Thermodynamic properties and superconducting transition temperature of dilute solutions of Hf, Ta and W in V

A. A. Shikov, N. A. Chernoplekov, G. Kh. Panova, B. N. Samoĭlov, and
A. P. Zhernov

I. V. Kurchatov Institute of Atomic Energy

(Submitted May 30, 1975)
Zh. Eksp. Teor. Fiz. 69, 1825–1833 (November 1975)

The specific heats of VHf alloys (0.9 at.%) and VW alloys (5.2 at.%) are measured between 1.2 and 40 K in the absence of a field and at 1.2–6 K in an 18 kOe field. Similar investigations were previously carried out (1973, 1975) with pure V and its alloy with Ta. Introduction of heavy impurity atoms of Hf, Ta or W into the V lattice results in an anomalous temperature behavior of the impurity part of the phonon specific heat. This indicates that quasilocal oscillations arise. Despite the almost equal masses of the impurity atoms, the magnitudes and positions of maxima of the quantity $\Delta C_{ph}/C_{ph}\eta$ is found to differ considerably for VHf, VTa and VW alloys due to variation of the effective force constants.

PACS numbers: 65.40.Fn, 74.10.+v, 74.20.Ef

Introduction of heavy impurity atoms into a crystal lattice leads to a resonant increase of the density of the phonon states in the low-frequency region.[2,4,5] There is a sufficiently widely accepted point of view, according to which the softening of the phonon spectrum should lead to an increase of the superconducting-transition temperature T_c,[6-8] and it might seem that there is a direct possibility of raising T_c noticeably in systems with heavy impurities. The influence of impurity phonon states on T_c of a metal was considered theoretically in [3,9,10]. Until recently, however, there were practically no experimental studies of the influence of quasi-local modes on T_c.

We are carrying out systematic investigations of the deformation of the phonon spectrum in solutions of V with heavy impurity atoms, and study the influence of this deformation on T_c.[1,2]

Alloys of V with heavy Ta impurity atoms were investigated using the method of inelastic scattering of neutrons, and by measuring the heat capacity and the electric conductivity. It was observed that quasi-local modes are produced at low frequencies and lead to a softening of the phonon spectrum, and at the same time to a lowering of T_c.

It is known that introduction of group-IV elements into vanadium increases T_c, while introduction of group-VI elements decreases it. Interest attaches therefore to alloys of V with Hf and W, which are the neighbors of Ta in the periodic table and which differ only in the number of electrons, having practically equal atomic masses.

We have measured in the present study the high-temperature heat capacity of the alloys VHf (0.9 at.%) and VW (5.2 at.%).

The investigated VHf (0.9 at.%) and VW (5.2 at.%) samples were prepared from brand VÉL-2 vanadium subjected to additional zone purification in a vacuum of 10^{-6} mm Hg in an electron-beam furnace. The alloys of V with Hf and W were prepared in the same furnace. Samples 18 mm in diameter and 50 mm long were cut from the obtained ingots. Owing to the poor solubility of Hf and W in V, the widths of the superconducting transitions of these samples were ~1.5–2°K, and additional prolonged homogenization of the samples in a vacuum of 10^{-6} mm Hg at 1400°K (~20 hours) was necessary, followed by rapid cooling. As a result of this homogenization, the width of the transition decreased to ~0.6°K for VW and ~0.1°K for VHf. The content of the Hf and W in the vanadium and the content of the extraneous impurities were determined by chemical and spectral analysis. The x-ray-structure and metallographic analysis methods did not reveal the presence of a second phase and allowed us to assume that the investigated alloys are single-phase and constitute solid solutions.

Measurements of the low-temperature heat capacity of the alloys VHf and VW were carried out in a vacuum adiabatic calorimeter[1] in the range 1.2–40°K without a field and in the field of a superconducting solenoid of intensity ~18 kOe in the region 1.2–6°K.

