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Dilatometric and X-Ray Thermal Expansion in Noncubic Crystals. I. Role of Dislocation Climb*

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Comparison of macroscopic (dilatometric) and microscopic (x-ray) precision thermal-expansion measurements at elevated temperatures has been widely used to obtain the equilibrium concentration of vacancies in cubic crystals. For noncubic crystals these measurements must be made in more than one orientation (e.g., in axial crystals, along both the *c* and *a* axes). Such measurements give information not only on the equilibrium vacancy concentration, but also on the relative rates of climb of the various dislocations in the crystal, which act as sources and sinks for the vacancies. Quantitative expressions are obtained for the ratio Δ_c/Δ_a, where Δ is the difference between fractional macroscopic and microscopic linear expansions along the *c* or *a* direction in an axial crystal. Consideration is given to the two extreme cases of dislocation climb, viz., the diffusion limited and climb-rate limited cases. An important point is that the measurements, in general, will be sample dependent, so that the samples of different orientation must be taken from the same single crystal.

I. INTRODUCTION

The use of precision thermal-expansion measurements, both macroscopic (dilatometry) and microscopic (x-ray lattice parameters), for determining the equilibrium vacancy concentration in cubic crystals is well known.[1-8] It has been widely used to obtain the concentrations of vacancies in thermal equilibrium in fcc metals (e.g., Al, Ag, Au, and Pb) and more recently in bcc alkali metals (e.g., Na and Li). The extension of such measurements to noncubic (specifically, hexagonal) crystals was recently reported.[9,10] We shall see that such studies of noncubic crystals offer the opportunity to obtain information about the sources and sinks for the vacancies, which could not be obtained in the case of cubic crystals. The present paper explores the theory behind such measurements, while the following paper (paper II) will apply this theory to a detailed study of single crystals of cadmium.

The determination of point-defect concentrations from thermal-expansion measurements derives from the relation

$$V = Nv \ , \tag{1}$$

which relates the volume V of a specimen to the average volume v of a unit cell, where N is the number of unit cells. If N is unchanged on heating the crystal from temperature T_0 to temperature T, and if the volumes at T_0 are V_0 and v_0, and those at T are V and v, respectively, then $\delta V/V_0 = \delta v/v_0$, where

$$\delta V = V - V_0 \ ,$$

$$\delta v = v - v_0 \ . \tag{2}$$

To relate δv to the change in volume of the unit cell as obtained from x-ray lattice-parameter measurements is actually a subtle point which was first discussed by Eshelby[11] who considered the distortions about the defect in the elastic approximation, and later in a more general way by Balluffi and Simmons.[12]

If, however, N changes upon heating up the sample due to the thermal generation of vacancies and/or interstitials, Eq. (1) leads to the more general result

$$\delta V(T)/V_0 = \delta N(T)/N_0 + \delta v(T)/v_0 \ , \tag{3}$$

where $\delta N = N(T) - N_0$ and N_0 is the number of unit cells at temperature T_0. In obtaining Eq. (3) we have dropped the term in $\delta N \delta V$ which is usually negligible. If, as is the case for most metals, only vacancies are produced thermally, and if T_0 is taken sufficiently low that the vacancy concentration at T_0 is negligible, then $\delta N/N_0$ simply becomes $\overline{C}_v(T)$, the equilibrium mole fraction of vacancies at temperature T.[13] Under these conditions

$$\overline{C}_v(T) = \delta V(T)/V_0 - \delta v(T)/v_0 \ . \tag{4}$$

Equation (4) is applicable to a crystal of any symmetry. For cubic crystals, one customarily writes

$$\overline{C}_v(T) = 3(\delta L(T)/L_0 - \delta a(T)/a_0) \quad \text{(cubic)} \ , \tag{5}$$

where L and a are, respectively, the macroscopic length and lattice parameter, again taken at both T and T_0, and δ is used in the same way as in Eq. (2). There are two assumptions made in going from Eq. (4) to (5): (a) The first is the obvious assumption that $\delta L/L_0 \ll 1$, so that higher terms are negligible. (If this were not valid, the equation could, of course, easily be corrected.) (b) The second is the more subtle assumption that the *sources and sinks for vacancies are distributed randomly with respect to the three cube axes*. If assumption (b) were not valid, macroscopic length measurements in different directions would not give the same results. As an extreme example, consider a long thin rod and suppose that the sources of vacancies are the external surfaces. Then the length change along the long axis would hardly show any evidence for defect formation, i.e., the right-hand side of Eq. (5) would give almost exactly zero. On the other hand, measurement of the diameter of the rod as a function of T *would* show the vacancy contribution.

