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Validity of Using Lattice Statics at All Temperatures*

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(Received 20 October 1976)

It is shown that zero-point and thermal vibrations change the vacancy formation volume calculated from classical lattice statistics by usually no more than 10^{-3} at all temperatures. In view of the recent interest in relating the temperature variation of the vacancy formation volume to Arrhenius plot curvature, the validity of lattice statics, as a tool for the calculation of temperature-dependent defect properties, is established.

As the name of the method implies, lattice statics (LS) is a technique used for calculating atomic relaxation displacements due to the presence of a defect in a nonvibrating, static lattice; that is, the usual formulation of LS[1-3] calculates the relaxation volume, ΔV_R^{stat}, hence the defect (for our purposes, the vacancy) volume of formation, $\Delta V_F^{\text{stat}} = \Omega + \Delta V_R^{\text{stat}}$ (Ω is the atomic volume), at 0°K in the absence of zero-point vibrations.

It has recently been shown by Gilder and Lazarus[4] that Arrhenius-plot curvature can be explained in terms of a vacancylike defect, in which the anharmonicity of the lattice modes gives rise to a large thermal coefficient of expansion associated with the vacancy activation volume of diffusion, $\Delta V = \Delta V_F + \Delta V_M$ (ΔV_M is the vacancy migration volume). As their analysis is based on the experimental result for zinc[5] and cadmium[6] that the activated-vacancy thermal coefficient of expansion $\beta_v = \Delta V^{-1}(\partial \Delta V/\partial T)_p = T^{-1} \approx 15\beta_0$ (β_0 is the thermal coefficient of expansion of the perfect lattice), the logical question that arises is whether a calculation of the thermal coefficient of expansion associated with the vacancy formation volume, $\beta_F = \Delta V_F^{-1}(\partial \Delta V_F/\partial T)_p$, in the absence of calculated or measured values of β_M (the thermal coefficient of expansion associated with the vacancy migration volume), would yield values comparable to the large experimental values of β_v necessary to make their explanation plausible from a theoretical point of view.

Since there are now, for the simple metals, reliable pseudopotential-derived interionic potentials[7] which have an intrinsic temperature dependence due to the variation of electronic charge density with lattice parameter or temperature, it is evident that a relaxation volume based on such a potential would exhibit a temperature dependence. But this volume would be the result, at each temperature, of the transformation of a portion of the discrete interionic, pairwise potential energy of the crystal to continuous elastic energy stored in the vacancy relaxation volume. However, we know that at all temperatures there exist both zero-point and thermal vibrations that can channel energy into the elastic deformation that represents the vacancy relaxation volume. The obvious question, then, is whether LS, in ignoring both zero-point and thermal vibrations as possible sources of energy available to the elastic deformation, introduces negligible errors in the calculation of $\Delta V_R(T)$, or whether these sources of energy change the calculated value of $\Delta V_R^{\text{stat}}(T)$ significantly.

It is the purpose, then, of this Letter to explore the influence of both zero-point and thermal vibrations on the LS calculated value of $\Delta V_R(T)$. We herein evaluate their contribution, ΔV_F^{vib}, to

ΔV_F, and show that for all metals $\Delta V_F^{\text{vib}} \ll \Delta V_F$. Thus, the usual formulation of LS is shown to be valid at all temperatures when calculating vacancy formation volumes in metals.

In the notation of Tewary,[8] the problem of calculating the vacancy relaxation volume is equivalent to that of calculating the vacancy dipole moment or "strength" G, since

$$\Delta V_R = G/3K\,, \tag{1}$$

where K is the isothermal bulk modulus of the perfect crystal. When zero-point and thermal vibrations are not taken into account, the equilibrium condition for the "crystal with defect" state is written as follows:

$$\textstyle\sum_\alpha (\partial/\partial q_\alpha)(U_1 + U_2) = 0, \tag{2}$$

where $\vec{q}$ is the vacancy-induced distortion (which for simplicity is assumed to be uniform), U_1 is the work done by the atoms at positions $\vec{r}(\vec{l})$ relaxing against the vacancy-created forces $\vec{F}^*(\vec{l})$ by an amount $\Delta r_\alpha(\vec{l}) = q_\alpha r_\alpha(\vec{l})$ ($\alpha = 1,2,3$ specifies the vector components at the site $\vec{l}$), and U_2 is the elastic energy associated with the crystal-volume change ΔV_R. Thus, under these conditions,

$$G = G^{\text{stat}} = \textstyle\sum_\alpha G_{\alpha\alpha}^{\text{stat}}\,, \tag{3}$$

where

$$G_{\alpha\alpha}^{\text{stat}} = \textstyle\sum_{\vec{l}} F_\alpha^*(\vec{l}) r_\alpha(\vec{l}). \tag{4}$$