The measured temperature dependence of the heat capacity of the initial V and of its alloys with Hf and W without a field and in a field of ~18 kOe in the 1.2–8°K range are shown in Fig. 1 as plots of C/T against T^2. A jump of the heat capacity on going to the superconducting state was observed in the measurements without the field.

However, in addition to the main jump for the VS alloy in the ~2.2°K region, a small jump of the heat capacity was observed, due apparently to the presence in the solid solution of a second phase not revealed by the x-ray methods. According to our estimates, the content of the second phase does not exceed 3%. The results made it possible to determine the superconducting-transition temperature T_c, the jump $\Delta C/\gamma T_c$ of the heat capacity at the transition, the ratio $(C_{es}/C_{en})T_c$ of the electronic heat capacities of the superconducting and normal states, and the width ΔT of the transition. Measurement of the heat capacity in a magnetic field made it possible to determine the coefficient of electronic specific heat γ and the Debye temperature Θ of the investigated samples. Our measurements of the electric conductivity have made it possible to determine T_c and the resistivity ratio $\rho(300K)/\rho(T_c)$. Good agreement was observed between the values of T_c obtained from measurements of the heat capacity and the electric conductivity.

The results of the measurement of the heat capacity of pure V and of its alloys with Hf and W in the normal state in the 1.2–40°K range are shown in Fig. 2. It is seen from this figure that at low temperatures the curve for VW lies lower than the curve for V, owing to the decrease of the electronic specific heat upon introduction of the impurity atoms W. With rising temperature, the curves intersect, after which the curve for VW lies somewhat higher than the curve for V.

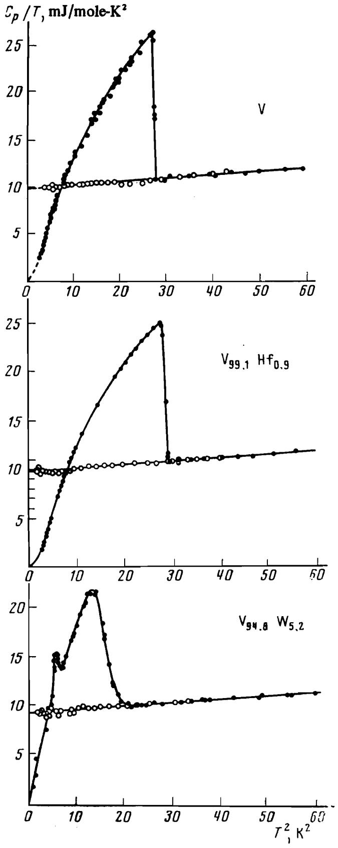

FIG. 1. Heat capacity of pure V and of its alloys with Hf and W without a field (●) and in a field ∿18 kOe (○).

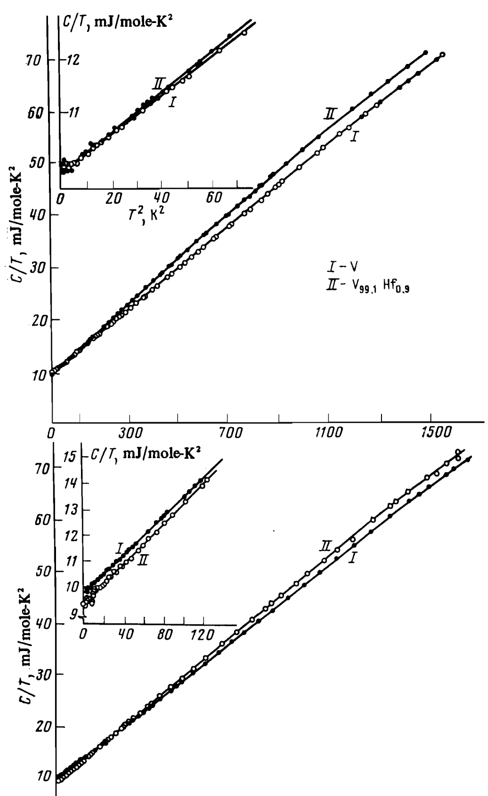

FIG. 2. Heat capacity of V and of its alloys with Hf and W in the normal state in the region 1.2–40°K. I and II in the lower figure are plots for V and $V_{94.8}W_{5.2}$, respectively.

