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Probability of the Mossbauer Effect in β-Sn at High Pressures and the Gruneisen Constant

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The probability f, of the Mössbauer effect in metallic tin is investigated at pressures ranging from 0 to 110 kbar. A discontinuity of the probability f is observed in the region of the first-order phase transition at 100 kbar. The discontinuity of f is compared (by means of the Debye approximation) with the known value of the phase-transition heat. The dependence of f on pressure up to the phase-transition point is discussed within the framework of the quasiharmonic model of a solid with allowance for the volume dependence of the Gruneisen constant γ. The volume dependence of γ is determined from the experimental data. In the immediate neighborhood of the phase transition, $\gamma \approx 0$; this suggests the presence in β-Sn of anomalous lattice modes whose frequency drops with pressure. On basis of the results some ideas are considered, wherein the phase transition under pressure is ascribed to peculiarities of the dynamics of the β-Sn lattice.

1. INTRODUCTION

THE properties of metallic tin (β-Sn) under pressure have been investigated sufficiently well. The compressibility of β-Sn in a wide pressure interval was investigated by Bridgman[1,2]. The PT phase diagram of tin was established in main outline by investigations of the melting curve of tin[3] under pressure and subsequent measurements of the electric resistance[4] as well as experiments by the method of differential thermal analysis[5], and a new crystalline modification Sn II was observed. The phase-transition point at room temperature is 100 ± 6 kbar (in the 1968 pressure scale[6]). X-ray diffraction investigations of β-Sn under pressure were also made[7-9]. These have established the phase diagram, the heat of the β-Sn – Sn II transition, and the structure of the new phase of tin. It turned out that Sn II has a simple tetragonal body-centered lattice (one atom per unit cell) with parameters a = 3.70 Å, c = 3.37 Å, and c/a = 0.91. The phase β-Sn (Sn I) has, as is well known[10], a tetragonal body-centered lattice with two atoms per unit cell; its parameters are a = 5.83 Å, c = 3.18 Å, and c/a ≈ 0.55.

The present work was undertaken for the purpose of studying the influence of pressure on the probability of the Mossbauer effect in tin up to pressures at which the phase Sn II already exists.

2. THEORY

A detailed quantum-mechanical study of the Mossbauer effect in the harmonic approximation was reported in a number of papers, for example[11,12]. In the case of a regular monatomic crystal with several atoms per unit cell, the fraction f of recoilless radiation is expressed in the following manner:

$$f = e^{-Z}, \tag{1}$$

$$Z = R\frac{u}{(2\pi)^3}\sum_\alpha \int d^3f\, \frac{|\mathbf{qv}(\mathbf{f},\alpha)|^2}{\hbar\omega(\mathbf{f},\alpha)}[2\bar{n}(\mathbf{f},\alpha)+1] \tag{2}$$

(the notation here is the same as in[11]). A theoretical investigation of the influence of pressure on the probability f was made in two studies[13,14]. The Debye approximation was used in the first, and a more general case was considered in the second. In both papers, a quasiharmonic model of a solid was used[15], based on the harmonic model, as well as the assumption that the frequencies of the normal oscillations vary with the lattice parameters. The latter makes it possible to take into account the anharmonicity of the thermal oscillations of the atoms in the lattice and leads to the well known[16] Gruneisen parameter. Using an expression given in[17] for the free energy of a solid in the harmonic approximation, we can obtain the Gruneisen formula (4) which will be used subsequently.

It is known that the volume coefficient of thermal expansion β is expressed in terms of the free energy F in the following manner[17]: $\beta = -\chi\partial^2 F/\partial T\partial V$, where χ is the isothermal compressibility, while T and V are the temperature and the volume. This yields for β the expression

$$\beta = \frac{\chi}{V}\sum_{\alpha=1}^{3N}\gamma_\alpha\frac{\partial E_\alpha}{\partial T};$$