Then

$$U_1 = -\textstyle\sum_{\alpha\vec{l}} F_\alpha^*(\vec{l})\Delta r_\alpha(\vec{l}) = -\sum_\alpha G_{\alpha\alpha}^{\text{stat}} q_\alpha\,, \tag{5}$$

and

$$U_2 = (N\Omega/2)\textstyle\sum_{\alpha\beta} C_{\alpha\beta}\, q_\alpha q_\beta\,, \tag{6}$$

where N is the number of atoms in the crystal, and $C_{\alpha\beta}$ is the elastic-constant tensor. Differentiating U_1 and U_2 with respect to q_α, it is easily shown that[8]

$$\textstyle\sum_\alpha \partial U_1/\partial q_\alpha = -G^{\text{stat}}\,, \tag{7}$$

and

$$\textstyle\sum_\alpha \partial U_2/\partial q_\alpha = 3K\Delta V_R. \tag{8}$$

Substitution of Eqs. (7) and (8) into Eq. (2) then yields Eq. (1) for $\Delta V_R = \Delta V_R^{\text{stat}}$. If, on the other hand, zero-point and thermal vibrations are taken into account, Eq. (2) must be modified. The equilibrium condition for the crystal with defect state is now

$$\textstyle\sum_\alpha (\partial/\partial q_\alpha)(U_1 + U_2 + U_3) = 0\,, \tag{9}$$

where U_3 is the difference in vibrational energy between the "defect-present" and "defect-free" states of the crystal. Since the vibrational part of the Helmholtz free energy of the crystal in the quasiharmonic approximation is given by the expression[9]

$$F_{\text{vib}} = \sum_{i=1}^{3N} h\nu_i/2 + k_B T \sum_{i=1}^{3N} \ln[1 - \exp(-h\nu_i/k_B T)]\,, \tag{10}$$

where ν_i is the ith normal-mode crystal frequency, it follows from the definition of U_3 that

$$U_3 = \Delta F_{\text{vib}} = h\sum_{i=1}^{3N} \Delta\nu_i \left\{\tfrac{1}{2} + \exp(-h\nu_i/k_B T)/[1 - \exp(-h\nu_i/k_B T)]\right\}, \tag{11}$$

where $\Delta\nu_i$ represents the change in the frequency ν_i induced by the presence of the vacancy. The presence of U_3 in Eq. (9) contributes the additional term ΔV_R^{vib} to ΔV_R^{stat}, or equivalently the term ΔV_F^{vib} to ΔV_F^{stat}:

$$\Delta V_{R,F} = \Delta V_{R,F}^{\text{stat}} + \Delta V_{R,F}^{\text{vib}}. \tag{12}$$

By substituting Eqs. (7), (8), and (12) in Eq. (9), the relation between ΔV_R^{vib} and U_3 is found to be

$$\Delta V_R^{\text{vib}} = -(1/3K)\textstyle\sum_\alpha \partial U_3/\partial q_\alpha. \tag{13}$$

Differentiating Eq. (11) with respect to q_α, substituting the result in Eq. (13), and making use of the dimensionless variable $x_i = h\nu_i/k_B T$, we then obtain

$$\Delta V_R^{\text{vib}} = -(k_B T/3K)\textstyle\sum_{i\alpha}\Big((\partial\Delta x_i/\partial q_\alpha)\{\tfrac{1}{2} + \exp(-x_i)/[1 - \exp(-x_i)]\} - (\partial x_i/\partial q_\alpha)\{x_i \exp(-x_i)/[1 - \exp(-x_i)]^2\}\Big). \tag{14}$$

As we are mainly interested in an order-of-magnitude estimation of $\Delta V_R^{\text{vib}}/\Omega$, the sum over normal-mode frequencies in Eq. (14) can be evaluated by means of either the Debye density of states, $g_D = (9N/$