When impurity Hf atoms (0.9 at. %) are introduced into V, the density of states remains practically unchanged ($\gamma_V = 9.80$, $\gamma_{VHf} = 9.78$), and therefore the plot of the specific heat of VHf in the entire investigated temperature region lies above the curve for V. A comparison of the temperature dependence of the heat capacities of VW and VHf shows that introduction of 0.9 at. % of Hf in V leads to a much larger increase of the heat capacity than introduction of 5.2 at. %W in V.

This difference manifests itself most clearly in the temperature dependence of the relative change of the phonon specific heat, shown in Fig. 3 for the alloys VHf, VTa, and VW. Introduction into V of the impurity atoms Hf, Ta, and W, which are practically equal in mass, as follows from Fig. 3, deforms the phonon spectrum differently. For the VW alloy, a small maximum $\Delta C_{ph}/C_{ph}^V \sim 1.1$ is observed at $T_{max} \sim 29$°K (η is the impurity concentration. For the alloys of V with Ta and Hf, the maximum shifts towards lower temperatures ($T_{max} \sim 20$°K), and the maxima for VTa and for VHf are 5 and 10 times larger, respectively, than the maximum observed for VW.

Comparison of the experimental results with the theory[11] has explained the causes of the observed difference. Theoretical calculations of the relative change of the impurity part of the phonon specific heat, performed in accord with [11] using the real phonon spectrum obtained for V from data on inelastic neutron scattering[12] with allowance for the change of the force constants, have shown that for the VW alloy the force constants are approximately doubled, and in the VTa alloys the increase by ~30%. When Hf impurity atoms are introduced into V, the effective force constants are greatly weakened: $\gamma_1/\gamma_0 \sim 0.6$ ($\gamma_{1,0}$ denotes here the effective force constants; the subscripts 0 and 1 pertain to the atoms of the matrix and of the impurity). To illustrate the numerical estimates of the parameter γ_1/γ_0, Fig. 4 shows both the experimental data for VHf and the calculated curves corresponding to different values of γ_1/γ_0.

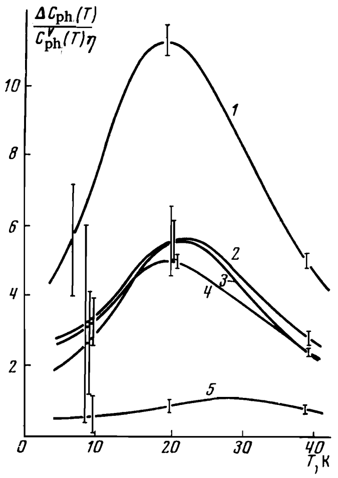

FIG. 3

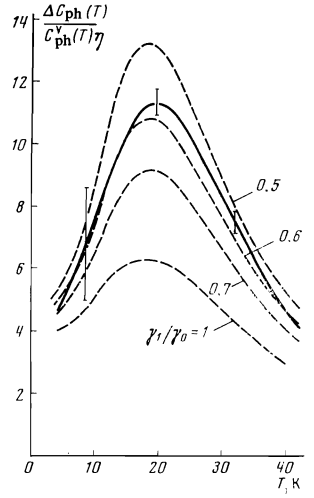

FIG. 4

FIG. 3. Temperature dependence of the relative change of the phonon specific heat of alloys of V with Hf, Ta, and W, normalized to the impurity concentration: 1—$V_{99.1}Hf_{0.9}$; 2—$V_{99.2}Ta_{0.8}$; 3—$V_{96.4}Ta_{3.6}$; 4—$V_{94.3}Ta_{5.7}$; 5—$V_{94.8}W_{5.2}$.

