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Thermal-Expansion Measurements of Vacancy Formation Parameters in Zinc Single Crystals*

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Extremely accurate measurements of the thermal expansion along the principal directions of zinc single crystals have been made over a temperature range of 45–410°C by means of a dilatometric technique. Present results seem to indicate rather large inward displacements parallel to the c axis of atoms surrounding vacancies, and possibly a large anisotropy in the rearrangement of atoms during the process of vacancy formation. The latter effect is consistent with a model involving dislocation climb put forward by Nowick, as well as with recent data on electromigration in zinc single crystals. In addition, the "extra" volumetric thermal expansion at high temperatures indicates a vacancy energy of formation of 0.50 ± 0.05 eV, and on entropy of formation of $(2.3\pm0.5)k$.

I. INTRODUCTION

As a metal is heated and vacancies are thermally generated we expect an anomalous increase in the thermal expansion of the specimen, especially near its melting point where the defect concentration is greatest. The extra thermal expansion can then be used to deduce the vacancy formation energy E_f and formation entropy S_f in basically two ways. The first method requires a knowledge of the ideal crystal thermal expansion over a temperature range extending from room temperature up to near the melting point. Since theories for the thermal expansion of both cubic[1] and noncubic[2,3] metals are usually based on such simplifying assumptions as the temperature independence of the Grueneisen constant γ, the elastic constants, and the Debye temperature Θ, these physical properties are then generally treated as parameters whose effective values are determined by a fit to the experimental data for temperatures at which defects are not present; i.e. the ideal thermal expansion is then extrapolated to the high-temperature region where differences between the extrapolated and measured values are attributed to the presence of the thermally generated defects. In addition, one needs to know the vacancy formation volume ΔV_f. ΔV_f is, of course, some fraction f of the atomic volume Ω owing to relaxation[4–6] of the lattice around the vacancy. The fractional equilibrium vacancy concentration $\Delta N/N$ at a temperature T is then presumably given by

$$\Delta N/N=(\Delta V/V_0-\Delta V^{\text{theoret}}/V_0)/f\,, \tag{1}$$

where V_0 is the volume of the specimen at a temperature low enough to ensure a negligible number of vacancies, ΔV is the experimentally determined volume change, and $\Delta V^{\text{theoret}}$ is the ideal crystal volume change. From thermodynamics we also have that

$$\Delta N/N=e^{S_f/k}\,e^{-E_f/kT}\,, \tag{2}$$

where k is Boltzmann's constant. Then according to Eqs. (1) and (2), the quantities $-E_f/k$ and S_f/k are given, respectively, by the slope and intercept of the expected straight-line plot of $\ln[(\Delta V/V_0-\Delta V^{\text{theoret}}/V_0)/f]$ versus $1/T$.

The extrapolation technique just described has been used with varying amounts of success by Gertsriken[7] to obtain a value of E_f for copper, by Jonenburger[8] to obtain values of E_f for copper and gold based on the thermal-expansion data of Nix and MacNair,[9] and by Gertsriken and Slyusar[10] to obtain formation energies for gold, copper, silver, aluminum, zinc, lead, cadmium, and tin.

The second method, and by far the superior one, avoids the problem of having to know the high-temperature thermal expansion of the "ideal" lattice by measuring both the fractional change in macroscopic volume and the fractional change in volume of the unit cell as functions of the temperature. Then $\Delta N/N$ for a cubic metal is given by[11]

$$\Delta N/N=3(\Delta L/L_0-\Delta a/a_0)\,, \tag{3}$$

where ΔL and Δa are the changes in specimen length and lattice parameter, respectively, and L_0 and a_0 are the corresponding reference length and lattice parameter at a low enough temperature so that vacancies are not present. By simultaneously making precision dilatometric and x-ray measurements to determine ΔL and Δa as functions of the temperature, Simmons and Balluffi quite accurately determined both E_f and S_f for aluminum,[12] silver,[13] gold,[14] and copper.[15] More recently,