Here N is the number of atoms in the crystal, V is the volume of the crystal, E_α is the energy of the α-th normal lattice vibration, and

$$\gamma_\alpha = -d\ln\omega_\alpha / d\ln V. \tag{3}$$

The quantity γ_α is a measure characterizing the influence of the change of volume on the frequency ω_α (for a harmonic oscillator, $\gamma_\alpha = 0$ and thus, γ_α is a certain measure of the anharmonicity of α-th normal vibration of the lattice). Further, following Gruneisen[18], we can assume that all γ_α are equal to one another, and take $\gamma_\alpha \equiv \gamma$ outside the summation sign. Then, recognizing that $\partial E_\alpha/\partial T$ is the Einstein specific heat[19] c_α of mode α, we have

$$\beta = \frac{\chi\gamma}{V}\sum_\alpha c_\alpha = \frac{\chi\gamma C_v}{V} \tag{4}$$

where C_V is the specific heat of the crystal at constant volume. From (4) we can calculate the experimental Gruneisen parameter γ, if all the remaining quantities in this formula are known from experiment. If we now write the expression for β in the form

$$\beta = \frac{\chi}{V}\sum_\alpha \gamma_\alpha c_\alpha = \frac{\chi C_v}{V}\Big(\sum_\alpha c_\alpha\Big)^{-1}\sum_\alpha \gamma_\alpha c_\alpha,$$

then we see that

$$\gamma = \left(\sum c_\alpha\right)^{-1} \sum \gamma_\alpha c_\alpha, \tag{5}$$

i.e., the Gruneisen parameter can be regarded as the mean value of all the individual γ_α with "weights" c_α. At high temperatures, when the law of equipartition of the thermal energy over all degrees of freedom of the crystal is valid, all the c_α are equal and

$$\bar{\gamma} = \frac{1}{3N}\sum_\alpha \gamma_\alpha, \tag{6}$$

i.e., it is simply the average of γ over all the lattice modes. It is important that formulas (5) and (6) introduce the parameter γ without the assumption that all the γ_α are equal to one another and to γ.

In the analysis of the influence of the pressure on the Mossbauer-effect probability[13,14], the Gruneisen approximation was actually used as a certain approximation to reality in order to take into account in the theory the change of the frequencies of the normal vibrations with pressure. It was assumed that all $\gamma_\alpha \equiv \gamma = \text{const}$, and then it follows from (3) that when the volume decreases from V_0 to V any frequency ω_0 of the phonon spectrum becomes equal to

$$\omega = \omega_0 (V/V_0)^{-\gamma}, \tag{7}$$

i.e., it increases with pressure. Since γ can be calculated by the Gruneisen formula (4), it becomes possible to estimate the probability f at different values of V from the known value f_0 at atmospheric pressure. Expanding in (2) the quantity $[2\bar{n} + 1] = \coth(\hbar\omega/2kT)$ in a series[20] in $\hbar\omega/2kT$, we obtain for $T > \Theta$ an approximate expression for f (with an error not larger than 1%)

$$f = e^{-R/6kT} e^{-Z_1(V)},$$

where Z_1 is given by

$$Z_1 = 2RkT\hbar^{-2}\langle\omega^{-2}\rangle.$$

Here $\langle\omega^{-2}\rangle$, according to[11], is averaged over all lattice vibration modes. Finally, using (7), we obtain

$$Z_1(V) = (V/V_0)^{2\gamma} Z_1(V_0). \tag{8}$$

Formula (8) is the basis for the discussion of the experimental results obtained under pressure.

3. PROCEDURE AND RESULTS

As follows from an analysis (see[21]) of the characteristics of Mossbauer spectra in absorption experiments, the area under the resonant Mossbauer curve is directly proportional to the value of f for the Mossbauer source and does not depend on the parasitic vibrations. Therefore, in the present experiments, a β-Sn source (foil 20 or 65 μ thick) was placed in the pressure chamber, and the influence of the pressure on f was investigated by the relative method of comparing the areas under the experimental curves at different pressures, with the area at atmospheric pressure. Control experiments without pressure yielded the corrections that must be introduced into the values of f to allow for certain changes in the geometry of the experiment and the density of the materials with increasing pressure, and also to take into account the change of the self-absorption in the source as the result of the variation of f with pressure.

Pressure was produced with a flat anvil of the Bridgman type[2], with a boron pellet ensuring hydrostatic support for the working plungers, similar to that realized in[22]. This has made it possible to obtain a chamber with a large working volume and rather uniform pressure, producing no changes whatever in the shape of the investigated sample in the entire interval 0 – 110 kbar. The chamber was calibrated beforehand against the jumps of the electric resistance of standard substances during the phase transitions[6], and the pressure in the chamber was monitored during the course of the experiments against the electric resistance of Bi or β-Sn[4].