FIG. 4. Temperature dependence of the relative change of the phonon specific heat of the V-Hf alloy (solid curve). The dashed curves are theoretical and calculated from the spectrum of V, with allowance for the change in the effective force constants.

The experimental results on the temperature dependence of the relative change of the phonon specific heat point to the presence in the phonon spectrum of VHf, VTa, and VW of an impurity quasi-local mode and to an appreciable change in the effective local strength constants.

The experimental data obtained by measuring the heat capacity are given in Table I. It is seen from the table that introduction of the heavy impurity atoms W and Ta into the V lattice decreases T_c, γ, and Θ. Introduction of 0.9 at.% Hf into V leads to an increase of T_c, while γ remains practically constant and Θ decreases. Further, Table I lists the calculated characteristics of the phonon spectra of alloys and pure V obtained using the results of neutron measurements. Owing to the softening of the phonon spectrum by introduction of the impurity atoms Hf, Ta, and W into V, the average frequency $\langle\omega\rangle$ of the phonon spectrum decreases. The obtained experimental data have made it possible to analyze the influence of the deformation of the phonon spectrum on T_c.

The causes of the change of T_c in the systems V-Hf, V-Ta, and V-W can be explained on the basis of the superconductivity theory developed directly for irregular metals. The question of the change of the T_c in metals following introduction of impurity atoms was considered by Appel,[9] Maksimov,[10] and Zhernov et al.[3] The latter considered anew the problem of the influence exerted on T_c by impurity atoms, with account taken of the changes in both the phonon and the electron subsystems of the metal with impurity. The analytic expression obtained in [3] on the basis of the Éliashberg equations[13] show that the quantity T_c brought about by the presence of impurity atoms and describing the change of the transition temperature is a complicated function of the parameters characterizing the electron and phonon spectra. In the usual situation, for example in the case of pure V, the expression for T_c in [3] actually coincides with the McMillan formula.[6] Uf the impurity atoms distort strongly the phonon spectrum, particularly when a quasilocal mode appears in the latter, then McMillan's relation can in general not be used for the description of T_c. In this case we have

$$\delta T_c = \frac{T_c(\eta)-T_c(\eta=0)}{\eta T_c(\eta=0)} = A_1+A_2+A_3 \qquad (1)$$

(explicit expressions for the coefficients A_i are given in the Appendix).

The coefficients A_1 and A_2 in (1) are connected by the impurity renormalization of the electron-phonon coupling constant λ_0. The scale of A_1 is determined by the difference between the values of the amplitudes of the scattering of the electrons by the ions and the effective force constants. The quantity A_2 reflects the role of the renormalization of the density of the electronic states on the Fermi surface. The presence of the coefficient A_3 is the consequence of allowance for the frequency dependence of the energy-gap parameter when T_c is determined.

Besides the terms already mentioned, Eq. (1) contains one more term due to impurity isotropization of the energy gap.[14] The initial samples of V are characterized by a resistivity ratio $\rho(300\text{K})/\rho(T_c) \sim 24$, i.e., are not pure enough. Therefore when impurity atoms are introduced in V having this degree of purity there should be practically no change in the value of T_c, owing to the isotropization of the energy gap. In the calculations, this contribution to T_c is not taken into account.

The variation of T_c of the investigated VHf, VTa, and VW alloys was estimated using relations (1) and (A.3)–(A.7). The results of the calculation are listed in Table II. The values of the parameters in the expressions for the coefficients A_i were estimated in the following manner. The quantities γ_1/γ_0 and $N_\gamma(0)$ (the density of the electronic states on the Fermi surface) were determined from the measured values of the heat capacity, and the pseudopotential ratio $\langle v_1\rangle^2/\langle v_0\rangle^2$ was estimated from the measurements of the electric conductivity.

An analysis of the data of Table II shows good agreement between the experimental and theoretical values of the relative change of T_c, both in sign and in order of magnitude.