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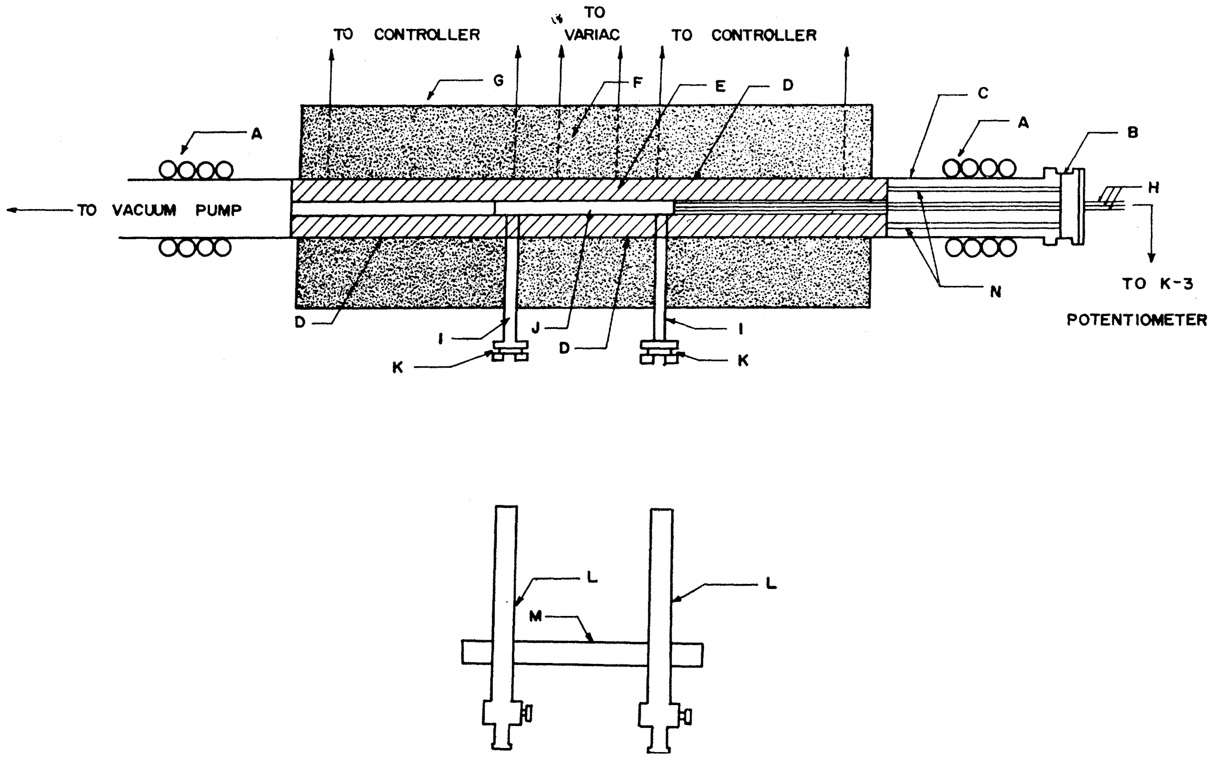

FIG. 1. Over-all view of furnace and measurement apparatus: A, cooling coils; B, vacuum seal; C, copper furnace tube; D, heating coils; E, graphite core; F, insulation; G, outer furnace jacket; H, thermocouples; I, viewing ports; J, specimen; K, quartz windows; L, filar micrometer microscopes; M, invar bar; and N, steel struts.

Feder and Nowick have used basically the same technique to determine vacancy-formation parameters for sodium,[16] lead,[17] and cadmium.[18] Cadmium has a hexagonal structure, so that Feder and Nowick's length measurements were done along the principal axes of oriented single crystals. For a crystal possessing the symmetry of cadmium, Eq. (3) must obviously be generalized to

$$\Delta N/N = 2[(\Delta L/L_0)_a - (\Delta a/a_0)_a] + [(\Delta L/L_0)_c - (\Delta a/a_0)_c], \quad (4)$$

where the subscript c refers to the c axis (hexad axis) and the subscript a to the a axis (perpendicular to the c axis). When both the quantities $\ln[(\Delta L/L_0)_a - (\Delta a/a_0)_a]$ and $\ln[(\Delta L/L_0)_c - (\Delta a/a_0)_c]$ were plotted versus $1/T$, straight lines having slopes corresponding to a vacancy formation energy of 0.40 eV were obtained. However, it was found that the ratio $\Delta_c/\Delta_a = 2.3$, where $\Delta_c \equiv (\Delta L/L_0)_c - (\Delta a/a_0)_c$ and $\Delta_a \equiv (\Delta L/L_0)_a - (\Delta a/a_0)_a$. Nowick[18] has suggested that this ratio can be understood in terms of the climb of various sets of edge dislocations, which are the sources and sinks for vacancies in the crystal.

