# Theory of a structural-volume effect and of the Invar anomaly in systems exhibiting structural transitions

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The Invar anomaly is associated with a striction effect in systems exhibiting structural transitions. This anomaly is described by developing a fluctuation theory of a structural-volume effect similar to a theory of magneto–volume effects in magnetically ordered metals. In addition to the usual phonons, there are also paraphonons which are characteristic relaxation fluctuations.

## 1. INTRODUCTION

The discoveries of the Invar[1] and Elinvar[2] effects, which earned the 1920 Nobel Prize, were followed by extensive experimental and theoretical investigations of these phenomena (see, for example, Ref. 3), and very interesting practical applications. The Invar effect, manifested by anomalously small values of the thermal expansion coefficient, is usually attributed to magnetic properties or materials. It is assumed specifically that the magnetostrictive contribution to the change in the volume, which in the case of magnetic materials is usually negative, can under certain conditions compensate the usual lattice and electron thermal expansion effects.[3]

In recent years a theory of the magnetovolume effect and Invar anomalies have been developed much further using a theory of spin fluctuations[4–7] that play—as already established—an extremely important role in weak ferromagnets, which include the majority of the alloys that exhibit the Invar effect (Invar alloys).

We shall indicate another possible reason for the Invar anomalies associated with a striction-induced structural-volume effect. In contrast to the familiar analysis of striction phenomena in systems with structural transitions (see, for example, Ref. 8) based on the Landau theory of phase transitions and ignoring fluctuation effects, we shall propose a simple model theory based on the approaches of Ginzburg[9] and Levanyuk[10,11] and we shall allow for fluctuations of the order parameter. In the theory of the structural-volume effect proposed below the thermally induced change in the volume is described by the average of the square of the order parameter and, in contrast to Ref. 8 where it is proportional to the square of the average order parameter, it differs also from zero even in the disordered phase. The structural-volume effect discussed by us is closely related to the magneto-volume effect in a spin fluctuation theory developed in Refs. 6 and 7 and, like the latter effect, may compensate for the usual thermal expansion and give rise to Invar anomalies. In the absence of such compensation the influence of the structural-volume effect may be manifested by a negative thermal expansion coefficient which is exhibited by a number of nonmagnetic materials. We can mention here, for example, the striking anomalies of the low-temperature expansion of uranium[12,13] which are in our opinion associated with the recently discovered transition to a state with a charge density wave[14] (see below).

## 2. GENERAL RELATIONSHIPS

In discussing the properties of the structural-volume effect we shall employ a simple model of a crystal with one branch of lattice vibrations corresponding to "soft" optical phonons (see, for example, Refs. 15–18). Such a model can be illustrated employing the following expression for the free energy density

$$F(u_0, V, T)=F_0(V, T)+{}^1/_2A_0u_0^2+{}^1/_4Bu_0^4+\Delta F(u_0, V, T). \tag{2.1}$$

Here, $u_0$ is a one-component order parameter which we shall assume to be small, $V$ is the volume, $T$ is the absolute temperature, and $F_0(V, T)$ is the free-energy contribution unrelated to fluctuations of the order parameter. The term (see Ref. 19)

$$\Delta F(u_0, V, T)=\frac{2}{\pi}\varkappa T\int_0^\infty d\omega \ln(1-e^{-\hbar\omega/\varkappa T}) \times\int\frac{d\mathbf{k}}{(2\pi)^3}\frac{\gamma(\mathbf{k})[\omega^2(\mathbf{k})+\omega^2]}{[\omega^2(\mathbf{k})-\omega^2]^2+[2\omega\gamma(\mathbf{k})]^2} \tag{2.2}$$

describes the fluctuation contribution, whereas $\omega(\mathbf{k})$ and $\gamma(\mathbf{k})$ are, respectively, the frequency and damping decrement of phonons.

We shall allow for a nonlinear (anharmonic) dependence of the frequency $\omega(\mathbf{k})$ on the order parameter $u_0$, and we shall use the following simple equation of motion:[15–18]

$$\rho[\ddot{\hat{u}}(\mathbf{k}, t)-2\gamma(\mathbf{k})\dot{\hat{u}}(\mathbf{k}, t)]+A(\mathbf{k})\hat{u}(\mathbf{k}, t) +B\int\frac{d\mathbf{k}'}{(2\pi)^3}\frac{d\mathbf{k}''}{(2\pi)^3}\hat{u}(\mathbf{k}-\mathbf{k}', t)\hat{u}(\mathbf{k}'-\mathbf{k}'', t)\hat{u}(\mathbf{k}'', t)=0, \tag{2.3}$$

where $\rho$ is the density of the investigated crystal and $u(\mathbf{k},t)$ is a dynamic variable the averaging of which for a specific wave vector $\mathbf{k}=\mathbf{k}_m$, representing an ordered state, governs the order parameter: $\langle u(\mathbf{k}_m,t)\rangle = u_0$. We shall use also $A(\mathbf{k}_m)\equiv A_0<0$. We shall ignore the influence of anharmonicity on the phonon damping decrement $\gamma(\mathbf{k})$. Averaging Eq. (2.3) on the assumption of a weak anharmonicity, we can write down the following expression (see Refs. 15 and 16)

$$\rho\omega^2(\mathbf{k})=A(\mathbf{k})+3B(u_0^2+\delta u^2)\equiv\rho\omega_0^2+A(\mathbf{k})-A(\mathbf{k}_m), \tag{2.4}$$

which governs the dependence of the phonon frequency

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$\omega(\mathbf{k})$ on the order parameter and on the average of the square of the fluctuation amplitudes

$$\delta u^2(T)=\frac{4\hbar}{\pi\rho}\int_0^\infty d\omega\, N(\omega)\int\frac{d\mathbf{k}}{(2\pi)^3}\frac{\omega\gamma(\mathbf{k})}{[\omega^2(\mathbf{k})-\omega^2]^2+[2\omega\gamma(\mathbf{k})]^2}, \tag{2.5}$$

where

$$N(\omega)=[\exp(\hbar\omega/\varkappa T)-1]^{-1}$$

and

$$\omega_0^2\equiv\omega^2(\mathbf{k}_m)=[A_0+3B(u_0^2+\delta u^2)]/\rho. \tag{2.6}$$

In writing down the equation of state we have to minimize Eq. (2.1) with respect to the order parameter $u_0$. We shall do this using an approximate expression

$$\rho\frac{\partial(\omega_0^2)}{\partial u_0^2}=6Bu_0\left[1+\frac{\partial(\delta u^2)}{\partial u_0^2}\right]\approx 6Bu_0, \tag{2.7}$$

which becomes invalid only near the phase transition temperature [see Sec. 4, Eqs. (4.40)–(4.44)].