It is well known that dislocations rather than the external surfaces provide the sources and sinks for vacancies via the climb mechanism. Accordingly, the above assumption (b) means, in fact, that the climbing dislocations are distributed randomly in a manner consistent with the cubic symmetry of the crystal. Thus, for example, edge dislocations with Burgers vector $\vec{b}$ along [110] are equally probable to those for which $\vec{b}$ is along $[1\overline{1}0]$, [101], etc. Since samples used for dilatational measurements are often relatively long thin single crystals, or if polycrystalline, worked into long thin rods, it is by no means obvious that the rod axis will not in some way be preferred. This point has not been given the discussion in the literature that it deserves. Nevertheless, in a number of past (unpublished) experiments on Pb using a differential dilatometer, the present authors looked for deviations in $L(T)$ among different samples with negative results; fully systematic experiments were not carried out, however.

If we accept the assumption of randomly distributed sources and sinks, it is then clear that dilatometric measurements in cubic crystals give no information on the relative effectiveness of various types of dislocations which serve as sources and sinks for vacancies. In the present paper, we will show that as soon as one turns to crystals of lower-than-cubic symmetry this statement is no longer true. Rather, the combination of dilatometric and x-ray measurements gives information not only on the concentration of vacancies but also on the dislocations which equilibrate them. In view of the greater interest in axial crystals (hexagonal, tetragonal and trigonal) as compared to those of still lower symmetry, we will confine our analysis to axial crystals.

In the case of axial crystals there are two independent thermal-expansion coefficients, one parallel to the c axis (the major symmetry axis) and the other perpendicular to the c axis or in the basal plane.[14] Expansion in the basal plane is isotropic. For the comparison of macroscopic and microscopic expansion, one may define two quantities Δ_c and Δ_a by

$$\Delta_c = (\delta L(T)/L_0)_c - \delta c(T)/c_0 \tag{6}$$

and

$$\Delta_a = (\delta L(T)/L_0)_a - \delta a(T)/a_0 \ , \tag{7}$$

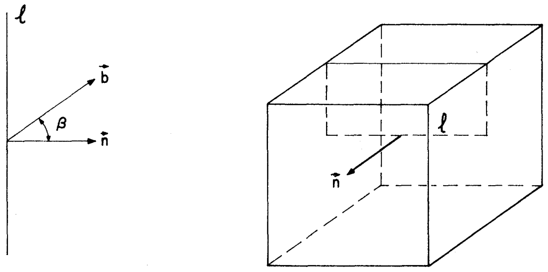
where L_c and L_a are macroscopic lengths parallel and perpendicular to the c axis, respectively, and c and a are the corresponding lattice parameters. The subscript zero and the difference δ have the same meanings as in Eq. (3). Since Eq. (4) is also valid for noncubic crystals, we may make similar assumptions as we did in going from Eq. (4) to (5) for the cubic case, and obtain, for axial crystals

$$\overline{C}_v(T) = 2\Delta_a(T) + \Delta_c(T) \ . \tag{8}$$

Equation (8) is the basic relation from which the vacancy concentration may be obtained from combined dilatometric and x-ray measurements on two properly oriented samples. The experiments, however, provide *two* independent functions of temperature, $\Delta_c(T)$ and $\Delta_a(T)$, while Eq. (8) utilizes only a linear combination of these measured functions. There is, therefore, information contained in the experiments in addition to $\bar{C}_v(T)$. This additional information is most conveniently expressed as the ratio $\Delta_c(T)/\Delta_a(T)$. It is the significance of this ratio that we wish to determine. We will show in this paper that the quantity Δ_c/Δ_a measures an over-all property of the totality of dislocation sources and sinks for vacancies in the crystal, which may be sample dependent.