In the present experiment precision dilatometric measurements along the principal axes of oriented single crystals of zinc were undertaken to see whether the extrapolation technique could disclose dislocation effects similar to those previously observed in cadmium by means of the combined dilatometric–x-ray technique. In addition, since the only other determination of vacancy-formation parameters by means of the extrapolation technique involved polycrystalline specimens, it was of interest to see whether significantly different values of E_f and S_f resulted when single crystals were used. Finally, it was also significant to see how consistent the high-temperature thermal-expansion data for zinc in the present experiment were with those of previous investigators.[19,20]

II. EXPERIMENTAL PROCEDURE

A. Apparatus

The linear-expansion measurements on the zinc crystals were made in a vacuum furnace constructed by Genoni.[21] The combination of a copper furnace tube, graphite core (in which the specimen was placed), and

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separately controlled heating coils served to establish a temperature gradient no greater than 6×10^{-3} C°/cm ever the entire 15-cm length of the specimen. The furnace is shown in Fig. 1.

The length measurement apparatus consisted of two parallel-mounted filar micrometer microscopes (purchased from Gaertner Scientific Corp., Chicago) having a working distance of approximately 8 in. and verniers with smallest division of 0.5 μ. The microscope mount was constructed of stainless steel, with the exception of an invar bar to which both microscopes were rigidly clamped. Room temperature was controlled to reduce any possible error due to the expansion or contraction of the invar bar. The arrangement is shown in Fig. 1.

For the temperature measurements, three chromel-versus-alumel thermocouples were equally spaced along the length of the specimen, and located in grooves provided in the graphite core. The distance between the specimen and thermocouples was about $\frac{1}{32}$ in. In a series of earlier thermal-expansion measurements on nickel, a fourth thermocouple located at the same position as one of the three in the grooves was allowed to touch the specimen. The difference in emf of the two thermocouples was noted over the range 30–420°C. This provided a correction to the temperatures recorded by the three thermocouples during the actual runs. All temperatures were measured to a precision of at least 0.1°C and an absolute accuracy of 1°C.

TABLE I. *a*-axis thermal expansion of zinc.

Cooling run		Heating run	
T (°C)	$10^5\ (\Delta L/L_0)_a$	T (°C)	$10^5\ (\Delta L/L_0)_a$
46.2	0	46.2	0
54.4	11.03	76.0	40.62
68.8	30.84	98.2	71.59
83.7	51.45	120.5	107.25
98.1	71.52	141.5	136.51
113.2	93.51	164.5	173.75
127.8	115.57	184.9	208.23
143.1	139.48	205.2	243.96
158.1	163.32	223.3	277.57
172.3	186.57	244.4	317.20
185.1	208.89	266.1	360.12
197.9	230.81	287.7	404.70
210.9	254.85	309.5	453.44
224.7	280.61	330.5	501.78
238.2	305.97	349.7	548.41
252.3	333.38	363.6	583.34
267.3	362.90	374.6	612.07
282.0	394.14	383.7	636.90
296.7	424.05	394.4	667.48
311.3	457.93	401.3	686.90
325.7	490.62	409.4	711.07
340.5	525.23		
350.7	549.46		
361.5	577.40		
368.7	596.35		
375.2	613.46		
381.8	631.16		
388.3	648.53		
395.2	667.88		

TABLE II. *c*-axis thermal expansion of zinc.

Cooling run		Heating run	
T (°C)	$10^5\ (\Delta L/L_0)_c$	T (°C)	$10^5\ (\Delta L/L_0)_c$
47.9	0	47.9	0
63.6	102.25	87.8	253.62
78.9	198.29	116.9	435.85
93.3	290.41	154.6	672.47
107.7	378.12	177.4	815.90
123.7	479.90	200.1	956.34
139.2	577.42	222.5	1098.65
153.5	667.80	244.4	1231.62
154.6	674.73	266.0	1363.79
169.9	771.98	287.0	1489.50
185.1	867.43	306.0	1605.48
200.0	956.47	327.4	1729.65
214.4	1049.59	347.7	1845.96
229.7	1144.50	362.7	1928.61
244.5	1235.15	371.2	1974.41
259.2	1324.74	380.6	2023.40
272.7	1408.25	389.3	2066.79
287.4	1490.77	398.1	2108.44
299.8	1569.02	403.0	2132.77
313.1	1648.60	408.4	2158.77
326.6	1725.32		
342.5	1819.10		
352.1	1870.96		
362.6	1929.01		
368.2	1958.54		
374.1	1990.14		
380.0	2019.46		
386.2	2052.92		
391.2	2080.45		
398.3	2114.44		

B. Specimen Preparation

Thermal-expansion measurements were made on *a*-axis and *c*-axis zinc crystals (purchased from Mono-Crystals, Cleveland, Ohio), both having dimensions of approximately 1×1×15 cm. A series of Laue back-reflection photographs of each crystal indicated alignment of the crystallographic and body axes to within $\frac{1}{2}$°.