The Mossbauer spectra were plotted with a setup containing an electrodynamic vibrator in the constant-velocity mode. The resonance spectrum consisted of a single line at all pressures. The experimental data were reduced with electronic computer by least squares relative to a single Lorentz curve, the result being the ratios S_p/S_0 of the areas under the experimental spectra. These results, the summary correction Δ, and the final values of f_p/f_0 as functions of the pressure P are listed in the table. The errors in the values of the areas S, resulting from certain differences between the experimental resonance line and the Lorentz line, turned out to be negligible because the relative quantities S_p/S_0 were used.

When the pressure was removed, the probability of the effect resumed its initial value within ±10%. The source and absorber temperature in the experiments was 18 ± 2°C.

4. DISCUSSION OF RESULTS

From the known dependence of f_p/f_0 on the pressure, it is possible to obtain the absolute values of f_p if one uses for f_0 the previously measured value. According to[23], $f_0 = 0.046 \pm 0.010$ at $T = 291°\text{K}$. The values of f_p at different pressures are given in the table. Certain deviations from the earlier data[24] are connected mainly with the use of different values of f_0. Let us examine the results in light of the theory developed above. Assuming initially that the Debye approximation is valid for tin[25], we estimate from f_p the effective Debye temperature Θ at different pressures. Since the value of Θ at P = 1 atm is ~130 – 140°K, it is permissible to use at room temperatures the approximate expression[12] for f in the Debye model:

$$f = e^{-Z}, \qquad Z = \frac{6RT}{k\Theta^2} + \frac{R}{6kT}$$

(R is the recoil energy of the free tin nucleus and k is Boltzmann's constant). The effective Debye temperature Θ determined from this, as a function of the pressure, is shown in Fig. 1. Starting with the point

P	S_p/S_0	Δ, %	f_p/f_0	f_p
1 atm	1	0	1	0.046
42 kbar	1.69±0.06	9	1.84±0.06	0.085±0.003
79 »	1.96±0.07	15	2.26±0.08	0.104±0.004
96 »	1.98±0.10	18	2.33±0.12	0.107±0.006
100 »	1.47±0.12	18	1.75±0.15	0.081±0.007
105 »	1.58±0.12	18	1.88±0.15	0.087±0.007
110 »	1.68±0.12	18	2.00±0.15	0.092±0.007

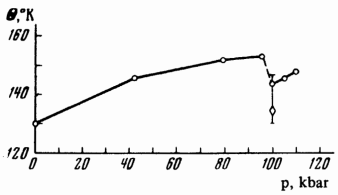

FIG. 1. Effective Debye temperature Θ as a function of the pressure (circles); the diamond represents the value of Θ for the Sn II phase, calculated from the β-Sn–Sn II transition.

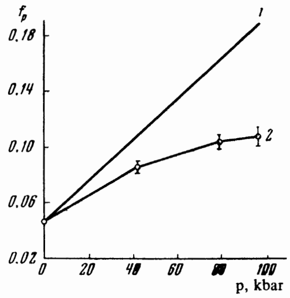

FIG. 2. Probability of the Mossbauer effect f_p in β-Sn as a function of the pressure: 1–theory, formula (8); 2–experiment.

100 kbar, Θ already assumes the values for the Sn II phase. These Mossbauer-effect results can be compared with the thermodynamic data. According to[26], the ratio of the Debye temperatures of two phases at the transition point is $\Theta_I/\Theta_{II} = \exp(L/3BT)$, where L is the heat of transition and B is the gas constant. Assuming for Θ_I the value of Θ at 96 kbar, we obtain from the known[9] value L = 225 ± 45 cal/g-at the value of Θ_{II} near the transition point. This value of Θ_{II}, with the spread resulting from the inaccuracy in the determination of L, is shown in Fig. 1. We see that the agreement between the presented data is good. We note that these data are the results of two independent experiments treated in the Debye approximation.

We consider now the results of the influence of pressure on f in the interval 0 – 96 kbar, without representing the phonon spectrum with the aid of a model. To this end, we use formula (8), in which we put $\gamma = 2.22$[27]. We can then estimate from the known function V = V(p) for tin the predicted course of f as a function of P in β-Sn. It is shown in Fig. 2 together with the experimental values of f_p.