Experiment reveals a small increase of T_c of the alloy VHf. Our measurements of the heat capacity have shown that the electronic spectrum remains almost unchanged, therefore $A_2 \sim 0$. Owing to the anomalous increase of the density of the phonon states at low frequencies, we have $A_3 < 0$. In VHf, the effective force constants are reduced by almost one-half. As a result, A_1 is positive and relatively large. This causes an increase of T_c.

When Ta impurity atoms are introduced in V, the density of the electronic states on the Fermi surface decreases, and therefore A_2 is negative and relatively large. The interaction of the electron with the quasilocal mode also leads to a decrease of T_c, with $A_3 < 0$. In spite of the enhancement of the effective force constants, due to the fact that $\langle v_1\rangle^2/\langle v_0\rangle^2 > 1$, the quantity A_1 makes a small positive contribution to T_c. The experimentally observed decrease of T_c is due mainly to a restructuring of the electronic spectrum and to a lesser degree to deformation of the phonon spectrum.

In the VW alloy the density of the electronic states on the Fermi surface again decreases noticeably, $A_2 < 0$. The quasi-local mode in this system lie relatively high on the frequency scale, and therefore the $A_3 < 0$ and is numerically small. In spite of the fact that the ratio $\langle v_1\rangle^2/\langle v_0\rangle^2 > 1$, and owing to the abrupt enhancement of the effective force constants the coefficient A_1 is negative. All this leads to a decrease of T_c when the impurity atoms W are introduced into V.

Our investigations of the heat capacity of the alloys of V with Hf, W, and Ta[1, 2] lead to the following conclusion: Introduction of heavy impurity atoms leads to an anomalous temperature behavior of the impurity part of the phonon specific heat ΔC_{ph}. For impurity atoms with practically equal masses, however, the scale and position of the maximum of $\Delta C_{ph}/C_{ph}^{V}\,\eta$ turn out to be

Table I

Composition	$\frac{\rho(300\text{ K})}{\rho(T_c)}$	T_c, K		γ, $\frac{\text{mJ}}{\text{mole-K}}$	Θ, K	$\frac{\Delta C}{\gamma T_c}$	$\left(\frac{C_{es}}{C_{en}}\right)_{T_c}$	$\frac{\langle\omega\rangle}{\omega_0}$
		From heat capacity	From electric conductivity					
V	24	5.24	5.21	9.80	373	1.40	2.52	0.679
$V_{99,1}Hf_{0,9}$	29.5	5.34	5.35	9.78	368	1.44	2.45	0.676
$V_{96,4}Ta_{3,6}$	5.6	4.55	4.57	9.25	359	1.42	2.48	0.670
$V_{94,8}W_{5,2}$	3.8	4.08	4.08	9.36	364	1.22	2.25	0.662

Table II

Composition	$\frac{\gamma_1}{\gamma_0}$	$N_\gamma(0)$ (eV-at)$^{-1}$	$\frac{M_0}{M_1}$	$\frac{\gamma_1 M_0}{\gamma_0 M_1}$	$\frac{\langle v_1\rangle^2}{\langle v_0\rangle^2}$	A_1	A_2	A_3	δT_c	
									Calculation	Experiment
$V_{99,1}Hf_{0,9}$	0.6	2.07	0.286	0.17	1.48	4.93	−0.57	−1.96	0.02	0.02
$V_{96,4}Ta_{3,6}$	1.3	1.96	0.272	0.35	1.56	0.67	−4.12	−0.44	−0.14	−0.13
$V_{94,8}W_{5,2}$	2	1.98	0.280	0.55	1.64	−0.60	−2.26	−0.14	−0.16	−0.22

significantly different, owing to the change of the effective local force constants. The appearance in the phonon spectrum of a quasilocal mode, if the force constants for the impurity change weakly, leads generally speaking to the small negative corrections to T_c. In the case of a strong change of the local force constants, T_c changes appreciably.

The authors are grateful to L. I. Voronenko and L. F. Myzenkova for preparing the samples and to V. V. Stepanov for help with the measurements.