A series of 25 to 30 markers, spaced about a millimeter apart, were then placed at each end of the specimens with a 90° pyramidal diamond indentor (purchased from Rel-Tok Diamond Tool Company, Watertown, Mass.). Because a particular marker would eventually move out of the field of view of a microscope as the specimen expanded, a series of markers was required to follow the entire thermal expansion.

Finally, to prevent vaporization of the zinc at the highest temperatures encountered in a run, the specimens were oxidized in air prior to an actual run. The zinc oxide layer thus formed not only served as a protective "blanket" for the specimen, but also improved the appearance of the markers as viewed with the microscopes.

C. Procedure

After oxidizing a specimen, it was positioned in the graphite core so that each set of markers was aligned with the viewing ports of the furnace. The invar bar on which the microscopes were mounted was then optically aligned parallel to the zinc specimen. In addition, the

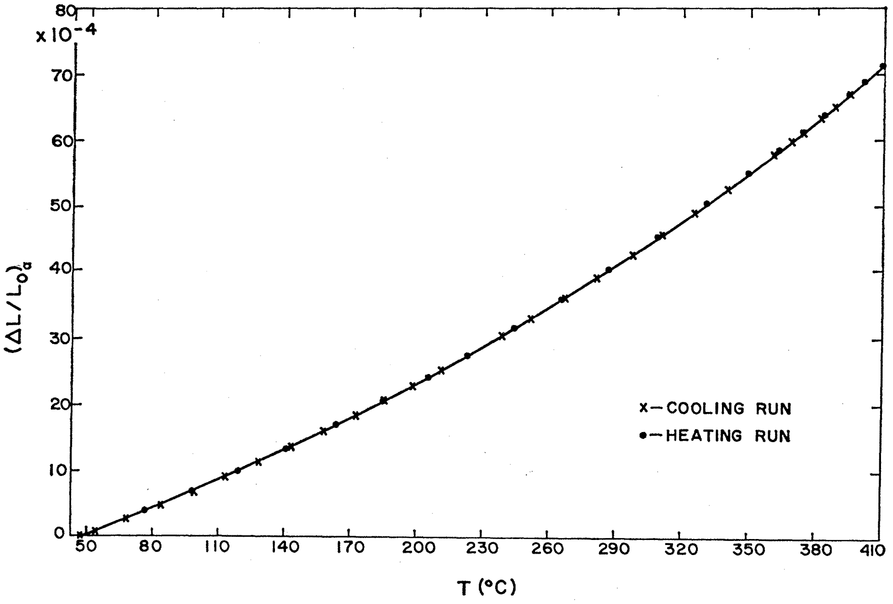

FIG. 2. Graph of $(\Delta L/L_0)_a$ versus T.

quartz windows in the viewing ports were oriented in such a way as to prevent significant refraction of the microscopes' axial light beams (used to view the markers) as they passed through the windows.

The furnace was then evacuated and the temperature of the specimen raised to approximately 400°C. After thermal equilibrium was established a series of length measurements was taken over a period of hours to determine possible changes in the crystal's length due to stress relaxation. When no relaxation was observed, the temperature was decreased in steps until the specimen reached a temperature of ~45°C. At each step, equilibrium was established in ~3 h, and a series of microscope readings then taken. During the time that the readings were taken, the temperature of the specimen was continuously monitored so as to make certain the specimen remained in thermal equilibrium. After reaching the lowest temperature of ~45°C, the temperature of the specimen was then raised to ~410°C through another series of steps to constitute a "heating" run. The heating run, in conjunction with the "cooling" run, served to check the reproducibility of the data.

Upon completion of a run, the value of L_0 was obtained with a glass scale (purchased from Gurley