II. THEORY OF Δ_c/Δ_a FOR AXIAL CRYSTALS

The dislocations which should be considered as sources and sinks for vacancies at temperatures close to the melting point are those originally present in the well-annealed crystal in local thermal equilibrium. The basis for this statement is that cooling and heating rates in dilatometric experiments are sufficiently slow that the sample is not strained, and also that supersaturations are never great enough to give rise to the nucleation of dislocation loops of the type produced upon rapid quenching.[15]



(a) (b)

FIG. 1. (a) Diagram of slip plane, showing a segment of dislocation line l, its Burgers vector $\vec{b}$, and the unit normal $\vec{n}$. (b) Three-dimensional view showing the extra half-plane which increases or decreases in area as climb occurs.

Consider a dislocation segment l shown in Fig. 1(a), which is a diagram of the slip plane defined by both l and the Burgers vector $\vec{b}$. Let $\vec{n}$ be the unit normal to l which lies in the slip plane, and β the angle between $\vec{b}$ and $\vec{n}$. Thus $\beta = 0$ for an edge and $\frac{1}{2}\pi$ for a screw dislocation. Climb of the dislocation segment takes place in the plane perpendicular to $\vec{n}$, as shown in Fig. 1(b). Thus, to first order, all dimensional changes resulting from such climb must be parallel to $\vec{n}$. Let us define $(\Delta_n)_i$ by

$$(\Delta_n)_i = [(\delta L/L_0)_n - (\delta d/d_0)_n]_i \ , \tag{9}$$

where $(\Delta L/L_0)_n$ and $(\Delta d/d_0)_n$ are, respectively, the fractional change in macroscopic dimensions and in lattice spacing parallel to $\vec{n}$, and the subscript i refers to the dislocation *type*, defined by $\vec{b}$ and $\vec{n}$. Thus $(\Delta_n)_i$ is the difference between fractional macroscopic and microscopic dimensional changes in direction $\vec{n}$ due to climb of dislocations of type i. By an argument analogous to that which led from Eq. (1) to (4), it follows that $(\Delta_n)_i = (C_v)_i$, where $(C_v)_i$ is the concentration of vacancies generated by the climb of dislocations of type i. Since $(\delta L/L_0)_n$ and $(\delta d/d_0)_n$ are (to first order) components of a strain tensor, like thermal-expansion coefficients, these quantities and their difference may be resolved into components $(\Delta_c)_i$ parallel to the c axis and $(\Delta_a)_i$ parallel to the a axis, according to[14]

$$\begin{aligned} (\Delta_c)_i &= (\Delta_n)_i \cos^2\psi_i \ , \\ (\Delta_a)_i &= (\Delta_n)_i \sin^2\psi_i \cos^2\phi_i \ . \end{aligned} \tag{10}$$

Here ψ and ϕ are the polar coordinates of $\vec{n}$ with respect to the crystal axis, i.e., ψ is the angle between $\vec{n}$ and the c axes, while ϕ is the angle between the projection of $\vec{n}$ in the basal plane and the a axis. Equation (10) represents the purely geometrical aspect of dislocation climb.

We now consider the presence of a distribution of dislocation types each having its own density, Burgers vector and polar angles, as well as *climb rate* $r_i(T)$ defined as the number of vacancies absorbed per second, per unit dislocation length, and per unit vacancy supersaturation. The supersaturation $\sigma(T, t)$, which depends on both temperature and time, is defined in the usual way, as

$$\sigma \equiv \ln(C_v/\bar{C}_v) \simeq (C_v/\bar{C}_v) - 1 \ , \tag{11}$$

where C_v is the actual vacancy concentration and $\bar{C}_v$ its equilibrium value at that temperature, and the approximate equality applies when $\sigma \ll 1$. In the present type of experiment σ is always small, but depends on the time-temperature history of the sample. Because of the small value of σ, it is reasonable to take the climb per second as proportional to σ (as implied by our definition of r_i). From these definitions, the concentration of vacancies generated in time dt by dislocations of type i is

$$(dC_v)_i = (d\Delta_n)_i = -v_a \Lambda_i r_i \sigma\, dt \ , \tag{12}$$

where v_a is the atomic volume, Λ_i the dislocation density (length per cm^3) of type i, and the minus sign comes from the fact that *generation* of vacancies requires a negative σ. It is easily shown that the speed s_i of dislocation climb is related to the climb rate r_i by

$$s_i = v_a r_i \sigma/(b \cos\beta_i) \ . \tag{13}$$

From the first of Eqs. (10), together with Eq. (12), we may obtain the total Δ_c of the crystal by summing over all dislocation types and integrating over time:

$$\Delta_c(T)=v_a\sum_i\Lambda_i\cos^2\psi_i I_i(T)\ , \tag{14}$$

where $I_i(T)$ is the time-temperature integral

$$I_i(T)=-\int_{T_0(t=0)}^{T(t)} r_i(T)\sigma(T,\,t)\,dt \tag{15}$$

from a relatively low temperature T_0 at $t=0$ over a time-temperature history $T(t)$. $I_i(T)$ is thus the total number of vacancies generated by a unit length of dislocation line of type i in going from T_0 to T. The summation $\sum_i$ over dislocation types may be over a continuous distribution (where integration is then implied), e.g., it may be thought of as a summation over Burgers vectors and an integration over the polar angles (ψ and ϕ) of the unit normal $\vec{n}$. Similarly, we obtain for Δ_a,

$$\Delta_a=v_a\sum_i\Lambda_i\sin^2\psi_i\cos^2\phi_i\,I_i(T)\ . \tag{16}$$

Just as in the cubic case [assumption (b), following Eq. (5)], in the absence of information to the contrary, we assume that climbing dislocations are distributed in a crystallographically random manner. This means that the length Λ_i of all crystallographically equivalent dislocations is the same. Obviously, ψ_i and I_i are the same for equivalent dislocations. Thus $\cos^2\phi_i$ may be replaced by its average value. For an axial crystal, it is not difficult to show that $\langle\cos^2\phi_i\rangle_{\text{av}}=\frac{1}{2}$. We therefore obtain, for the desired ratio, the result

$$\frac{\Delta_c(T)}{\Delta_a(T)}=\frac{2\sum_i\Lambda_i\cos^2\psi_i I_i(T)}{\sum_i\Lambda_i\sin^2\psi_i I_i(T)}\ . \tag{17}$$

To proceed further, one must examine the integral $I_i(T)$. Based upon what has been said so far, it might be expected that $I_i(T)$ is a function of the time-temperature history in arriving at final temperature T. However, we will now show that under the conditions of a dilatation experiment, I_i for each dislocation type is independent of history and is a function only of the final temperature T. The basis for this conclusion is that the temperature is varied slowly enough that the vacancy concentration is always very close to equilibrium. Thus, consider the case of constant temperature T and apply Eqs. (11) and (12) to get

$$\frac{dC_v}{dt}=\overline{C}_v\frac{d\sigma}{dt}=-v_a\sigma\sum_i\Lambda_i r_i\ , \tag{18}$$

which may be written

$$\frac{d\sigma}{dt}=-\frac{\sigma\zeta}{\overline{C}_v}\equiv-\frac{\sigma}{\tau}\ , \tag{19}$$

where

$$\zeta(T)\equiv v_a\sum_i\Lambda_i r_i \tag{20}$$

and $\tau^{-1}\equiv\zeta/\overline{C}_v$. This result means that at a constant temperature, σ decays exponentially with time constant τ. Let us assume that this equilibration time is much less than the time to raise the temperature appreciably. This latter time is $\delta T/\gamma$, where γ is the heating rate and δT is a small temperature change, of the order of 1 °C. (Experimentally, we have ample evidence for the validity of this assumption, see paper II.) We may write the total change in σ in an infinitesimally small time-temperature interval. However, since the temperature is considered to be increasing with time, it is more convenient to use the undersaturation $-\sigma$ rather than the supersaturation as the quantity of interest. Thus,

$$d(-\sigma)=\frac{\sigma}{\tau}\,dt+\overline{C}_v^{-1}\frac{d\overline{C}_v}{dT}\,dT\ . \tag{21}$$

The first term on the right-hand side is the change in $(-\sigma)$ with time at constant T, taken from Eq. (19). The meaning of the last term in Eq. (21) is $-(\partial\sigma/\partial T)_t$, i.e., the increase in $(-\sigma)$ that would occur due to heating by dT if the time-dependent decay did not take place. In view of our assumption of a very rapid equilibration, however, over a small finite temperature interval δT the time-dependent decay given by the first term will eliminate the increase in $(-\sigma)$ just as rapidly as it is produced by the heating. The total increment $\delta(-\sigma)$ is then very nearly zero. This means that the quantity σdt which appears in the integral (15) may be calculated from Eq. (21) by setting $d(-\sigma)$ equal to zero. Accordingly,

$$I_i(T)=\int_{T_0}^{T}\frac{r_i(T)}{\zeta(T)}\frac{d\overline{C}_v}{dT}\,dT\ , \tag{22}$$

where $\zeta(T)$ is given by Eq. (20). The integral is independent of the time-temperature history of the sample, which completes the proof. Inserting Eq. (22) into (7) then given a general expression for Δ_c/Δ_a.