The discrepancy between theory and experiment becomes quite appreciable when P is increased. The reason lies apparently in the fact that the employed theory[14] assumes that γ is independent of the pressure. According to experiment[28], however, γ varies with pressure. Then, assuming that $\gamma = \gamma(V)$ and modifying correspondingly the conclusions of the theory, let us discuss the results of our experiments in terms of a variable Gruneisen parameter. We obtain in place of (7)

$$\omega = \omega_0 \exp\left(-\int_{V_0}^{V} \frac{\gamma(v)}{v}\,dv\right), \tag{9}$$

and in place of (8)

$$Z_1(V) = Z_1(V_0)\exp\left[2\int_{V_0}^{V} \frac{\gamma(v)}{v}\,dv\right]. \tag{10}$$

As seen from (10), to calculate $Z_1(V)$ it is necessary to know the function $\gamma = \gamma(V)$. It is known from experiments[2] only up to 12 kbar. Therefore, instead of calculating $Z_1 = Z_1(V)$ from these data, we use our experiments and expression (10) to determine the parameter γ as a function of the pressure (volume). We assume here that γ varies linearly with V in the intervals between the points at which f is measured. This is reasonable, if account is taken of the estimates of the course of $\gamma = \gamma(V)$ given in[29,28]. We can then write for each interval

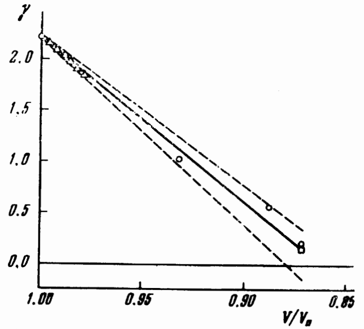

FIG. 3. Variation of the Gruneisen parameter γ with decreasing volume. ○, □–Mossbauer-effect data, Δ–data obtained from (4) and from the dependence of the bulk expansion coefficient of β-Sn on the pressure.

$$\gamma(V) = a + b(1 - V/V_0), \tag{11}$$

where $a = \gamma$ at P equal to the initial pressure in the corresponding interval, and b is a constant to be determined. We can then obtain an analytic expression for the integral in (10), substitute this expression in (10), and determine b from the experimentally known Z(V) for each of the intervals 0 – 42, 42 – 79, and 79 – 96 kbar. The results of this calculation of $\gamma = \gamma(V)$ are shown in Fig. 3 (circles). The same figure shows a continuous line which is the result of the calculation for the entire interval 0 – 96 kbar, assuming the linear dependence (11) to be valid in the entire interval. We see that in both cases, taking into account the measurement errors, the results can be regarded to be the same and that the last method of calculating $\gamma = \gamma(V)$ can be used henceforth. We use this method to estimate the possible deviations of γ from the straight line as a result of the presence of uncertainties in the initial value $f_0 = 0.046 \pm 0.010$ and as a result of the experimental errors in the determination of f_p from the pressure. These deviations lie within the area bounded by the dashed lines. Figure 3 shows also the plot of $\gamma = \gamma(V)$ obtained on the basis of formula (4) and of $\beta = \beta(V)$ calculated from measurements of the compressibility of β-Sn at different temperatures up to 12 kbar[2]. The agreement between the two experiments is quite adequate.

We have used so far the assumption that all $\gamma_\alpha \equiv \gamma$ = const. In real bodies, however, this may not hold[30]. In this case the mean value $\bar{\gamma}$ is determined from formula (6), and since $\gamma \equiv \bar{\gamma}$ at $T > \Theta$, it is legitimate to assume that the dependence of $\bar{\gamma}$ on P will be similar to $\gamma = \gamma(P)$. It is seen from Fig. 3 that at $V/V_0 = 0.872$ (P = 96 kbar), in the immediate vicinity of the Sn I – Sn II phase transition, the value of γ is close to zero. Assuming that an increase of the elastic constants with pressure[31] constitutes the normal behavior, then the tendency $\bar{\gamma} \to 0$ may indicate the presence of certain frequencies ω_β with $\gamma_\beta < 0$ in the phonon spectrum of β-Sn; these frequencies, consequently, de-

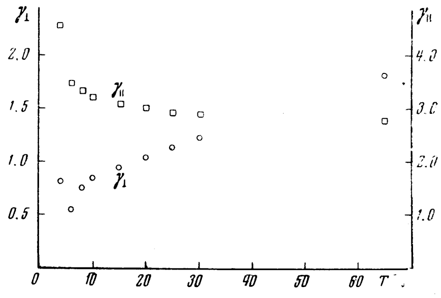

FIG. 4. Components $\gamma_\perp$ and $\gamma_\parallel$ of the Gruneisen-parameter tensor as functions of the temperature (°K). Their values at room temperature are 2.16 and 2.68, respectively.