In the approximation described by Eq. (2.7) the process of minimization of the free energy [Eq. (2.1)] of the ordered phase, when $u_0\neq 0$, gives an equation of state describing the change in the order parameter $u_0(T)$ (compare with Refs. 15 and 16):

$$u_0^2(T)=u_0^2(0)-3\delta u^2(T), \tag{2.8}$$

where $u_0^2(0)=-A_0/B>0$. Equation (2.8) allows us to derive the following relationships governing the temperature dependence of the soft-mode frequency:

$$\omega_0^2(T)=\frac{2B}{\rho}u_0^2(T)=\omega_0^2(0)\frac{u_0^2(T)}{u_0^2(0)} \tag{2.9}$$

in the ordered phase ($T<T_m$) and

$$\omega_0^2(T)=\frac{3B}{\rho}[\delta u^2(T)-\delta u^2(T_m)]=\frac{1}{2}\omega_0^2(0)\left[\frac{\delta u^2(T)}{\delta u^2(T_m)}-1\right] \tag{2.10}$$

in the disordered phase ($T>T_m$). Naturally, the phase transition temperature $T_m$ is governed by vanishing of the right-hand side of Eq. (2.8) and we then have $\delta u^2(T_m)=\frac{1}{3}U_0^2(0)$. Consequently, the soft-mode frequency vanishes at the phase transition temperature $T_m$.

## 3. INVAR ANOMALY

We shall now consider the influence of fluctuations of the order parameter on the thermal expansion crystal. If we define, as usual, the pressure by $P=-[\partial(FV)/\partial V]_T$, we find that in the approximation of Eq. (2.7) the equation of state becomes

$$P=P_0(V,T)+C_s u_L^2(T), \tag{3.1}$$

where

$$u_L^2(T)=u_0^2(T)+\delta u^2(T) \tag{3.2}$$

is the average of the square of the order parameter,

$$P_0=-(\partial(F_0V)/\partial V)_T,\quad C_s=\tfrac{1}{4}\rho\partial\omega_0^2(0)/\partial\ln V$$

is a striction constant which we shall assume to be positive. It should be stressed that Eq. (3.1) is derived ignoring the volume dependences of the quantities $[A(k)-A_0]V$ and $\gamma(\mathbf{k})V$, which we shall assume to be weak compared with the volume dependence of the soft phonon frequency $\omega_0$. The equation of state (3.1) makes it possible to determine the temperature dependence of the volume of a crystal

$$V=V_0\left[1+\frac{\Delta V(T)}{V_0}\right], \tag{3.3}$$

where

$$\Delta V(T)=\Delta V_n(T)+\Delta V_s(T)$$

and

$$\frac{\Delta V_n(T)}{V_0}=\frac{1}{K_0(V,T)}[P_0(V,T)-P_0(V,0)]=\frac{1}{K(V_0,T)}[P_0(V_0,T)-P_0(V_0,0)]$$

describes the usual contributions of electrons and phonons, whereas

$$\frac{\Delta V_s(T)}{V}=\frac{C_s(T)}{K_0(V,T)}u_L^2(T)=\frac{C_s(V_0)}{K(V_0,T)}u_L^2(T)\,|_{V=V_0} \tag{3.4}$$

is the change in the volume due to striction. The volume $V_0=V_0(P)$ is governed by the relationship $P=P_0(V,0)$ and then the bulk modulus $K(V,T)$ is described by

$$K(V,T)=-\left(\frac{\partial P}{\partial\ln V}\right)_T=K_0(V,T)-\frac{\partial}{\partial\ln V}[C_s(V)u_L^2(T)], \tag{3.5}$$

where

$$K_0(V,T)=-(\partial P_0/\partial\ln V)_T.$$

Equations (3.4) and (3.5) can be used in elucidating the Invar and Elinvar effects that are manifested by the anomalously weak temperature dependences of the volume and elastic modulus of a crystal. We shall therefore consider the qualitative temperature dependence of $u_L^2(T)$. In the case of the ordered phase (which exists at temperatures $T<T_m$) it follows from Eq. (2.8) that the average square

$$u_L^2(T)=u_0^2(0)-2\delta u^2(T) \tag{3.6}$$

decreases with increase in temperature, reaching its minimum value $\frac{1}{3}u_0^2(0)=u_L^2(T_m)$ at the transition temperature $T=T_m$. Above the transition temperature ($T>T_m$), we find that the quantity

$$u_L^2(T)=\delta u^2(T) \tag{3.7}$$

rises with temperature. These qualitative properties of $u_L^2(T)$ make it possible, on the basis of Eq. (3.4), to conclude that on increase in temperature in the range $T>T_m$ the fluctuation contribution of the soft mode results in the usual increase in the volume of a crystal with temperature. On the other hand, in the ordered phase ($T<T_m$), when $u_L^2(T)$ decreases with rising temperature, the fluctuation contribution of the soft mode to the volume decreases. Therefore, at $T=T_m$ there is a change in the sign of the structural-volume effect which we are considering here. This property is typical of the Invar anomalies and it may

result, under certain conditions, in compensation of the usual electron and phonon contributions and thus weaken the temperature dependence of the volume of a crystal. Similarly, a reduction in the bulk modulus $K_0(V, T)$ on increase in temperature, which is due to the influence of electrons and of the phonon anharmonicity, may be compensated by an increasing striction contribution described by the second term on the right-hand side of Eq. (3.5), which corresponds to the Elinvar anomaly.

Ignoring the temperature-induced changes in the striction constant and allowing for the smallness of the corresponding change in the bulk modulus, we can write down the following simple expression for the striction-induced volume change:

$$\frac{\Delta V_s(T)}{V_0}=\frac{\Delta V_s(0)}{V_0}+\frac{2}{3}\frac{C_s}{K_0}[u_0^2(T)-u_0^2(0)] \qquad (3.8)$$

considered as a function of the order parameter varying with temperature, where

$$\Delta V_s(0)/V_0=(C_s/K_0)u_0^2(0).$$

The relative change in the volume of the ordered phase (which exists in the range $0<T<T_m$) due to the striction is given by

$$\frac{\Delta V_s(T_m)}{\Delta V_s(0)}\approx\frac{u_L^2(T_m)}{u_0^2(0)}=\frac{1}{3}. \qquad (3.9)$$

Above the phase transition temperature ($T>T_m$) the striction contribution to the change in the volume increases with temperature:

$$\frac{\Delta V_s(T)}{V_0}=\frac{C_s}{K_0}\delta u^2(T). \qquad (3.10)$$

It should be pointed out that using Eqs. (2.9) and (2.10) we obtain the following simple relationship:

$$\frac{\Delta V_s(T)}{V_0}=\frac{\Delta V_s(T_m)}{V_0}\left[1+2\frac{\omega_0^2(T)}{\omega_0^2(0)}\right], \qquad (3.11)$$

which relates the striction-induced volume change $\Delta V_s(T)$ to the soft mode frequency $\omega_0(T)$ and is valid both below and above the structural transition temperature. Figure 1 illustrates schematically the temperature dependence of this structural-volume effect. A comparison of the relationships obtained by us with the familiar laws governing the magnetovolume effect, described by the spin-fluctuation theory of magnetism,[6,7] reveals a qualitative analogy between these two phenomena and makes it possible to draw general conclusions about the possibility of such effects as a result of fluctuations of the order parameter even in the case of substances with different types of second-order phase transitions.

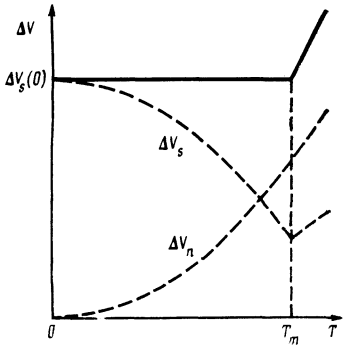


FIG. 1. Invar anomaly in a system with structural transitions.