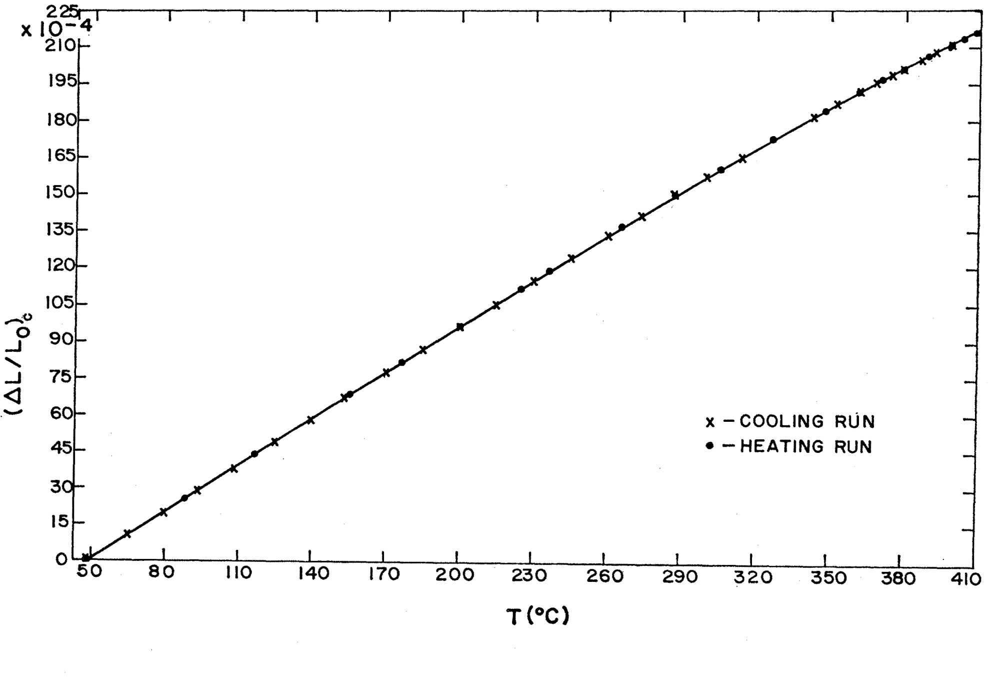

FIG. 3. Graph of $(\Delta L/L_0)_c$ versus T.

Engineering Instruments, Troy, N. Y.). This scale had smallest divisions of 0.1 mm. Also, the microscope verniers were calibrated against a glass slide having smallest divisions of 0.01 mm.

III. EXPERIMENTAL RESULTS

The values of $(\Delta L/L_0)_a$ and $(\Delta L/L_0)_c$ are tabulated in Tables I and II, and are shown plotted against temperature in Figs. 2 and 3. The a-axis data span the temperature range 409.4–46.2°C (a-axis reference temperature), while the c-axis data were taken over the range 408.4–47.9°C (c-axis reference temperature). The curves include data from both cooling and heating runs. The standard deviations of the experimental points from the smoothed curves of $(\Delta L/L_0)_a$ versus T and $(\Delta L/L_0)_c$ versus T are 5×10^{-6} and 14×10^{-6}, respectively. These deviations are reasonably consistent with the typical standard deviation of 0.3 μ for repeated microscope readings, i.e., for $L_0=150$ mm and $\delta(\Delta L)=0.3$ μ, $\delta(\Delta L/L_0)\sim\delta(\Delta L)/L_0\sim2\times10^{-6}$. Within this experimental uncertainty there is absolutely no evidence for any systematic lack of reversibility during heating and cooling. In addition, the consistency of the data indicates that thermal equilibrium of the specimen was established prior to and during each length measurement.

IV. DISCUSSION AND INTERPRETATION OF DATA

A. Comparison with Previous Thermal-Expansion Data

The data of Medoff and Cadoff[20] were available only in the form of principal-axis instantaneous coefficients of linear thermal expansion. Therefore, the curves of $(\Delta L/L_0)_a$ and $(\Delta L/L_0)_c$ versus T obtained in the present experiment, as well as those of Owen and Yates,[19] were graphically differentiated to permit a comparison of all three sets of data. The principal-axis instantaneous coefficients of thermal expansion, α_a and α_c, are defined as $\alpha_a\equiv(dL_a/dT)/L_a$ and $\alpha_c\equiv(dL_c/dT)/L_c$. Curves of α_a and α_c versus T for all three sets of data are shown in Figs. 4 and 5, respectively. While Medoff and Cadoff assigned an experimental uncertainty of $\sim5\%$ to their values of α, an estimated uncertainty of $\sim10\%$ was assigned to the measurements of Owen and Yates on the basis of the accuracy they claim for their x-ray lattice parameter and temperature measurements. We conservatively estimate our uncertainty in α_a and α_c to be $\sim1\%$.

It is apparent that, at the highest temperatures, the values of α obtained in the present experiment are systematically smaller than those of either Medoff and Cadoff or Owen and Yates. Owen and Yates take pains to discuss their difficulties with establishing a temperature scale. Medoff and Cadoff do not mention any details of temperature measurement. Obviously, any systematic differences in the temperature scales of each experiment will produce the most pronounced systematic differences in the α's in the high-temperature region where both $d\alpha_a/dT$ and $-d\alpha_c/dT$ are both increasing most rapidly with T. Conversely, the best agreement is achieved at the lower temperatures.

