3}. However, he cautions, "Bearing in mind the crudeness of the treatment, all that can safely be concluded is that, at T_m, concentrations of defects of the order of $1/10\%$ are not inconsistent with the specific-heat data." This agrees well with our results. Machlup[24] used Carpenter's data, but the value of E from MacDonald, to revise $\Delta N/N_0$ to 5×10^{-3}. Martin, on the other hand, solved for the Boltzmann expression at the melting point, using his values of E and A obtained by the semilog fitting to ΔC, and obtained 1×10^{-3} for the defect concentration, again in good agreement with our results.

The resistivity determinations, it would seem to us, are open to more questions. MacDonald considered relative resistance which was excess with respect to a linear extrapolation and fitted this to a Boltzmann factor, arriving at his $E=0.395\pm0.004$ eV. In order to estimate a defect concentration, Machlup combined his own calculation for resistivity per defect with MacDonald's data to arrive at his estimate of a melting point defect concentration of 2.5×10^{-3}. The data of Bradshaw and Pearson on resistivity seem more reliable. Their "excess" resistivity was obtained by com-

parison with a Bloch-Grüneisen relation and the results depend on what Debye temperature is used. Also, an estimated value for resistivity per defect was used to arrive at the defect concentration of 0.7×10^{-3}. The result agrees well with ours. The energy was obtained by calculating the Boltzmann factor at the melting point and setting the entropy factor to unity.

We have taken the resistivity data given by Bradshaw and Pearson in their article and have used the less sophisticated approach that the normal resistivity is proportional to the temperature. Fitting a straight line over the range of about 100 to 210°K, we obtained from the excess resistivity a semilog plot which yields a formation energy $E=0.16\pm0.01$ eV, in very good agreement with our results.

From our assessment of the relative worth of these results we offer the following reactions. The specific-heat approach is more direct, but it would appear that the only convincing data in the important region above 300°K obtained within the last 25 years are those of Ginnings *et al.* However, their sodium was distilled once in glass. As we have remarked in this article, this could lead to pickup of boron and silicon in not insignificant amounts. It thus seems very desirable that specific-heat measurements in this temperature region be repeated using high-purity sodium.

The resistivity approach is more indirect. First, it shares with the specific-heat approach the question of what constitutes a normal curve from which excesses are derived. We suspect the problems here are more subtle than that in the specific-heat case. Secondly, all the values of defect concentration at the melting point depend on the correctness of the calculated or estimated resistivity per defect. The more recent data of Bradshaw and Pearson seem quite valid, but a more careful analysis of them with regard to the energy of formation is needed.

It should be realized that both specific heat and resistivity excesses will be positive for interstitials as well as vacancies. Thus, if there is an interstitial contribution, our defect concentration and energy of formation values should be lower than those from specific heat or resistivity data. If interstitial formation occurs with a larger energy than that for vacancies, the high-temperature end of our semilog plot would be lowered, with a reduction in the energy of formation calculated from this plot on the assumption of monovacancies only. This difficulty is aggravated by the fact that the weighting of the points in the curve fitting involves relative errors. Thus, the high-temperature points, which more strongly reflect possible interstitial contributions, are more heavily weighted. It is difficult to estimate the size of this effect. A theoretical energy for interstitials in fcc copper has been calculated to be about 3 eV,[25] or three times that for monovacancies. Paneth[26] has

[21] D. C. Ginnings, T. B. Douglas, and A. F. Ball, J. Res. Natl. Bur. Std. 45, 23 (1950).

[22] D. L. Martin, Chem. Phys. Solids (to be published) (private communication).

[23] F. G. Fumi, Phil. Mag. 46, 1007 (1955).

[24] S. Machlup, J. Chem. Phys. 24, 169 (1956).

[25] L. Tewordt, Phys. Rev. 109, 61 (1958).