## 4. TEMPERATURE DEPENDENCE OF THE STRUCTURAL-VOLUME EFFECT

In this section we shall consider the explicit dependences of the average squares of the fluctuation amplitudes $\delta u^2(T)$, of the order parameter $u_0(T)$, and of its average square $u_L^2(T)$, of the soft-mode frequency $\omega_0(T)$, and finally of the structural-volume effect $\Delta V_s(T)$. The softening of an optical phonon mode will be related to the following simple mode of the optical spectrum. In a wide range of wave vectors the optical phonon frequency is assumed to be independent of the wave vector and equal to $\omega(\mathbf{k})\approx\omega_1$. Therefore, in a range of wave vectors limited by the inequality $|\mathbf{k}-\mathbf{k}_m|<k_c$ we shall assume that this is an anomaly of the smallness of $\omega(\mathbf{k})$, which is usually attributed to a soft mode (see Ref. 17). In this range the spectrum of an optical mode can be modeled by the expression

$$\omega^2(\mathbf{k})=\omega_0^2(T)+c^2(\mathbf{k}-\mathbf{k}_m)^2, \qquad (4.1)$$

where

$$c^2=(2\rho)^{-1}\partial^2 A(\mathbf{k}_m)/\partial\mathbf{k}_m^2.$$

It then follows from Eq. (2.9) that $\omega_0(T)$ vanishes at the structural transition point. However, even far from such a transition we shall assume that

$$\omega_0(T)\ll\omega_c, \qquad (4.2)$$

where $\omega_c\equiv ck_c\sim\omega_i$.

We shall discuss first the properties of the spectral density of fluctuations (see Refs. 16 and 18):

$$g(\omega)=\frac{4\hbar}{\pi\rho}\int\frac{d\mathbf{k}}{(2\pi)^3}\frac{\omega\gamma(\mathbf{k})}{[\omega^2(\mathbf{k})-\omega^2]^2+[2\omega\gamma(\mathbf{k})]^2}, \qquad (4.3)$$

which governs, in accordance with Eq. (2.5), the temperature dependence of fluctuations of the order parameter. In the adopted model we shall assume that the damping of optical phonons is independent of the wave vector $\gamma(\mathbf{k})=\gamma=$ const and is relatively small ($\gamma\ll\omega_c$). In particular, such a model allows us to consider in detail the spectral properties of the function $g(\omega)$.

Firstly, it should be noted that the integral expression on the right-hand side of Eq. (4.3) contains the usual contribution to the spectral density, which appears at optical phonon frequencies $\omega=\omega(\mathbf{k})$ and if we ignore the damping of phonons ($\gamma=0$), we find that this contribution is (see Ref. 15)

$$g(\omega)\approx\frac{\hbar}{\rho}\int\frac{d\mathbf{k}}{(2\pi)^3}\frac{1}{\omega(\mathbf{k})}\delta[\omega-\omega(\mathbf{k})]$$
$$=\frac{\hbar}{2\pi^2\rho c^3}[\omega^2-\omega_0^2(T)]^{1/2}$$
$$\times\theta\{[\omega^2-\omega_0^2(T)]/[\omega_0^2(T)+\omega_c^2-\omega^2]\}+(\hbar V_k/\rho\omega_1)\delta(\omega-\omega_1), \qquad (4.4)$$

where $\theta(x)=1$, if $x>0$ and $\theta(x)=0$ if $x<0$, whereas $V_k$ is the phase volume corresponding to "hard" hf phonons of

frequency $\omega(\mathbf{k}) = \omega_1$. The first term on the right-hand side of Eq. (4.4) describes the influence of lf soft phonons with the spectrum given by Eq. (4.1) and it differs from zero in the frequency range

$$\omega_0(T) < \omega < [\omega_0^2(T) + \omega_c^2]^{1/2} \approx \omega_c. \tag{4.5}$$

The second term is due to the effects of hf phonons ($\omega \approx \omega_1$). Secondly, in addition to this phonon contribution the spectral density $g(\omega)$ includes a contribution due to "relaxation" fluctuations of the order parameter which in the equation of motion (2.3) correspond to neglect of the term $\sim \hat{u}(\mathbf{k},t)$. By analogy with magnetic fluctuations (paramagnons) we suggested in Ref. 19 to call these paraphonons.

In discussing the relative contributions of phonons and paraphonons to the spectral density of fluctuations, we shall use the condition (4.2) to write down the following explicit expression:

$$g(\omega) = \frac{\hbar\gamma\omega}{\pi^3\rho c^3} \frac{1}{[2(r^2+\omega_0^2-\omega^2)]^{1/2}} \left\{ \operatorname{arctg} \frac{(\omega_c+\omega)2^{1/2}}{(r^2+\omega_0^2-\omega^2)^{1/2}} + \operatorname{arctg} \frac{(\omega_c-\omega)2^{1/2}}{(r^2+\omega_0^2-\omega^2)^{1/2}} - \left[\frac{r^2+\omega_0^2-\omega^2}{r^2-\omega_0^2+\omega^2}\right]^{1/2} \ln\left|\frac{\omega_c+\omega}{\omega_c-\omega}\right| \right\} + \frac{4\hbar V_k}{\pi\rho} \frac{\omega\gamma}{(\omega_1^2-\omega^2)^2+(2\omega\gamma)^2}, \tag{4.6}$$

where $r^2 = [(\omega_0^2 - \omega^2)^2 + (2\omega\gamma)^2]^{1/2}$. The first and second terms on the right-hand side of Eq. (4.6) are due to, respectively, lf (Eq. (4.1) and hf $[\omega(\mathbf{k}) \approx \omega_1]$ parts of the spectrum.

It should be pointed out that inclusion in Eq. (4.6) of just the first term corresponds to a model which is usually attributed to the soft mode concept (see the review in Ref. 17). Then, neglect in such a term of the spatial dispersion of the soft mode, which corresponds to the limit $\omega_c = ck_c \to 0$ in Eq. (4.6), gives rise to a spectral density of fluctuations that has been used in a number of investigations (for reviews see Refs. 17 and 18). We shall allow for the effects of the spatial dispersion of a soft mode and for the influence of "hard" hf phonons.

At moderately high frequencies defined by $\omega \ll \omega_c$, we find that the spectral density of fluctuations deduced from Eq. (4.6) is described by the following simple expression:

$$g(\omega) \approx \frac{\hbar\omega\gamma}{2^{1/2}\pi^2\rho c^3} \{[(\omega_0^2-\omega^2)^2+(2\omega\gamma)^2]^{1/2}+\omega_0^2-\omega^2\}^{-1/2} + \frac{4\hbar V_k}{\pi\rho} \frac{\omega\gamma}{\omega_1^4}. \tag{4.7}$$

Here, the first term on the right-hand side represents the influence of a soft mode, whereas the second corresponds to inclusion of paraphonons associated with the hf spectrum $[\omega(k) \sim \omega_i]$, which we shall call "hard." We shall consider first the spectral properties of Eq. (4.7) for the function $g(\omega)$.