An interesting special (but unrealistic) case is that which only one dislocation type is present. In that case the integral $I(T)$ and the dislocation density cancel in Eq. (17), to give

$$\Delta_c/\Delta_a=2\cot^2\psi\ , \tag{23}$$

i.e., the ratio depends only on the angle ψ between $\vec{n}$ and the c axis.

The general problem may be simplified further by considering two extreme situations under which climb may take place, namely, diffusion-limited and climb-rate-limited processes. These two cases have been discussed by Lothe,[16] and Friedel,[17] Thomson and Balluffi,[18] and others. We consider the two cases in turn.

A. Diffusion-Limited Climb

In this case the creation (or annihilation) of vacancies at the dislocation core is rapid enough

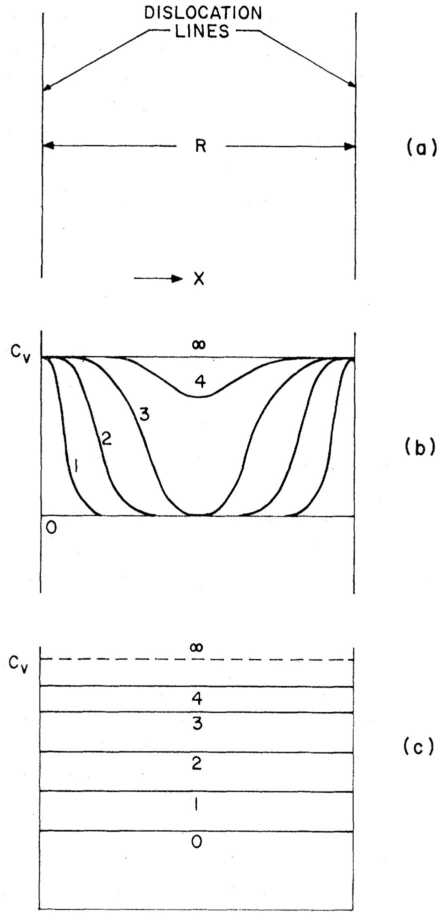


FIG. 2. (a) Two dislocation lines separated by a distance R. (b) Schematic illustration of the profiles of vacancy concentration at successive times (0, 1, 2, ..., ∞) in the case of diffusion-limited climb, and (c) the corresponding vacancy concentration profiles in the case of climb-rate limitation.

to maintain equilibrium immediately adjacent to the dislocation. The rate of climb is then controlled by the rate at which vacancies diffuse toward or away from the dislocation line. Recall that $I_i(T)$ is the total number of vacancies generated by a unit length of dislocation line of type i when the sample is heated from T_0 to T. In the diffusion-limited case, this integral depends only on the rate of diffusion of vacancies away from the dislocation line. This involves, approximately, a cylindrical diffusion problem as illustrated in Fig. 2(b), in which R is the mean spacing between parallel dislocations.

If diffusion were isotropic, and the distance R over which diffusion occurs were independent of dislocation type i, then $I_i(T)$ would be independent of i, i.e., all unit dislocation lines would generate vacancies to the same extent. Actually neither of these two requirements are met. First, in an axial crystal, the coefficients of self-diffusion parallel and perpendicular to the c axis (D_c and D_a, respectively) are, in general unequal. This anisotropy is probably not too serious, however, since at least for metallic axial crystals, D_a and D_c usually differ by less than a factor of two near the melting point.[19] Furthermore, most dislocation lines are so oriented that the diffusion illustrated in Fig. 2(b) involves both D_a and D_c rather than just one of these coefficients. The second problem relates to the dependence of climb rate on dislocation separation R which is given by[17, 20]

$$r = D/[v_a \ln(R/R_0)] , \tag{24}$$

in which D is the coefficient of self-diffusion (assuming isotropic diffusion) and R_0 is a small cutoff distance. This dependence of climb rate on R is only through the logarithmic term, and it is therefore reasonable to consider that even if R were to depend on dislocation type i, the effect upon r_i is relatively unimportant. Thus we conclude that, in the case of diffusion-limited climb, the integral I_i is approximately independent of i, and it therefore cancels out of Eq. (17) to give

$$\frac{\Delta_c}{\Delta_a} \approx 2\frac{\sum_i \Lambda_i \cos^2\psi_i}{\sum_i \Lambda_i \sin^2\psi_i} . \tag{25}$$