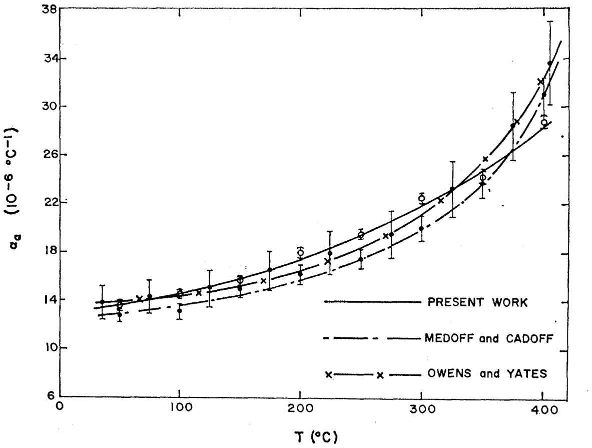

FIG. 4. Comparison of present measurements of the a-axis instantaneous coefficient of linear expansion with those of Medoff and Cadoff and of Owen and Yates.

B. Relaxation and Dislocation Effects

A theory developed by Riley,[3] and patterned after an earlier theory of Grueneisen and Goens[2] for the thermal expansion of hexagonal crystals, indicates that the coefficients of thermal expansion can be written

$$\alpha_a^{\text{theoret}}=AC_{va}+BC_{vc}+CT, \qquad (4')$$

$$\alpha_c^{\text{theoret}}=LC_{va}+MC_{vc}+NT, \qquad (4'')$$

where C_{va} and C_{vc} are the contributions from vibrational modes perpendicular and parallel to the c axis, respectively, to the total heat capacity C_v of the crystal at constant volume; i.e., it is assumed that "parallel" and "perpendicular" normal modes are weakly coupled, so that $C_v=\frac{1}{3}(2C_{va}+C_{vc})$. The constants A, B, C, L, M, and N are related to the elastic moduli and are assumed to be temperature-independent. For $T>50$°C both C_{va} and C_{vc} are essentially independent of T; i.e., from low-temperature thermal-expansion data[2] the characteristic temperature Θ_c associated with c-axis vibrations is ~200°K, while $\Theta_a\sim300$°K. Therefore, for the purposes of the present experiment, the result of integrating Eqs. (4′) and (4″) with respect to temperature is

$$(\Delta L/L_0)_a^{\text{theoret}}=A'T^2+B'T+C', \qquad \text{(5a)}$$

$$(\Delta L/L_0)_c^{\text{theoret}}=D'T^2+E'T+F', \qquad \text{(5b)}$$

where the constants A', etc., are again all considered temperature-independent.

The constants in Eqs. (5a) and (5b) were determined by fitting the above second-degree polynomials to the experimentally determined values of $(\Delta L/L_0)_a$ and $(\Delta L/L_0)_c$ in the temperature range 215–275°C. Vacancy

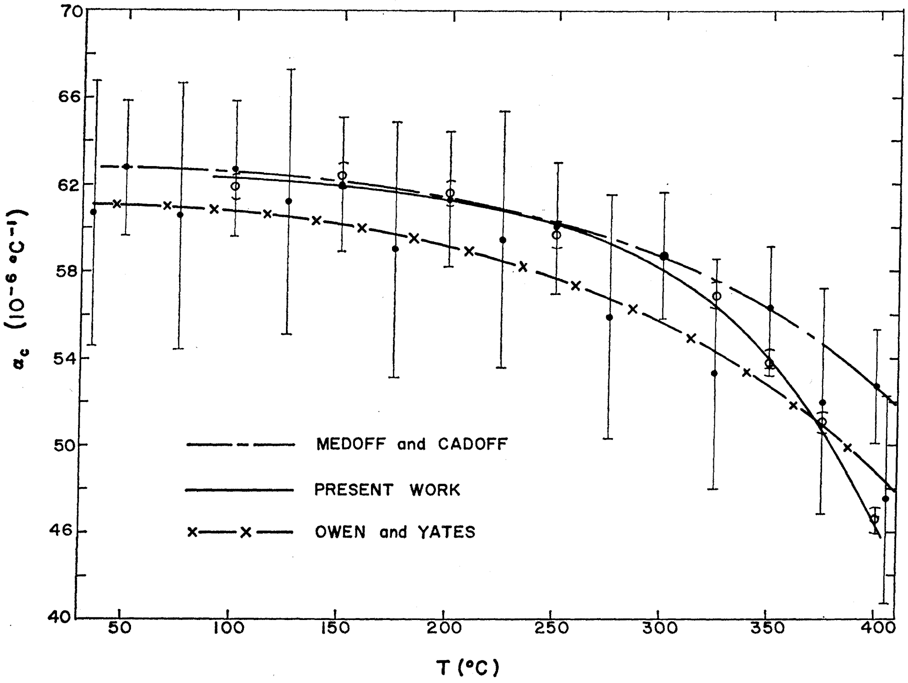

FIG. 5. Comparison of present measurements of the c-axis instantaneous coefficient of linear expansion with those of Medoff and Cadoff and of Owen and Yates.