In the low-frequency limit

$$\omega \ll \omega_0^2(T)/\gamma, \quad \omega_0(T), \tag{4.8}$$

where according to Eq. (4.5) there are no phonons, we find that Eq. (4.7) for the spectral density yields the expression

$$g(\omega) \approx \frac{\hbar}{2\pi^2\rho} \omega\gamma \left[\frac{1}{c^3\omega_0(T)} + \frac{8\pi V_k}{\omega_1^4}\right], \tag{4.9}$$

where the first term with $\omega_0(T)$ and the second term with $\omega_1$ are due to, respectively, the "soft" and "hard" paraphonons. In the frequency range

$$\omega_0^2(T)/\gamma \ll \omega \ll \gamma \tag{4.10}$$

it follows from Eq. (4.7) that

$$g(\omega) \approx \frac{\hbar}{2\pi^2\rho} \left[\frac{(\omega\gamma)^{1/2}}{c^3} + 8\pi V_k \frac{\omega\gamma}{\omega_1^4}\right], \tag{4.11}$$

which is again due to paraphonons. The frequency range (4.10) appears in the $\omega_0(T) \ll \gamma$ case, when the soft phonons are strongly damped (for example, near the structural transition temperature). Under these conditions, the soft mode is frequently called "overdamped" (see Refs. 15, 16, and 18).

It should be stressed that the paraphonon effects considered by us do not just appear when soft phonons are strongly damped (or overdamped). It follows from Eqs. (4.8) and (4.9) that the lf $[\omega \ll \omega_0(T)]$ paraphonons play an important role also when $\omega_0(T) \gg \gamma$. Therefore, the case of an overdamped soft mode discussed earlier[15,16,18] does not exhaust all the situations in which the paraphonon role is predominant.

Finally, in the frequency range

$$\gamma, \ \omega_0(T) \ll \omega \ll \omega_c \tag{4.12}$$

we find that Eq. (4.7) yields the following expression for the spectral density of fluctuations (see, for example, Ref. 15):

$$g(\omega) \approx \frac{\hbar\omega}{2\pi^2\rho} \left[\frac{1}{c^3} + 8\pi V_k \frac{\gamma}{\omega_1^4}\right], \tag{4.13}$$

where the terms proportional to $c^{-3}$ and $\gamma$ are due to, respectively, soft phonons and hard paraphonons. We shall complete a discussion of the spectral properties of the function $g(\omega)$ by noting that in the hf limit $\omega \gg \omega_c$ it falls on increase in the frequency in accordance with the $\omega^{-3}$ law, as deduced from Eq. (4.6).

We shall now discuss the temperature dependence of the fluctuation amplitudes by noting first of all that when the phase volume corresponding to a soft mode is negligible so that $k_c^3/6\pi^2 V_k \ll \omega_0(0)/\omega_1, \gamma/\omega_1$, its influence is unimportant and the quantity $\delta u^2(T)$ is governed by the fluctuations associated with the hf part of the spectrum $[\omega(k) \approx \omega_1]$. We shall ignore this case but assume that the phase volume of a soft mode is comparable with the dimensions of the Brillouin zone. We shall consider only the situation when the damping and frequency of soft phonons are not too high:.

$$\gamma, \ \omega_0(0) \ll \omega_c. \tag{4.14}$$

The condition (4.14) imposes certain restrictions on the parameters of the investigated systems:

$$\frac{u_1^2}{g} \equiv \frac{\rho\gamma^2}{B}, \quad u_0^2(0) \ll \frac{\hbar k_c^2}{g\rho c} \equiv \frac{u_2^2}{g}, \tag{4.15}$$

where $g = \hbar B/2\rho^2 c^3$ is a dimensionless parameter representing the anharmonicity. We shall assume that the condition $g \ll 1$ is satisfied (see Ref. 15).

The asymptotic expression for the spectral density $g(\omega)$ allows us to write down the square of the fluctuation amplitudes

$$\delta u^2(T)=\delta u_p^2(T)+\delta u_{ph}^2(T) \tag{4.16}$$

in the form of a sum of the contributions $\delta u_p^2$ and $\delta u_{ph}^2$, which are due to paraphonons and phonons, respectively. Under the conditions assumed here, when the influence of hard paraphonons can be ignored, the quantity $\delta u_p^2$ is governed by paraphonons associated with the soft mode.

In the low-temperature limit

$$\varkappa T \ll \frac{\hbar\omega_0^2(T)}{\gamma}, \quad \hbar\omega_0(T) \tag{4.17}$$

the contribution $\delta u_p^2$ governed by paraphonons is, according to Eq. (4.9), given by

$$\delta u_p^2(T)=\frac{\varkappa^2T^2}{12\hbar\rho c^3}\frac{\gamma}{\omega_0(T)}, \tag{4.18}$$

and the contribution of phonons is found to be exponentially small (see, for example, Ref. 15) and is described by

$$\delta u_{ph}^2(T)\sim\exp\left[-\hbar\omega_0(T)/\varkappa T\right].$$

Using the general relationships governing the square of the order parameter, the soft mode frequency, and the fluctuation-induced change in the volume (deduced in the preceding section) we can apply Eq. (4.18) to find that in the case of an ordered Phase ($T<T_m$) we have

$$\begin{aligned}
&u_0^2(T)=u_0^2(0)\,(1-T^2/T_0^2), \quad u_L^2(T)=u_0^2(0)\,(1-2T^2/3T_0^2),\\
&\omega_0^2(T)=\omega_0^2(0)\,(1-T^2/T_0^2),\\
&\Delta V_s(T)=\Delta V_s(0)\,(1-2T^2/3T_0^2),
\end{aligned} \tag{4.19}$$

where

$$T_0=(\hbar\omega_0(0)/\varkappa)\,(\omega_0(0)/g\gamma)^{1/2}$$

is the characteristic temperature governed by paraphonons. We shall ignore the phonon contribution and allow for the smallness of the ratio $T^2/T_0^2\ll 1$, which follows from the estimates

$$\begin{aligned}
&\frac{T^2}{T_0^2}\ll\left[\frac{\hbar\omega_0(0)}{\varkappa T_0}\right]^2\sim g\frac{\gamma}{\omega_0(0)}\ll 1,\\
&\frac{T^2}{T_0^2}\ll\left[\frac{\hbar\omega_0^2(0)}{\gamma\varkappa T_0}\right]^2\sim g\frac{\omega_0(0)}{\gamma}\ll 1
\end{aligned} \tag{4.20}$$

applicable to the cases of, respectively, weak damping of phonons $[\omega_0(0)\gg\gamma]$ and strong damping of phonons $[\omega_0(0)\gg\gamma]$ associated with an overdamped mode. Bearing in mind that, according to Eq. (4.20), the soft phonon frequency varies only slightly $[\omega_0(T)\approx\omega_0(0)]$, we can use Eq. (4.14) to rewrite the range [Eq. (4.17)] of validity of the relationships given in Eq. (4.19) in the following simple form:

$$\varkappa T\ll\hbar\omega_0^2(0)/\gamma, \quad \hbar\omega_0(0). \tag{4.21}$$

It should be stressed that the relatively weak, because of the condition (4.20), temperature dependences in Eq. (4.19) nevertheless play the main role in the low-temperature limit and they govern, for example, the thermal expansion coefficient.