crease with pressure. The presence of such anomalous frequencies in the phonon spectrum of β-Sn even at atmospheric pressure is indicated by data on the dependence of the coefficients of linear expansion of β-Sn single crystals on the temperature[32] in the interval 4–100°K. The components $\gamma_\parallel$ and $\gamma_\perp$ (parallel and perpendicular to the c axis) of the Gruneisen-parameter tensor[33], calculated on their basis, are shown in Fig. 4. We see that $\gamma_\perp$ decreases at $T \sim 10°K$, when the bulk of the high-frequency lattice modes has already been "quenched" and the relative fraction of the anomalous low-lying frequencies of the phonon spectrum has increased (formula (5)). At $T \sim 4°K$ the anomalous modes also begin to be "quenched" and $\gamma_\perp$ increases.

The facts listed above have a direct bearing on the ideas advanced in[34 24], where the Sn I – Sn II phase transition was discussed from the point of view of the dynamics of the β-Sn lattice. It was indicated there that certain soft lattice modes of β-Sn can exhibit an instability that increases with pressure and is manifest in a lowering of their frequencies with increasing pressure. It was assumed that this instability might be the cause of the phase transition. A detailed mechanism of the Sn I – Sn II transition, based on the assumption that a decisive role in the instability of the β-Sn lattice is played by two low-frequency transverse optical moments with wave vectors along the [100] directions, with values zero and $2\pi/a$ and with displacements parallel to the c axis, has also been considered. Under the condition that the maximum displacements of the atoms in these unstable modes reach $c_0/8$ and $c_0/4$, respectively, with increasing pressure ($c_0 = 3.18$ Å), it was possible to obtain from β-Sn a structure similar to Sn II (ratio $c/a = 0.83$).

Our experiments indeed point to the presence in β-Sn of certain lattice modes whose frequencies decrease with pressure. It is also seen from the results of the experiments that this instability progresses when the phase transition is approached.

According to[36], such a progressive decrease of the frequencies of a number of lattice modes can lead to a phase transition since, starting with a certain pressure (transition point), the thermodynamic potential of the initial phase may be so increased by the presence of the unstable modes, that this phase turns out to be less favored in comparison with the other possible crystalline modification.

Furthermore, a comparison of the data on the dependence of $\gamma_\perp$ and $\gamma_\parallel$ on T (Fig. 4) and the data on the anisotropy of the Mossbauer effect in β-Sn single crystals at different temperatures[37] (all at atmospheric pressure) does not contradict the idea of the instability of low-lying transverse optical (or acoustic) modes with polarization vectors parallel to the c axis, since the anomaly in the temperature behavior of $\gamma_\perp$ corresponds to a decreased probability of the effect in the direction of the c axis, and since the anisotropy of the Mossbauer effect vanishes at temperatures close to absolute zero, when the low-lying modes begin to be "quenched".

No definite conclusion can be drawn as yet from the existing experiments concerning the role of the two particular optical modes mentioned above and concerning the values of their amplitudes.

5. CONCLUSIONS

1. The employed theory, which takes into account the influence of the pressure on the probability of the Mossbauer effect, describes satisfactorily the results of experiments on β-Sn only when account is taken of the dependence of the Gruneisen parameter γ on the pressure.

2. An investigation of the change (jump) of the Mossbauer-effect probability in a first-order phase transition makes it possible to estimate the heat of the phase transition, provided the Debye approximation can be used for both phases.

3. Measurement of the probability of the Mossbauer effect under pressure can be used to determine the dependence of the Gruneisen parameter on the volume; this is important for problems connected with the equation of state of solids at high pressures.

4. The results of the experiments confirm the previously advanced hypothesis that the instability of certain low-lying lattice modes of β-Sn increases with increasing pressure. This instability may be the cause of the phase transition in tin under pressure.