${\nu_D}^3)\nu^2$ (ν_D is the Debye cutoff frequency), or by the Einstein density of states, $g_E = 3N\delta(\nu-\nu_E)$ (ν_E is the Einstein frequency). In addition, we need to know the dependence of each frequency shift Δx on the frequency x. To determine this dependence, we suppose that there is no dispersion in the phonon spectra; that is, that $\nu = Qc/2\pi$, where $\vec{Q}$ is the phonon wave vector and c is a suitably averaged sound velocity. The change in sound velocity, Δc, and the change in wave vector, $\Delta\vec{Q}$, induced by the presence of the vacancy are then related to Δx in the following way:

$$\Delta x = \mu x, \tag{15}$$

where

$$\mu = \Delta c/c + \Delta Q/Q = \Delta c/c - \Delta V_F/3V_0,$$

since $Q \sim {V_0}^{-1/3}$, V_0 being the defect-free crystal volume. Taking into account the "breathing-like" local mode introduced by the vacancy, Gilder and Lazarus[4] find that $\mu = -1/6N$. This result appears to be reasonable in view of the fact that we expect that the vacancy does not change the solid's frequencies by more than $\sim N^{-1}$. Thus, from Eq. (15), $\Delta x = -x/6N$. Replacing Δx by this value in Eq. (14), we obtain

$$\Delta {V_R}^{\text{vib}} = (k_B T/18kN)\textstyle\sum_i \sum_\alpha (\partial x_i/\partial q_\alpha)\{\frac{1}{2} + \exp(-x_i)/[1-\exp(-x_i)] - x_i \exp(-x_i)/[1-\exp(-x_i)]^2\}. \tag{16}$$

Since each frequency of the Debye solid is fractionally shifted by the same amount μ, we suppose that Eq. (16) is equally valid for the single frequency of the Einstein solid. The quantity $\sum_\alpha \partial x/\partial q_\alpha$ is evaluated as follows:

$$\textstyle\sum_\alpha \partial x/\partial q_\alpha = \sum_\alpha (\partial x/\partial V)_T(\partial V/\partial q_\alpha)_T = -\sum_\alpha V^{-1}(\partial V/\partial q_\alpha)_T, \tag{17}$$

where the Grüneisen constant $\gamma = -(V/\nu)(\partial\nu/\partial V)_T = -(V/x)(\partial x/\partial V)_T$. Since $V = V_0(1+q_\alpha)(1+q_\beta)(1+q_\gamma)$, we then obtain

$$\textstyle\sum_\alpha V^{-1}(\partial V/\partial q_\alpha)_T = \sum_\alpha (1+q_\alpha)^{-1} \cong \sum_\alpha (1-q_\alpha) \cong 3, \tag{18}$$

since $\sum_\alpha q_\alpha = V_R/N\Omega \sim N^{-1}$. Between Eqs. (17) and (18) we have

$$\textstyle\sum_\alpha \partial x/\partial q_\alpha = -3\gamma x. \tag{19}$$

Thus, in the Debye model, substituting Eq. (19) in (16) yields

$$\begin{aligned}\Delta {V_{R(D)}}^{\text{vib}}/\Omega &= -(3k_B\gamma T/2K{x_D}^3\Omega)\int_0^{x_D} x^3[\tfrac{1}{2} + e^{-x}/(1-e^{-x}) - xe^{-x}/(1-e^{-x})^2]\,dx \\ &= \Delta {V_{F(D)}}^{\text{vib}}/\Omega = -(\gamma k_B\Theta_D/2K\Omega)F_D,\end{aligned} \tag{20}$$

where

$$F_D = \tfrac{3}{8} + (3/{x_D}^4)\int_0^{x_D}[x^3e^{-x}/(1-e^{-x})][1-x/(1-e^{-x})]\,dx, \tag{21}$$

Θ_D is the Debye temperature, and x_D is the dimensionless cutoff frequency. By a similar procedure, Eq. (16) yields, in the Einstein approximation, the following expression for $\Delta {V_{R(E)}}^{\text{vib}}/\Omega$:

$$\Delta {V_{R(E)}}^{\text{vib}}/\Omega = \Delta {V_{F(E)}}^{\text{vib}}/\Omega = -(\gamma k_B\Theta_D/2K\Omega)F_E, \tag{22}$$

where

$$F_E = 0.775\{\tfrac{1}{2} + \exp(-x_E)[1-\exp(-x_E)] - x_E\exp(-x_E)/[1-\exp(-x_E)]^2\}, \tag{23}$$

x_E is the dimensionless Einstein frequency, and the Einstein temperature $\Theta_E = 0.775\Theta_D$.[10]