At temperatures obeying the condition

$$\hbar\omega_0^2(T)/\gamma\ll\varkappa T\ll\hbar\gamma, \tag{4.22}$$

the contribution $\delta u_p^2$ of paraphonons to the square of the amplitude of fluctuations given by Eq. (4.16) is described by the following expression[20] which is obtained from Eq. (4.11):

$$\delta u_p^2\approx\frac{1}{8}\zeta\left(\frac{3}{2}\right)\frac{\hbar\gamma^{1/2}}{\rho c^3}\left(\frac{\varkappa T}{\hbar}\right)^{3/2}. \tag{4.23}$$

Ignoring the exponentially small contribution of phonons $\delta u_{ph}^2$ and using Eq. (4.23), we obtained the following relationships:

$$\begin{aligned}
&u_0^2(T)=u_0^2(0)\left[1-\left(\frac{T}{T_1}\right)^{3/2}\right], \quad u_0^2(T)=0,\\
&u_L^2(T)=u_0^2(0)\left[1-\frac{2}{3}\left(\frac{T}{T_1}\right)^{3/2}\right],\\
&u_L^2(T)=\frac{1}{3}u_0^2(0)\left(\frac{T}{T_1}\right)^{3/2},\\
&\omega_0^2(T)=\omega_0^2(0)\left[1-\left(\frac{T}{T_1}\right)^{3/2}\right],\\
&\omega_0^2(T)=\frac{1}{2}\omega_0^2(0)\left[\left(\frac{T}{T_1}\right)^{3/2}-1\right],\\
&\Delta V_s(T)=\Delta V_s(0)\left[1-\frac{2}{3}\left(\frac{T}{T_1}\right)^{3/2}\right],\\
&\Delta V_s(T)=\frac{1}{3}\Delta V_s(0)\left(\frac{T}{T_1}\right)^{3/2},
\end{aligned} \tag{4.24}$$

which govern the temperature dependences of the order parameter, of the soft mode frequency, and of the volume in the ordered ($T<T_m$) and disordered ($T>T_m$) phases. In the above expressions the quantity

$$\varkappa T_1=\pi c^2\left\{\frac{8}{3}\frac{1}{\zeta(3/2)}\rho u_0^2(0)\left(\frac{\hbar}{\gamma}\right)^{1/2}\right\}^{2/3} \tag{4.25}$$

represents the characteristic energy of paraphonons, whereas $\zeta(x)$ is the Riemann zeta function.

If a structural phase transition occurs in the temperature range described by Eq. (4.22), then the transition temperature $T_m=T_1$ is given by Eq. (4.25) and is governed by paraphonons. We should mention here that the low-temperature mechanism of structural transitions due to paraphonons was considered by us briefly in Ref. 20, where we discussed the temperature dependences of the type given by Eq. (4.24). In the systems exhibiting such a transition the order parameter satisfies the condition

$$u_0^2(0)\ll u_1^2. \tag{4.26}$$

However, if the condition (4.26) is not obeyed, the transition temperature is higher $T_m\gtrsim\hbar\gamma/\varkappa$ (see below).

If we allow for the estimate $\hbar\omega_0^2(T)/\gamma\varkappa T_1\lesssim g\ll 1$, we can write down the condition (4.22) in the form

$$\hbar\omega_0^2(0)/\gamma\ll\varkappa T\ll\hbar\gamma, \tag{4.27}$$

which defines the range of validity of the temperature dependences of Eq. (4.24) due to paraphonons. It should be stressed that the inequalities of Eq. (4.27) can be satisfied only when the mode frequency is overdamped at low temperatures $[\omega_0(0)\ll\gamma]$, which corresponds to the limit

$$u_0^2(0) \ll \frac{1}{g} u_1^2. \tag{4.28}$$

In the systems in which the order parameter satisfies the condition $u_1^2 \lesssim u_0^2(0) \ll u_1^2/g$ and the temperature of the structural transition is, in accordance with Eq. (4.26), not too low ($T_m > T_1$), we obtain an estimate of the upper limit of the temperature range in Eq. (4.27) which is $T/T_1 \ll \hbar\gamma/\varkappa T_1 \sim u_1/u_0(0) \lesssim 1$ and which demonstrates the relative weakness of the temperature dependences described by the equations in the system (4.24).

At temperatures

$$\hbar\gamma, \quad \hbar\omega_0(T) \ll \hbar\omega_c \tag{4.29}$$

the contribution of phonons to the square of the fluctuation amplitude is governed mainly, according to Eq. (4.13), by soft phonons [15,21,22]

$$\delta u_{ph}^2(T) \approx \frac{\varkappa^2 T^2}{12\hbar\rho c^3}. \tag{4.30}$$

The influence of hf phonons is then exponentially small, $\sim \exp(-\hbar\omega_1/\varkappa T)$, whereas the contribution of paraphonons associated mainly with the soft mode is $\sim \varkappa T/\max[\hbar\omega_0(T), \hbar\gamma] \gg 1$ times smaller than the phonon contribution $\delta u_{ph}^2$.

Using Eq. (4.30), we obtain the following relationships:

$$u_0^2(T) = u_0^2(0)\left(1 - \frac{T^2}{T_2^2}\right), \quad u_0^2(T) = 0,$$
$$u_L^2(T) = u_0^2(0)\left(1 - \frac{2}{3}\frac{T^2}{T_2^2}\right), \quad u_L^2(T) = \frac{1}{3} u_0^2(0) \frac{T^2}{T_2^2},$$
$$\omega_0^2(T) = \omega_0^2(0)\left(1 - \frac{T^2}{T_2^2}\right), \quad \omega_0^2(T) = \frac{1}{2}\omega_0^2(0)\left(\frac{T^2}{T_2^2} - 1\right), \tag{4.31}$$
$$\Delta V_s(T) = \Delta V_s(0)\left(1 - \frac{2}{3}\frac{T^2}{T_2^2}\right),$$
$$\Delta V_s(T) = \frac{1}{3}\Delta V_s(0)\frac{T^2}{T_2^2},$$

which govern the temperature dependences of the characteristics of the ordered ($T < T_m$) and disordered ($T > T_m$) phases, where [15,21,22] the characteristic temperature due to soft phonons is $T_2 = \hbar\omega_0(0)/\varkappa g^{1/2}$.

If a structural transition appears in the temperature range defined by Eq. (4.29), it then follows from Eq. (4.31) that the transition temperature $T_m = T_2$ is governed by soft phonons. Such low-temperature structural transitions were discussed in Ref. 15, 21, and 22 where a dependence of the type given by Eq. (4.31) was obtained for the soft-mode frequency $\omega_0(T)$ in the disordered phase ($T > T_m$). The change in the volume of the disordered phase, proportional to $T^2$ and due to soft phonons, was also discussed in Refs. 15 and 22. However, no attention was given to reversal of the sign of the structural-volume effect at the phase transition point or to the possibility of appearance of thermal expansion anomalies.