APPENDIX

The phonon spectrum of a metal with impurity ions can differ significantly from the spectrum of the matrix. An expression obtained in [3] for T_c makes it possible to estimate the scale of the correction to T_c due to the deformation of the spectrum in the general case. For a direct analysis of the behavior of T_c in the presence of impurity modes in the vibrational spectrum, it is necessary to know the form of the kernel of the Éliashberg integral equation, $\alpha^2F(\omega)$. Bearing in mind the qualitative aspect of the phenomenon, we choose the simplest model. We assume the spectrum to consist of two Einstein modes. The frequencies of these modes are determined approximately by the average phonon frequency of the unperturbed crystal lattice ω_0 and by the value of the characteristic frequency ω_1 of the oscillations of the impurity atom. (Here and below, the subscripts 0 and 1 label quantities pertaining to the host-lattice and impurity atoms, respectively.) It is assumed that the frequencies ω_0 and ω_1 are of the same order. There is a simple connection between the frequencies ω_0 and ω_1. If we denote by γ the effective force constant and by M the mass of the atom, then

$$\omega_1^2/\omega_0^2=\gamma_1 M_0/\gamma_0 M_1. \qquad (A.1)$$

Taking the foregoing into account and making use of the results obtained for $\alpha^2F(\omega)$ in [15], we have

$$\alpha^2F(\omega)=N_c\left\{(1-\eta)\frac{\langle\langle v_0^2\rangle\rangle}{M_0}\delta(\omega^2-\omega_0^2)+\eta\frac{\langle\langle v_1^2\rangle\rangle}{M_1}\delta(\omega^2-\omega_1^2)\right\}, \qquad (A.2)$$

where η is the concentration of the impurities and $\langle\langle v^2\rangle\rangle$ is the electron-ion pseudopotential twice-averaged over the Fermi surface.

We substitute (A.2) in formula (19) of [3] for T_c. Simple transformations yield for the coefficients A_i in (1) the relations

$$A_1=\left(\frac{\gamma_0}{\gamma_1}\frac{\langle\langle v_1^2\rangle\rangle}{\langle\langle v_0^2\rangle\rangle}-1\right)\left(\frac{g_0^2}{\lambda_0}+\tilde{\mu}_*^{(0)}\frac{\lambda^0}{1+\lambda_0}\right)(g_0-\tilde{\mu}_*^{(0)})^{-2}, \qquad (A.3)$$

$$A_2=\left(\frac{g_0^2}{\lambda_0}+\tilde{\mu}_*^{(0)}\frac{\lambda_0}{1+\lambda_0}-\frac{\tilde{\mu}_*^{(0)}\mu_*^{(0)}}{\mu_0}\right)(\sigma-\tilde{\mu}_*^{(0)})^{-2}\frac{N(\eta)-N(\eta=0)}{\eta N(\eta=0)} \qquad (A.4)$$

$$A_3=\frac{g_0^2}{(g_0-\tilde{\mu}_*^{(0)})^2}\frac{\gamma_0}{\gamma_1}\frac{\langle\langle v_1^2\rangle\rangle}{\langle\langle v_0^2\rangle\rangle}\left[1+\left(\frac{1}{1-\gamma_1M_0/\gamma_0M_1}-\frac{\tilde{\mu}_*^{(0)}}{g_0}\right)\ln\frac{\gamma_1M_0}{\gamma_0M_1}\right]. \qquad (A.5)$$

We have introduced here the notation

$$g_0^{-1}=\lambda_0^{-1}+1.5, \qquad (A.6)$$

$$\tilde{\mu}_*^{(0)}=\frac{\mu_*^{(0)}}{1+\lambda_0},\qquad \mu_*^{(0)}=\frac{\mu_0}{1+\mu_0\ln(\varepsilon_F/\omega_0)}, \qquad (A.7)$$

λ_0 is the constant of the electron-phonon coupling for a regular superconductor, μ_0 is the Coulomb-interaction matrix element averaged over the Fermi surface and multiplied by the density N (η = 0) of the normal electronic states.