A numerical evaluation of the functions F_D and F_E for the case of aluminum indicates that they are very closely equal at all temperatures, the fractional difference between them varying from 2×10^{-3} at the melting point (933°K) to 3×10^{-2} at 0°K. However, the important aspect of the present result for the case of aluminum is that $\Delta {V_R}^{\text{vib}}/\Delta {V_R}^{\text{stat}} \sim 3\times10^{-3}$ at 0°K and $\sim 5\times10^{-4}$ at the melting point. As the explicit contribution of the vacancy-induced local mode to the sum of Eq. (14) can increase $\Delta {V_R}^{\text{vib}}/\Omega$ by about at most a factor of 2,[4] we are indeed justified in neglecting it.

But the size of this vibrational effect is not peculiar to aluminum. Of all the metals, the effect is most pronounced in lithium, for which $(\Delta {V_F}^{\text{vib}}/$

$\Delta V_F^{\rm stat})_{\rm max} = 10^{-2}$ at 0°K. Silver and copper exhibit one of the smallest effects: about one-third of that for lithium.

Considering the fact that the uncertainty in the most precise measurement[5,6] of ΔV is $\sim 10^{-2}$, the contribution of both zero-point and thermal vibrations to the usual LS-calculated vacancy formation volume is indeed negligible. Thus, the usual formulation of LS suffices for the calculation of the vacancy formation volume at all temperatures.

The authors wish to express their deepest thanks to Dr. Roger Taylor of the Physics Division, National Research Council of Canada, for many helpful discussions and exchanges of scientific materials.

*Supported by the Centre National de la Recherche Scientifique, France.

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Trigonal-to-Tetragonal Transition in Stressed SrTiO$_3$: A Realization of the Three-State Potts Model

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(Received 18 October 1976)

The trigonal-to-pseudotetragonal structural first-order transition in [111]-stressed SrTiO$_3$ is shown to be a realization of the continuous three-state Potts model. The measured order-parameter discontinuity at the transition, $\langle \Delta\vec{\varphi}\rangle$, depends on the trigonal order parameter $\langle \varphi_{[111]}\rangle \propto M$ as $|\langle\Delta\vec{\varphi}\rangle| \propto |M|^{\delta^*}$, with $\delta^* = 0.62 \pm 0.10$ (mean-field theory predicts $\delta^* = 1$). This agrees with renormalization-group predictions, and proves that the model has a first-order transition even in the fluctuation-dominated region.

Multicritical points in stressed perovskite crystals undergoing displacive phase transitions have been the subject of much recent interest.[1-4] It has been shown[4] that stress p along the [100] axis leads to a bicritical point[5] in SrTiO$_3$[3] and to a tetracritical point in LaAlO$_3$. Stress p along the [111] diagonal in SrTiO$_3$ leads to a rather more complicated phase diagram, studied both experimentally and using mean-field theory in Refs. 1, 2, and 4 and shown in Fig. 1. At constant stress p (>0), one first observes a second-order transition from the "pseudocubic" phase into a trigonal phase at temperature $T_1(p)$, and then, at $T_2(p)$, a first-order transition into a "pseudotetragonal" phase. For $p<0$ there is a direct second-order pseudocubic-to-pseudotetragonal transition. The point $p=0$, $T=T_1(0)=T_2(0)$ is thus bicritical.[4] However, it is not identical to the one discussed in Refs. 3 and 5. A renormalization-group study of this phase diagram showed[4] that the transition at $T_1(p)$ is Ising-like, while that at $T_1(0)=T_2(0)$

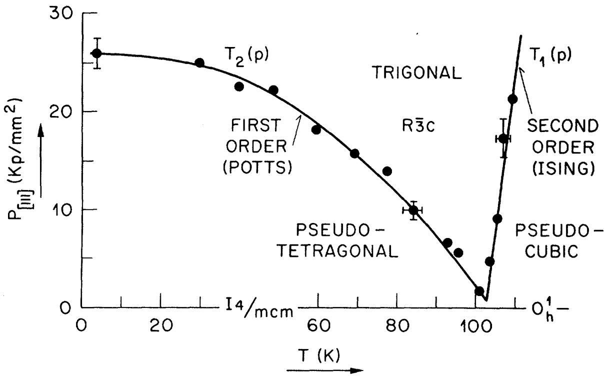

FIG. 1. Experimental phase diagram of SrTiO$_3$ for stress along the [111] diagonal, from Ref. 1.