The conditions of Eqs. (4.15) and (4.29) impose the following restrictions on the order parameter of systems with low-temperature structural transitions due to the phonon mechanism:

$$u_1^2 \ll u_0^2(0) \ll u_2^2. \tag{4.32}$$

It should be pointed out that if the order parameter satisfies also the condition of Eq. (4.28), it then follows from the system (4.31) that the soft mode is overdamped [$\omega_0(T) < \gamma$] in a wide range of temperatures $T \lesssim T_2 u_1/u_0(0) g^{1/2}$, including the range of existence of the ordered phase ($T < T_m$).

If the right-hand inequality in Eq. (4.32) is not obeyed, the temperature of the transition is higher: $T_m \gtrsim \hbar\omega_c/\varkappa$ (see above). In this case the temperature dependences described by the system (4.31) represent the ordered phase ($T < T_m$) and estimates yield $T/T_2 \ll \hbar\omega_c/\varkappa T_2 \sim u_2/u_0(0) \lesssim 1$. In both cases if we assumed that $\hbar\omega_0(0)/\varkappa T_2 \propto g^{1/2} \ll 1$, the condition of validity [Eq. (4.29)] of the dependences given by the system (4.31) can be written in the form

$$\hbar\gamma, \quad \hbar\omega_0(0) \ll \varkappa T \ll \hbar\omega_c. \tag{4.33}$$

We shall finally consider the limit of high temperatures

$$\varkappa T \gg \hbar\omega_c. \tag{4.34}$$

Allowing for the properties of the spectral density of fluctuations described above, we find that in this limit the main contribution to the square of the amplitude of the fluctuations is made by phonons (see, for example, Ref. 15):

$$\delta u_{ph}^2(T) \approx \frac{\varkappa T}{2\pi^2\rho}\left[\frac{k_c}{c^2} + \frac{2\pi^2 V_k}{\omega_1^2}\right]. \tag{4.35}$$

The terms on the right-hand side of Eq. (4.35) with $k_c$ and $V_k$, describing respectively the influence of soft lf and hard hf phonons are of the same order of magnitude in the model adopted by us and, in contrast to the cases discussed above, the fluctuations associated with the soft mode do not play the dominant role. The contribution of paraphonons $\delta u_p^2$ is then $\sim \omega_1/\max[\omega_0(T), \gamma] \gg 1$ times less than the quantity $\delta u_{ph}^2$, so that we should ignore this contribution, exactly as in the case described by Eq. (4.33). It follows from Eq. (4.35) that the temperature dependences of the characteristics of the ordered ($T < T_m$) and disordered ($T > T_m$) states are

$$u_0^2(T) = u_0^2(0)\left(1 - \frac{T}{T_3}\right), \quad u_0^2(T) = 0,$$
$$u_L^2(T) = u_0^2(0)\left(1 - \frac{2}{3}\frac{T}{T_3}\right), \quad u_L^2(T) = \frac{1}{3} u_0^2(0)\frac{T}{T_3}, \tag{4.36}$$
$$\omega_0^2(T) = \omega_0^2(0)\left(1 - \frac{T}{T_3}\right), \quad \omega_0^2(T) = \frac{1}{2}\omega_0^2(0)\left(\frac{T}{T_3} - 1\right),$$
$$\Delta V_s(T) = \Delta V_s(0)\left(1 - \frac{2}{3}\frac{T}{T_3}\right), \quad \Delta V_s(T) = \frac{1}{3}\Delta V_s(0)\frac{T}{T_3},$$

where

$$T_3 = \frac{2\pi^2}{3}\frac{\hbar\omega_c}{\varkappa}\frac{u_0^2(0)}{u_2^2}\Big/\left(1 + \frac{2\pi^2 V_k \omega_c^2}{\mathbf{K}_c^3 k_1^2}\right) \tag{4.37}$$

is the characteristic phonon temperature.

Substituting into the condition (4.2) the expression for $\omega_0(T)$ from Eq. (4.36) and allowing for the inequality of Eq. (4.34), we find that the range of validity of the high-temperature relationships given by the system (4.36) is

$$\hbar\omega_c \ll \varkappa T \ll \hbar\omega_c/g. \tag{4.38}$$

If a structural transition appears in the high-temperature range defined by Eq. (4.38), it then follows from the system (4.36) that the transition temperature $T_m = T_3$ is governed by Eq. (4.37). High-temperature structural transitions and the associated temperature dependences of the type described by the system (4.36) have been discussed widely in the literature (see, for example, monographs[15,16] and reviews[17,18]). The temperature dependence of the fluctuation contribution to the volume $\Delta V_s(T)$ obtained allowing for the soft mode was first discussed by Levanyuk,[10] leading to the results (after correction for some errors) that represent expressions derived from Eqs. (4.36) and (4.37) in the limit $V_k \to 0$.

The order parameter of systems with high-temperature structural transitions obeys the following conditions:

$$u_2^2 \ll u_0^2(0) \ll \frac{1}{g} u_2^2. \tag{4.39}$$

At low values of the order parameter a structural transition is governed by the low-temperature mechanisms discussed above. The case of large values of $u_0(0)$ corresponds to transitions at the temperature $T_m$, which is outside the inverval of Eq. (4.38). However, this violates the condition (4.15) of validity of the approach adopted here.

The above analysis of the temperature dependences of the order parameter $u_0(T)$, of their average square of the atomic displacements $u_L^2(T)$, of the soft mode frequency $\omega_0(T)$, and of the fluctuation contribution to the volume $\Delta V_s(T)$ complete our analysis of the physical picture of structural phase transitions within the framework of the adopted simple model of a crystal.

Equations (4.24), (4.31), and (4.36) for the fluctuation contribution to the volume $\Delta V_s(T)$ illustrates a general qualitative relationship associated with a change in the sign of the structural-volume effect and a kink in the temperature dependence of the volume of a crystal in the vicinity of a structural phase transition. The analytic temperature dependences of the volume of a crystal corresponding to the mechanisms of structural transitions discussed above are very different. We find that there is a difference between the jumps in the volume thermal expansion coefficient at the point $T = T_m$, due to the kinks in the temperature dependence $\Delta V_s(T)$ and given respectively by $\frac{3}{2}\Delta V_s(0)/V_0 T_1$, $2\Delta V_s(0)/V_0 T_2$, and $\Delta V_s(0)/V_0 T_3$, for low-temperature structural transitions due to paraphonons ($T_m = T_1$) and soft phonons ($T_m = T_2$) and for high-temperature transitions ($T_m = T_3$).

We shall conclude by considering the condition employed by us in Sec. 2:

$$\left| \frac{\partial(\delta u^2)}{\partial u_0^2} \right| \ll 1, \tag{4.40}$$

which corresponds to the self-consistent field approximation (see Refs. 15 and 16). Substitution in the above condition of the low-temperature expression given by Eq. (4.19) together with Eq. (4.20) gives $|\partial(\delta u^2)/\partial u_0^2| \sim T^2/T_0^2 \ll 1$. Therefore, the condition (4.40) is satisfied in the limit of low temperatures given by Eq. (4.21).