We call attention to the following circumstance. Since usually $\lambda_0 \gg \mu_*^{(0)}$, we can use instead of Eqs. (A.3)–(A.5) the set of equations

$$A_1=\left(\frac{\gamma_0}{\gamma_1}\frac{\langle\langle v_1^2\rangle\rangle}{\langle\langle v_0^2\rangle\rangle}-1\right)\Big/\lambda_0', \qquad (A.8)$$

$$A_2=[N(\eta)-N(\eta=0)]/\eta N(\eta=0)\lambda_0', \qquad (A.9)$$

$$A_3=\frac{\gamma_0\langle\langle v_{12}\rangle\rangle}{\gamma_1\langle\langle v_0^2\rangle\rangle}\left(1+\frac{\ln(\gamma_1M_0/\gamma_0M_1)}{1-\gamma_1M_0/\gamma_0M_1}\right). \qquad (A.10)$$

The constant λ_0' is defined by the formula

$$\lambda_0'=\ln\left(\frac{\omega_0}{3.92T_c^{(0)}}\right). \qquad (A.11)$$

---

[1] N. A. Chernoplekov, G. Kh. Panova, B. N. Samoĭlov, and A. A. Shikov, Zh. Eksp. Teor. Fiz. 63, 1381 (1972); 64, 195 (1973) [Sov. Phys.-JETP 36, 731 (1973); 37, 102 (1973)].
[2] N. A. Chernoplekov, Doctoral dissertation, Atomic Energy Inst., 1975.
[3] A. P. Zhernov, G. Kh. Panova, and Yu. A. Malov, Zh. Eksp. Teor. Fiz. 69, 255 (1975) [Sov. Phys.-JETP 42, 131 (1976)].
[4] Yu. Kagan and Ya. Iosilevskiĭ, Zh. Eksp. Teor. Fiz. 42, 259 (1962); 45, 610 (1963) [Sov. Phys.-JETP 15, 182 (1962); 18, 419 (1964)].
[5] N. A. Chernoplekov and M. G. Zemlyanov, Zh. Eksp. Teor. Fiz. 49, 449 (1965) [Sov. Phys.-JETP 22, 315 (1966)].
[6] W. L. McMillan, Phys. Rev. 167, 331 (1968).
[7] P. B. Allen and M. L. Cohen, Phys. Rev. 187, 525 (1969).
[8] M. V. Medvedev, É. A. Pashitskiĭ, Yu. S. Pyatiletov, Zh. Eksp. Teor. Fiz. 65, 1186 (1973) [Sov. Phys.-JETP 38, 587 (1974)].
[9] J. Appel, Phys. Rev. 165, 421 (1967).
[10] E. G. Maksimov, Pis'ma Zh. Eksp. Teor. Fiz. 9, 527 (1969) [JETP Lett. 9, 319 (1969)].
[11] A. P. Zhernov and G. R. August, Fiz. Tverd. Tela 9, 2196 (1967) [Sov. Phys. Solid State 9, 1724 (1968)].
[12] N. A. Chernoplekov, M. G. Zemlyanov, and A. G. Chicherin, Zh. Eksp. Teor. Fiz. 43, 2080 (1962) [Sov. Phys.-JETP 16, 1472 (1962)].
[13] G. M. Eliashberg, Zh. Eksp. Teor. Fiz. 38, 966 (1960); 39, 1437 (1960) [Sov. Phys.-JETP 11, 696 (1960); 12, 1000 (1961)].
[14] D. Markowitz and L. P. Kadanoff, Phys. Rev. 131, 563 (1963).
[15] Yu. Kagan and A. P. Zhernov, Zh. Eksp. Teor. Fiz. 50, 1107 (1966) [Sov. Phys.-JETP 23, 737 (1966)].

Translated by J. G. Adashko
195