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[1] P. W. Bridgman, Phys. Rev. **60**, 351 (1941).
[2] P. W. Bridgman, The Physics of High Pressure, Bell, 1931.
[3] J. D. Dudley and H. T. Hall, Phys. Rev. **118**, 1211 (1960).
[4] R. A. Stager, A. S. Balchan, and H. G. Drickamer, J. Chem. Phys. **37**, 1154 (1962).
[5] G. C. Kennedy and R. C. Newton, Solids under Pressure, McGraw, 1963, Chap. 7, p. 163 [Russ. transl., Mir, 1966, p. 187].
[6] L. F. Vereshchagin, A. A. Semerchan, N. N. Kuzin, and Yu. A. Sadkov, Dokl. Akad. Nauk SSSR **191**, 557 (1970) [Sov. Phys.-Dokl. **15**, 292 (1970)].
[7] J. D. Barnett, R. B. Bennion, and H. T. Hall, Science **141**, 1041 (1963).
[8] J. E. Martin and P. L. Smith, Br. J. Appl. Phys. **16**, 495 (1965).
[9] J. D. Barnett, V. E. Bean, and H. T. Hall, J. Appl. Phys. **37**, 875 (1966).
[10] Fizicheskiĭ éntsiklopedicheskiĭ slovar' (Physics Encyclopedic Dictionary), Sovetskaya éntsiklopediya, 1963, Vol. 3, p. 487.
[11] Yu. Kagan, in Effect Mossbauera (Mossbauer Effect), Collection of Translations, edited by Yu. Kagan.
[12] M. A. Krivoglaz, in: Fizika tverdogo tela (Solid State Physics), ed. by S. V. Tyablikov, Institute of Scientific Information, 1965, p. 5.
[13] R. V. Hanks, Phys. Rev. **124**, 1319 (1961).
[14] J. Dlouha, Chekh. fiz. zh. B **14**, 570 (1964).
[15] T. H. K. Barron, Proc. 7th Int. Conf. Low. Temp. Phys., Univ. Toronto Press, 1961, p. 655.
[16] C. Kittel, Introduction to Solid State Physics, Wiley, 1953.

[17] L. D. Landau and E. M. Lifshitz, Statisticheskaya fizika (Statistical Physics), Nauka, 1964 [Addison-Wesley, 1969].
[18] L. Knopoff, High Pressure Phys. and Chem., ed by R. S. Bradley, 1963, Vol. 1, p. 227.
[19] D. E. Schuele and C. S. Smith, J. Phys. Chem. Solids **25,** 801 (1964).
[20] I. N. Bronshteĭn and K. A. Semendyaev, Spravochnik po matematike (Mathematics Handbook), Gostekhizdat, 1955, p. 329.
[21] G. A. Bykov and Pham Zui Hien, Zh. Eksp. Teor. Fiz. **43,** 909 (1962) [Sov. Phys.-JETP **16,** 646 (1963)].
[22] D. N. Pipkorn, C. K. Edge, P. Debrunner, G. DePasquali, H. G. Drickamer, and H. Frauenfelder, Phys. Rev. A **135,** 1604 (1964).
[23] C. Hohenemser, Phys. Rev. A **139,** 185 (1965).
[24] V. N. Panyushkin and F. F. Voronov, Zh. Eksp. Teor. Fiz. Pis'ma Red. **2,** 153 (1965) [JETP Lett. **2,** 97 (1965)].
[25] A. J. F. Boyle, D. St. P. Bunbury, C. Edwards, and H. E. Hall, Proc. Phys. Soc. Lond. **77,** 129 (1961).
[26] C. Zener and S. Bilinsky, Phys. Rev. **50,** 101 (1936).
[27] K. A. Gschneidner, Jr., Solid State Phys. **16,** 275 (1964).
[28] B. J. Alder, Solids Under Pressure, McGraw-Hill Book Company, Inc., N. Y., 1963, Chap. 13, p. 385.
[29] V. N. Zharkov and V. A. Kalinin, Uravneniya sostoyaniya tverdykh tel pri vysokikh davleniyakh i temperaturakh (Equations of State of Solids at High Pressures and Temperatures), Nauka, 1968.
[30] G. A. Samara, Phys. Rev. B **2,** 4194 (1970).
[31] J. C. Slater, Introduction to Chemical Physics, N. Y., 1939, p. 199.
[32] G. K. White, Phys. Lett. **8,** 294 (1964).
[33] S. W. Key, J. Appl. Phys. **38,** 2923 (1967).
[34] M. J. P. Musgrave, J. Phys. Chem. Solids **24,** 557 (1963).
[35] M. J. P. Musgrave, J. Phys. Chem. Solids **30,** 1091 (1969).
[36] R. A. Cowley, Philos. Mag. **11,** 673 (1965).
[37] N. K. Alekseevskiĭ, A. P. Kir'yanov, V. I. Nizhankovskiĭ and Yu. A. Samarskiĭ, Zh. Eksp. Teor. Fiz. Pis'ma Red. **2,** 269 (1965) [JETP Lett. **2,** 171 (1965)].

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