In the temperature ranges described by Eqs. (4.27), (4.33), and (4.38) we can calculate the derivative in Eq. (4.40) if we know small corrections $\sim \varkappa T\omega_0(T)/\rho c^3$ to the squares of the amplitudes of the fluctuations described by Eqs. (4.23), (4.30), and (4.35), and due to paraphonons. Consequently, the inequality of Eq. (4.40) leads to the following restrictions on temperature:

$$\left| \frac{T - T_m}{T_m} \right| \gg \frac{1}{A_0 \rho^3} \left( \frac{\varkappa T_m B}{c^3} \right)^2 \sim \left[ g \frac{\varkappa T_m}{\hbar\omega_0(0)} \right]^2, \tag{4.41}$$

which is formally identical with the familiar criterion put forward by Ginzburg[9] and Levanyuk, [11] but—in contrast to Refs. 9 and 11—the phase transition temperature $T_m$ is governed by the fluctuation effects [see Eq. (2.8)].

It is in the case of the low-temperature phase transitions due to paraphonons that we can write down the condition of Eq. (4.41) in the following form[20] on the assumption that $T = T_1$:

$$\left| \frac{T - T_m}{T_m} \right| \gg \frac{\hbar\omega_0^2(0)}{\gamma \varkappa T_m} \sim g \left( \frac{u_0(0)}{u_1} \right)^{4/3}. \tag{4.42}$$

The inequality of Eq. (4.42) is a quantum analog of the criterion used in Refs. 9 and 11, and it appears similarly in a quantum spin-fluctuation theory of weak ferromagnets given in Ref. 4. In the case of low-temperature phase transitions due to phonons ($T_m = T_2$), we find that the condition (4.41) becomes

$$\left| \frac{T - T_m}{T_m} \right| \gg \left( \frac{\hbar\omega_0(0)}{\varkappa T_m} \right)^2 \sim g \tag{4.43}$$

and is identical with the condition of validity of expansion of the free Landau energy near a structural transition obtained in Ref. 22. The condition of Eq. (4.41) for high-temperature phase transitions ($T_m = T_3$) is identical with the criterion derived in Refs. 9 and 11:

$$\left| \frac{T - T_m}{T_m} \right| \gg \left( \frac{\omega_0(0)}{\omega_c} \right)^2 \sim g \frac{u_0^2(0)}{u_2^2}. \tag{4.44}$$

It should be noted that the conditions of Eqs. (4.42)–(4.44) break down, in accordance with Eqs. (4.28) and (4.39), in a narrow critical range of temperatures near the transition point where an important role is played by the effects of the interaction of fluctuations ignored in Eq. (2.7).

All the above results are easily generalized to the case of an anisotropic spectrum (compare with Ref. 21):

$$\omega^2(\mathbf{k}) = \omega_0^2(T) + \sum_{i=x,y,z} c_i^2 (\mathbf{k} - \mathbf{k}_m)^2,$$

which appears in the vicinity of $\omega(\mathbf{k}) < \omega_c$ of the vector $\mathbf{k} = \mathbf{k}_m$ outside of which we still can assume that $\mu(\mathbf{k}) \approx \omega_1 \sim \omega_c$. All that we need to do is to substitute $c \to (c_x c_y c_z)^{1/2}$, $k_c \to \omega_c (c_x c_y c_z)^{-1/2}$ in the above expressions.

Finally, we note that in the adopted model of a crystal with one soft mode we have ignored the excitations associated with fluctuations of the phase of the order parameter (see, for example, Ref. 16). Inclusion of such fluctuations does not alter qualitatively the temperature dependences of the structural-volume effect discussed above and simply changes the numerical coefficients in Eqs. (4.19), (4.24), (4.31) and (4.36) for the case when $\Delta V_s(T)$.

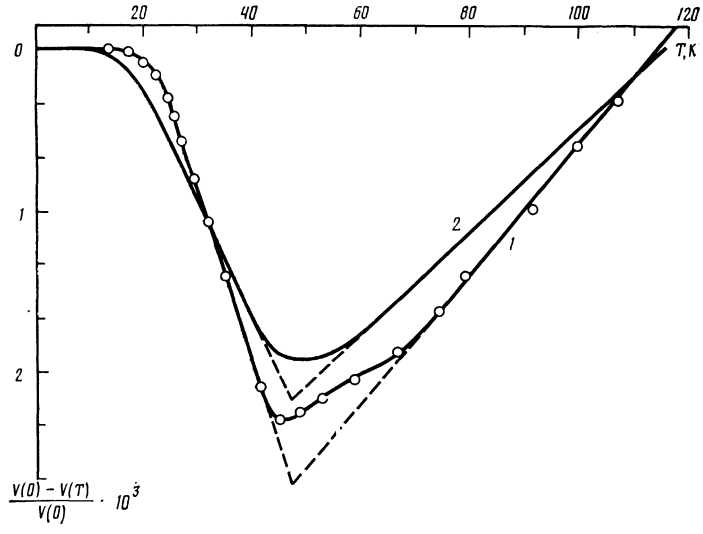


FIG. 2. Thermal expansion of $\alpha$-uranium: 1) based on Ref. 12; 2) based on Ref. 13; the dashed curves represent the results calculated using the system of equations (4.36).

## 5. TEMPERATURE DEPENDENCES OF THE VOLUME AND THE STRUCTURAL-VOLUME EFFECT

The influence of structural transitions on the temperature dependence of the volume is known in the case of $BaTiO_3$: according to Fig. 4.16 reproduced in the book of Jona and Shirane—reporting the results obtained during cooling—the thermal expansion coefficient of this compound decreases strongly near the structural phase transition points. In our discussion of this experimental dependence it corresponds to a change of the sign of the striction contribution to the volume [Eqs. (3.8) and (3.10)] at the structural transition point, reducing the thermal expansion coefficient of barium titanate as a result of cooling (see Ref. 8).

We can assume that our theory can explain, in particular, the anomaly of the thermal expansion of powder-metallurgy ceramic $YBa_2Cu_3O_{7-x}$, observed experimentally in Ref. 24 where in the range 110–120 K it was found that the thermal expansion coefficient decreased strongly (approximately by a factor of 2). As shown in Ref. 25, anomalies of the elastic moduli and of the internal friction are observed in the same temperature range. It follows from our treatment that such a change in the thermal expansion coefficient of $YBa_2Cu_3O_{7-x}$ can also occur in the vicinity of a structural phase transition in which the change in the striction contribution to the volume should show a reversal of the sign in accordance with the fluctuation theory. This conclusion agrees with the major change in the unit cell parameter $c$ observed with the aid of x-ray diffraction investigations[26,27] in the same temperature range.

Similar anomalies of the thermal expansion, preceding the superconducting transition in the lanthanum[26] and thallium[28] ceramics and appearing also in our opinion in $YBa_2Cu_3O_{7-x}$ are all due to the structural-volume effect and agree with the widely held view that structural instabilities are important in high-temperature superconductors.