concentrations are still negligible in this temperature range, so we expect $(\Delta L/L_0)_a^{\text{theoret}} = (\Delta L/L_0)_a$ and $(\Delta L/L_0)_c^{\text{theoret}} = (\Delta L/L_0)_c$. With the values of the constants so determined, the quantities $\Delta_a' \equiv (\Delta L/L_0)_a - (\Delta L/L_0)_a^{\text{theoret}}$ and $\Delta_c' \equiv (\Delta L/L_0)_c - (\Delta L/L_0)_c^{\text{theoret}}$ were computed in the temperature range 300–410°C. It was then found that $\Delta_c' \lesssim 0$ and $\Delta_a' > 0$ over the entire high-temperature range. It is probably reasonable to expect $\Delta_a' > \Delta_c'$ since both quantities depend on the relaxation of the lattice; Δ_a and Δ_c, on the other hand, are quantities which do not depend on the lattice relaxation.[12,18] The inward atomic displacements parallel to the c axis are expected to be greater than those parallel to the a axis since zinc is about 10 times stiffer along the a-axis direction than the c-axis direction. However, in any case we expect both Δ_a' and Δ_c' to be positive. The fact that we find $\Delta_c' \lesssim 0$ is a warning that Eqs. (5) are not to be taken too literally; i.e., in addition to previously mentioned assumptions, Riley's model ignores such effects as lattice anharmonicity[22] and alteration of the crystal's vibrational frequency spectrum[23] owing to the presence of the defects.

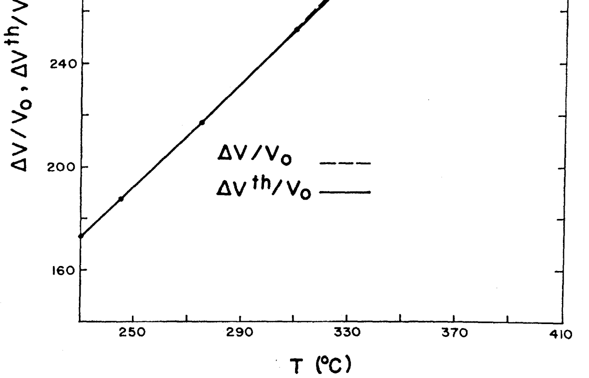

FIG. 6. Graph of $\Delta V/V_0$ and $\Delta V^{\text{theoret}}/V_0$ versus T.

On the other hand, in addition to the above factors, a dislocation climb effect could enhance Δ_a' over Δ_c'. It is well known that vacancies are generated or annihilated as dislocations climb in a crystal.[24] If the product of the density and climb velocity of edge dislocations climbing perpendicular to the basal plane exceeded that of dislocations climbing parallel to the basal plane, we would expect the growth rate of atomic planes parallel to the c axis to exceed that of planes perpendicular to the c axis. In a paper by Routbort[25] on electromigration in zinc single crystals, values for an isotropy factor σ were determined for two different orientations of the

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[25] J. L. Routbort, Bull. Am. Phys. Soc. **13**, 487 (1968).

c axis with respect to the applied electric field. σ is a proportionality factor between the velocities of specimen surface markers (used to measure the electromigration) and the actual drift velocity of the ions in the electric field. It has been shown that[26]

$$e_{rr}/e_{xx} = (1-\sigma)/2\sigma , \qquad (6)$$

where e_{rr} and e_{xx} are the dilatations of the crystal perpendicular and parallel to the electric field, respectively. From the electromigration data of Routbort we find the mean values of e_{rr}/e_{xx} over the temperature range 360–400°C to be 1.6 for the c axis parallel to the electric field, and 1.1 for the a axis parallel to the field. These values of e_{rr}/e_{xx} would appear to indicate preferential deposition of atomic planes parallel to the c axis. This would tend to make $\Delta_a' > \Delta_c'$.