In this approximation, the ratio Δ_c/Δ_a is therefore independent of temperature. The major contribution to Δ_c comes from dislocations for which ψ is near zero, while the contribution to Δ_a is mainly from those for which ψ is near $\frac{1}{2}\pi$.

It is also worth mentioning the intermediate case, in which the diffusion-limited approximation applies to a substantial fraction of the dislocation types, but not to all of them. In this case these types will dominate in the process of generation of vacancies, since they are able to generate vacancies just as fast as the defects can diffuse away into the surrounding lattice. Accordingly Eq. (25) may still be expected to be valid, but with the summation taken only over the diffusion-limited-dislocation types.

B. Climb-Rate Limitation

This is the opposite extreme to case A, in which diffusion is rapid enough relative to climb that almost no concentration gradient is present during the equilibration process. The concentration profiles are then, ideally, as shown in Fig. 2(c). In general, $I_i(T)$ is a different function of temperature for different types i, and Δ_c/Δ_a is then a function of temperature. On the other hand, it is still possible for this ratio to be nearly independent of temperature if for each type i, $r_i(T)$ takes the form

$$r_i(T) = \eta_i f(T) , \tag{26}$$

in which η_i depends on i but not on T, while $f(T)$ is independent of i. The quantity η_i may then be regarded as the *relative climb efficiency* for a dislocation of type i. Actually, Eq. (26) is predicted by the jog-model of climb considered by various authors (see, e.g., Friedel[17]) in which the activation energy E for the climb process turns out to be the sum of the activation energy for self-diffusion Q_{sd} and the jog-formation energy U_j. Other terms can appear, however, to complicate the situation.[18] Nevertheless, if $f(T)$ is dominated by $\exp[-(Q_{\text{sd}} + U_j)/kT]$ and, if U_j is independent of dislocation type i, then Eq. (26) is valid. In that case Δ_c/Δ_a is given by

$$\frac{\Delta_c}{\Delta_a} = 2\frac{\sum_i \Lambda_i \eta_i \cos^2\psi_i}{\sum_i \Lambda_i \eta_i \sin^2\psi_i} , \qquad (27)$$

which is the same as Eq. (25), except that the contribution of each dislocation type is weighted by its relative climb efficiency η_i.

Which of cases A and B is valid for specific materials may be difficult to evaluate, and in fact, the usual situation may be intermediate to these two cases. The most detailed model of dislocation climb is that of Thomson and Balluffi[18] who assumed that, for the case of subsaturation ($\sigma < 0$), vacancies are produced at jogs and then diffuse rapidly along the core where they either jump off into the lattice or are destroyed again at other jogs. For supersaturation ($\sigma > 0$), arriving vacancies diffuse along the core where they may either jump off or be annihilated at a jog. Thomson and Balluffi separate the above two cases A and B in terms of a parameter αL, where L is the average jog spacing and α^{-1} is the mean distance that a vacancy travels along the dislocation before jumping off. They show that if $\alpha L < 3$, the diffusion-limited case applies, since vacancies in excess of equilibrium have a higher probability of reaching a jog than of jumping off. On the other hand, if $\alpha L > 3$, many vacancies jump off the dislocation before they are annihilated. In this range the activation energy for climb contains Q_{sd} and U_j as well as other terms, but for crystals with a high jog energy, the sum $Q_{\text{sd}} + U_j$ will dominate. Seidman and Balluffi[21] have compared a variety of experiments (primarily on gold) with theoretical expectations and conclude that in a number of cases, climb occurs with high efficiency, i.e., under diffusion control. However, most of their work is done at moderate to high supersaturations, in contrast to the present type of experiment.