Manifestation of the thermal expansion anomaly discussed here and due to the structural-volume effect is particularly clear in the case of the anomalous temperature dependence of the volume obtained for $\alpha$-uranium by x-ray diffraction investigations of single crystals[12] and by a dilatometric study of polycrystalline samples[13] (see Fig. 2). In both cases it was found that the thermal expansion coefficient was negative at low temperatures, but at $T\sim 50$ K its sign was reversed. At temperatures $T>50$ K the change in the volume was of the usual type expected in the case of thermal expansion. The recently discovered (by neutron scattering[14]) transition of $\alpha$-uranium to a state with a charge density wave at 43 K demonstrated that the thermal expansion anomalies represented a manifestation of the structural-volume effect much greater than the usual thermal expansion. Then, bearing in mind that in the temperature range 0–50 K the relative change in the volume of uranium was $\sim 2\times 10^{-3}$ (Fig. 2), which was large and comparable with the giant spontaneous magnetostriction in magnetically ordered materials,[29] we concluded that this was a manifestation of a giant striction that accompanied structural transformations in $\alpha$-uranium.

Comparing the dependence $\Delta V_s(T)$ shown in Fig. 1 with the experimental curves in Fig. 2, we concluded that the structural-volume effect discussed above accounted qualitatively for the thermal expansion anomalies of uranium. The linear temperature dependence of the volume observed[12,13] in the temperature range 25–45 K and also at $T\gtrsim 75$ K corresponded to the high-temperature limit of Eq. (4.34), which according to an estimate $\omega_c\approx 2.6\times 10^{12}\ \mathrm{s}^{-1}$ obtained from the results of neutron-diffraction experiments,[14] appeared at temperatures $T>20$ K. The ratio of the thermal expansion coefficients below and above 50 K was, according to Refs. 12 and 13, $-2.3$, and $-2.4$, respectively (Fig. 2) and was close to the value of $-2$ obtained from Eq. (4.36). This result, in spite of the complexity of the ordered state of $\alpha$-uranium associated with the existence of several incommensurate charge density waves,[14] indicated the possibility of utilizing in other cases our simple model and demonstrated the smallness of the usual thermal expansion effects and of fluctuations of the phase of the order parameter at temperatures $T\lesssim 50$ K.

The system of equations (4.36) predicts a kink in the temperature dependence of the volume at the phase transition point (Fig. 2). The absence of kinks in the experimental curves plotted in Fig. 2 could be due to the influence of inho-

mogeneities and internal stresses which were clearly responsible for the difference between the results of measurements of the thermal expansion coefficient of single crystals[12] and polycrystalline samples.[13] Another cause of the "smearing out" of the phase transition could be the influence of critical fluctuations in the range of temperatures where the condition (4.32) was no longer obeyed. Assuming, in accordance with Ref. 14, that $\omega_0(0) \approx 1.10^{12}\ \mathrm{s}^{-1}$ we estimated the critical temperature range to be $|T - T_m| \lesssim 6$ K.


[1]Ch. E. Guillaume, C. R. Acad. Sci. **125**, 235 (1897).
[2]Ch. E. Guillaume, C. R. Acad. Sci. **170**, 1433 (1920).
[3]E. F. Wassermann, Invar: *Moment-Volume Instabilities in Transition Metals and Alloys* (Ferromagnetic Materials), North-Holland, Amsterdam (in press).
[4]I. E. Dzyaloshinskiĭ and P. S. Kondratenko, Zh. Eksp. Teor. Fiz. **70**, 1987 (1976) [Sov. Phys. JETP **43**, 1036 (1976)].
[5]T. Moriya, *Spin Fluctuations in Magnetics with Itinerant Electrons* [Russian translation], Mir, Moscow (1988).
[6]T. Moriya and K. Usami, Solid State Commun. **34**, 95 (1980).
[7]V. P. Silin and A. Z. Solontsov, Phys. Status Solidi B **147**, 373 (1988).
[8]G. A. Smolenskii, V. A. Bokov, V. A. Isupov *et al.*, *Ferroelectrics and Antiferroelectrics* [in Russian], 2nd ed., Nauka, Leningrad (1971).
[9]V. L. Ginzburg, Fiz. Tverd. Tela (Leningrad) **2**, 2031 (1960) [Sov. Phys. Solid State **2**, 1824 (1961)].
[10]A. P. Levanyuk, Fiz. Tverd. Tela (Leningrad) **5**, 1776 (1963) [Sov. Phys. Solid State **5**, 1294 (1964)].
[11]A. P. Levanyuk, Zh. Eksp. Teor. Fiz. **36**, 810 (1959) [Sov. Phys. JETP **9**, 571 (1959)].
[12]C. S. Barrett, M. H. Mueller, and R. L. Hitterman, Phys. Rev. **129**, 625 (1963).
[13]A. Hough, J. A. C. Marples, M. J. Mortimer, and J. A. Lee, Phys. Lett. A **27**, 222 (1968).
[14]G. H. Lander, J. Magn. Magn. Mater. **29**, 271 (1982); H. G. Smith and G. H. Lander, Phys. Rev B **30**, 5407 (1984).
[15]V. G. Vaks, *Introduction to the Microscopic Theory of Ferroelectricity* [in Russian], Nauka, Moscow (1973).
[16]A. D. Bruce and R. A. Cowley, *Structural Phase Transitions*, Taylor and Francis, London (1981).
[17]V. L. Ginzburg, Tr. Fiz. Inst. Akad. Nauk SSSR **180**, 3 (1987).
[18]V. L. Ginzburg, A. P. Levanyuk, and A. A. Sobyanin, Usp. Fiz. Nauk **130**, 615 (1980).
[19]V. P. Silin and A. Z. Solontsov, Kratk. Soobshch. Fiz. No. 11, 50 (1989).
[20]A. Z. Solontsov, Preprint No. 7-54 [in Russian], VNII NM 7-54, Moscow (1989); Dokl. Akad. Nauk SSSR **313**, 853 (1990).
[21]A. B. Rechester, Zh. Eksp. Teor. Fiz. **60**, 782 (1971) [Sov. Phys. JETP **33**, 423 (1971)].
[22]D. E. Khmel'nitskiĭ and V. L. Shneerson, Fiz. Tverd. Tela (Leningrad) **13**, 832 (1971) [Sov. Phys. Solid State **13**, 687 (1971)].
[23]F. Jona and G. Shirane, *Ferroelectric Crystals*, Pergamon Press, Oxford (1962).
[24]O. V. Basargin, L. A. Rudnitskiĭ, V. V. Moshchalkov, *et al.*, Fiz. Tverd. Tela (Leningrad) **30**, 877 (1988) [Sov. Phys. Solid State **30**, 507 (1988)].
[25]G. P. Vorob'ev, A. M. Kadomtseva, Z. A. Kazeĭ *et al.*, Sverkhprovodimost' (KIAE) **2**, 47 (1989) (Superconductivity **2**, 57 (1989)].
[26]V. V. Moshchalkov, N. B. Brandt, I. T. Muttik, *et al.*, Abstracts of Papers presented at Workshop on Problems in High-Temperature Superconductivity, Sverdlovsk, 1987 [in Russian], p. 11.
[27]A. I. Golovashkin, O. M. Ivanenko, G. M. Leĭtus *et al.*, *ibid.*, p. 20.
[28]A. I. Akimov, B. B. Boĭko, V. I. Gatal'skaya *et al.*, Sverkhprovodimost' (KIAE) **2**, 41 (1989) (Superconductivity **2**, 51 (1989)].
[29]K. P. Belov, *Magnetostriction Effects and Their Technical Applications* [in Russian], Nauka, Moscow (1987).


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