[26] H. R. Paneth, Phys. Rev. 80, 708 (1950).

calculated an energy of formation of only 0.07 ± 0.2 eV for an interstitial crowdion in sodium. In addition, this crowdion would have four possible orientations (closest packed directions) which would multiply its concentration fourfold. There is a slight suggestion in both samples that the semilog plots do flatten out at the high-temperature end. In any case, there is too much scatter in the data to draw a definite conclusion.

Although one would expect the entropies of formation to be positive because the creation of vacancies would result in decreased lattice frequencies,[27] our results are clearly negative within the errors. Again, the difficulty might be that the extrapolations to obtain these values proceed from the high-temperature ends of the semilog plots where interstitials might be pulling the curves down.

A word might be said about the effect of impurities on the point defect concentrations. The difference in the vacancy atomic fractions of the impure and pure metal is given by[10,28] $n_v{}^i - n_v{}^p = gC_i n_v{}^p [\exp(F_b/kT) - 1]$, where g is the number of possible orientations of the vacancy-impurity pair, C_i the concentration of the ith impurity, and F_b the free binding energy between the vacancy and impurity atom.

Analysis of our zone-refined sodium has shown only 53 ppm of impurities (PO_4 and K); the other 9 impurities for which tests were made could not be detected to less than a total of 150 ppm. It is possible that the samples picked up additional impurities in the casting and handling process, and in the sample holder. These most likely would be hydrogen, oxygen, and carbon. If one assumes typical values for these elements found in unpurified commercial sodium (60 ppm each for H_2 and O_2, 30 ppm for C [29]), then the total impurity concentration of the samples would be about 3.5×10^{-4}. In view of the fact that the sodium was handled very carefully, such high concentrations are unlikely. However, taking a total impurity concentration of 10^{-3} (which should almost certainly be an overestimate) and a typical binding energy of 0.1 eV, together with a binding entropy of zero, and assuming $z=2\times4=8$ for the bcc lattice (there are 4 close-packed directions), then the increase in the vacancy concentration at the melting point would be approximately 1.6×10^{-4}. This is about the limit of the measuring accuracy. Actually, the binding energy is probably much smaller than 0.1

eV.[30] This would result in yet a smaller effect on the vacancy concentration. Thus it is probable that differences in the impurity content of the various samples had a smaller effect on the observed differences in vacancy concentrations than did the random errors in the measurements.

VI. CONCLUSION

We have obtained values of net vacancy concentrations and of energies and entropies of vacancy formation in two samples of sodium. The melting point defect concentrations agree well with those from specific-heat data (Martin and Ginnings et al.) when the anharmonic contributions have been subtracted from the latter. The agreement with the concentrations derived from the most recent electrical resistivity data (Bradshaw and Pearson) without considering anharmonic contributions is good, but this depends on the proper choice for resistivity per defect, and thus any comparison is less significant. If this agreement is meaningful, however, it would give support to a previous suggestion[4] that the anharmonic contributions to the specific heat are greater than to the electrical resistivity.

Our energies of formation do not differ much from those obtained by the resistivity measurement referred to above, but this depends on the manner of interpreting the data. The largest discrepancy arises when we compare our energies with that derived by Martin from the specific-heat values or with the theoretical value of Fumi. Because of the possibility of other than mono-vacancy formation occurring, and because of the large relative errors in the low-temperature region of the semilog plots, the energy and entropy values may be less meaningful than the melting point concentration values.

ACKNOWLEDGMENTS

[27] H. B. Huntington, G. A. Shirn, and E. S. Wajda, Phys. Rev. 99, 1085 (1955).
[28] A. B. Lidiard, Phil. Mag. 5, 1171 (1960).
[29] M. Sittig, Sodium: Its Manufacture, Properties and Uses (Reinhold Publishing Corporation, New York, 1956), p. 350.

[30] D. R. Beaman, R. W. Balluffi, and R. O. Simmons, Phys. Rev. 134, A532 (1964). Assuming a binding entropy of zero, a binding energy of 0.08 eV for silver in aluminum has been deduced. This is only about 10% of the vacancy formation energy in pure aluminum.