III. CONCLUDING REMARKS

It has been shown that, unlike cubic crystals, the study of high-temperature thermal expansion by dilatometry and x rays in axial crystals does give information on dislocation climb. This information is lumped into one parameter Δ_c/Δ_a, the ratio of the dimensional changes caused by the climbing dislocations parallel to the c axis to that in the basal plane. This ratio may in general be a function of temperature, although in special cases discussed it is essentially independent of temperature. Although Δ_c/Δ_a is a composite measure of the overall dislocation effect, it gives an indication of the relative importance of nonbasal to basal dislocations in the climb process in axial crystals.

An important result of this work is the realization that in axial crystals, the measured values of the separate quantities Δ_c and Δ_a are dependent on the particular dislocation distribution in the samples and may therefore be dependent on the method of preparation of the sample. Only the combination $\Delta_c + 2\Delta_a$ should be sample independent. In order to obtain the correct vacancy concentration from Eq. (8), therefore, both the c-oriented and a-oriented samples should come from the same crystal. This point will be given special attention in the work on cadmium in the paper that follows.

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Dilatometric and X-Ray Thermal Expansion in Noncubic Crystals. II. Experiments on Cadmium†

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Precision measurements of macroscopic thermal expansion $\delta l/l_0$ and microscopic (x-ray) thermal expansion $\delta d/d_0$ have been carried out for cadmium single crystals in both the a and c directions, between room temperature and the melting point. In accordance with the prediction of the previous paper (paper I) it was found that the difference $\Delta=(\delta L/L_0)-(\delta d/d_0)$ in a given direction is sample dependent. Accordingly, information on the equilibrium defect concentration was obtained from samples cut from the same large crystal. The mole fraction of vacancies in equilibrium, given by $2\Delta_a+\Delta_c$, has the value 5.6×10^{-4} at the melting point. The results as a function of temperature are consistent with an interpretation in terms of monovacancies only, with enthalpy and entropy of formation, respectively, of (0.40 ± 0.02) eV and $(0.3\pm0.4)\,k$. With the aid of self-diffusion data, appropriate vacancy-migration parameters are also obtained. In addition, the ratio Δ_c/Δ_a is found to be independent of temperature, and is interpreted in accordance with the theory of paper I. In particular, it is found that nonbasal dislocations play a large role as sources and sinks for vacancies.

I. INTRODUCTION

The previous paper[1] (henceforth called paper I) discusses the theory involved in the comparison of precision dilatometric and x-ray thermal-expansion measurements at high temperatures for axial crystals. It is shown that if vacancies are the predominant defects present in thermal equilibrium at temperatures near the melting point, the vacancy concentration is given by

$$\overline{C}_v(T)=2\Delta_a(T)+\Delta_c(T)\ , \tag{1}$$

where $\Delta\equiv(\delta L/L_0)-(\delta d/d_0)$ is the difference between the macroscopic and microscopic expansions between the reference temperature T_0 and an elevated temperature T. The quantity $\overline{C}_v(T)$ is a thermodynamic quantity and, therefore, should be independent of the sample studied. On the other hand, it is pointed out that the separate quantities Δ_a and Δ_c may be sample dependent. The major emphasis of paper I is on the interpretation of the ratio Δ_c/Δ_a in terms of the parameters of dislocation climb.

Equation (1) gives the total number of vacant lattice sites regardless of whether or not vacancies are combined into higher clusters (divacancies, trivacancies, etc.). If, however, primarily monovacancies are present (as has usually been the case for cubic crystals[2]), $\overline{C}_v(T)$ is given by

$$\overline{C}_v(T)=A\,e^{-H_v^f/kT}\ , \tag{2}$$

with

$$A=e^{S_v^f/k}\ , \tag{3}$$

in which H_v^f and S_v^f are, respectively, the enthalpy and entropy of formation of a vacancy. These two parameters may then be obtained, in the usual way, from the slope and intercept, respectively, of a plot of $\ln\overline{C}_v$ vs T^{-1}.

The present paper is concerned with describing measurements of $\Delta_a(T)$ and $\Delta_c(T)$ for metallic cadmium, in order to obtain the quantities H_v^f and S_v^f, as well as to examine the ratio Δ_c/Δ_a in terms of the dislocation-climb theory presented in paper I. In view of the indication in that paper of possible sample dependence of Δ_a and Δ_c, we have carried out the principal measurements on samples cut from one large single crystal. In addition, however, data were taken on several other crystals to see if the predicted sample dependence does, in fact, occur. The results are then compared with those reported recently for other hexagonal metals