C. Determination of Vacancy-Formation Parameters E_f and S_f

The experimentally determined and extrapolated values of the fractional length changes were used to compute $\Delta V/V_0$ and $\Delta V^{\text{theoret}}/V_0$ over the high-temperature range. These quantities are shown plotted against temperature in Fig. 6. We note that $\Delta V/V_0 > \Delta V^{\text{theoret}}/V_0$, consistent with the formation of vacancies. In addition, when $\ln(\Delta V/V_0 - \Delta V^{\text{theoret}}/V_0)$ is plotted against $1/T$, a straight line results, as shown in Fig. 7. From Eqs. (1) and (2) the slope of this straight line corresponds to $E_f = 0.50 \pm 0.05$ eV. The intercept is found to be $(1.2\pm0.3)k$; i.e., $\ln f + S_f/k = (1.2\pm0.3)k$. Now the relaxation parameter f can be estimated from recent high-pressure data of Styris and Tomizuka.[27] They have found that the activation volumes for diffusion parallel and perpendicular to the c axis are 3.7 and 5.8 cm^3/mole, respectively. This means that the vacancy formation volume $\Delta V_f \leqslant 3.7$ cm^3/mole, assuming the migration volume $\Delta V_m{}^c$ for diffusion along the c axis to be positive. Since for zinc $\Omega = 9.2$ cm^3/mole, we expect that ΔV_f is probably not too much smaller than 3 cm^3/mole. Typically, $f \gtrsim 0.5$.[28] Thus we take $f = 0.33 \pm 0.08$ corresponding to $\Delta V_f = 3 \pm 0.7$ cm^3/mole. Then $\ln f = -1.1 \pm 0.2$, and hence $S_f = (2.3\pm0.5)k$. At the melting point of zinc (~692.2°K) then, corresponding to $E_f = 0.5$ eV and $S_f = 2.3k$, $\Delta N/N = 2\times10^{-3}$.

From the "extra" thermal-expansion measurements of Gertsriken and Slyusar,[10] $E_f = 0.47$ eV, $S_f = 1.6k$, and at the melting point $\Delta N/N = 3\times10^{-3}$. Although their value of E_f is in good agreement with that determined in the present experiment, there is not quite as good agreement between values of $\Delta N/N$ since Gertsriken and Slyusar ignore relaxation effects.

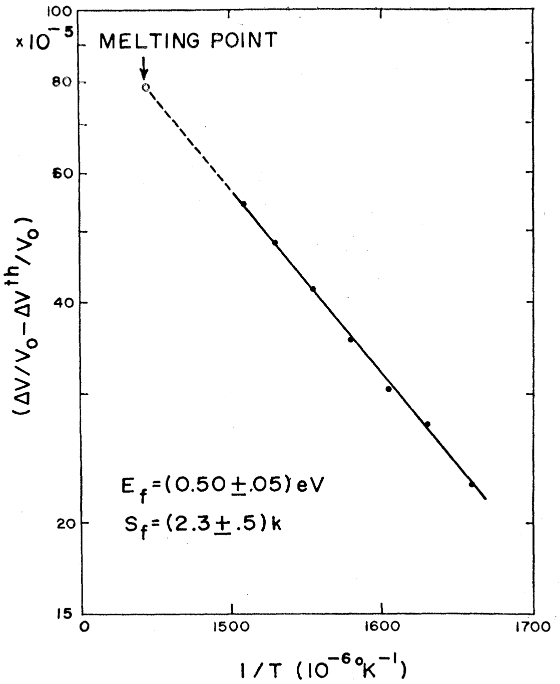

FIG. 7. Graph of $\ln(\Delta V/V_0 - \Delta V^{\text{theoret}}/V_0)$ versus $1/T$.

The present value of E_f also appears to be consistent with data for the recovery of neutron-irradiated zinc. Nihoul[29] has found that, besides a main recovery stage located at 105°K, there was a second but less pronounced stage around 155°K associated with an activation energy of 0.5 eV, and perhaps connected with vacancy migration.

In addition, the vacancy-formation parameters obtained in the present experiment appear to satisfy some empirical rules developed for the cubic metals. In particular, with Q being the activation energy for self-diffusion, for a number of the cubic metals such as Pb, Al, Au, Ag, and Cu, $E_f/Q \sim 0.5$ and $S_f \sim k$. For zinc, $Q = 0.98$ eV,[30,31] so that the present value of $E_f = 0.5$ eV gives $E_f/Q \sim 0.5$. The present value of $S_f = 2.3k$ is also consistent with $S_f \sim k$. In addition, the values of the vacancy-formation parameters ascertained for zinc in the present experiment also appear to be consistent with the values of Feder *et al.*[18] for cadmium of $E_f = 0.40$ eV ($Q = 0.81$ eV) and $S_f = 0.7k$.

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