

to understand the specifics of the phenomenon of exciton condensation in thin and thick germanium samples.

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¹The observed phenomena cannot be attributed to overheating of the sample by the laser light, since the exciton line present at 4.2 °K was not observed at 1.8 °K, and the width of the cyclotron resonance lines at $I \approx I_{thr}$ was much less at 1.8 °K than at 4.2 °K.

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Effect of impurity oscillations on the superconducting transition point in dilute U or Be solutions in V

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The specific heat of the alloys $V_{97.2}U_{2.8}$ and $V_{96.9}Be_{3.1}$ was measured in the temperature range 1.2-40°K without a field and in fields of 18 and 40 kOe at 1.2-6°K. An anomalous behavior was observed in the phonon specific heat, related to the appearance of quasilocal and local oscillations in the phonon spectrum upon the introduction in the V of heavy impurity atoms of U and light atoms Be. The effect of modification of the phonon spectrum on T_c is studied. Estimate of the scale of change of T_c from deformation of the phonon spectrum showed that softening of the phonon spectrum in the alloy $V_{97.2}U_{2.8}$ leads to a decrease in T_c ; on the other hand, hardening of the spectrum of $V_{96.9}Be_{3.1}$ gives a positive contribution to δT_c .

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1. INTRODUCTION

As follows from a theoretical analysis,^[1] the transition temperature T_c of superconductors with tight binding depends essentially on the details of the phonon spectrum. For the study of the connection between the deformations of the phonon spectrum and T_c , the weak solid substitution solutions are of interest, in which the mass of the impurity atoms differs markedly from the mass of the matrix atoms. It is well known that in such impurity systems, quasilocal and local modes can exist and the phonon spectrum turns out to be anomalously restructured. The possibility of the existence of specific impurity modes was predicted by I. Lifshitz^[2] and Yu. Kagan.^[3] These modes were discovered experimentally in a number of metals in the measurement of inelastic neutron scattering,^[4,5] low-tem-

perature specific heat,^[5,6] electric conductivity,^[7] and tunnel characteristics.^[8]

The problem of the change in T_c in metals due to direct deformation of the phonon spectrum by impurity modes has been studied theoretically in a number of researches. The analysis was carried out on the basis of the Eliashberg equations.^[9] Appel^[10] carried out an analysis using a model description of the kernel of the integral of the Eliashberg equation. The form of the characteristic function α of the electron-phonon interaction was not specified. Actually, however, the value of α depends on the relation between the characteristic phonon frequency of the regular lattice and that of the alloy. The results of Appel were criticized by Maksimov^[11] who, analyzing the behavior of T_c in impurity systems, obtained a formula for T_c similar to the for-

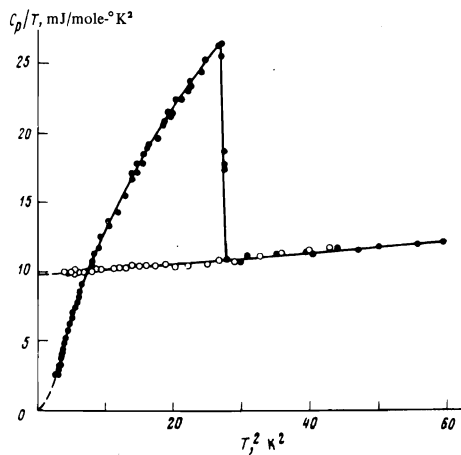


FIG. 1. Specific heat of pure V: ●—without field and ○—in a field of 18 kOe.

mula of McMillan,^[1] In particular, he showed that if the impurity atom is an isotopic defect, then the electron-phonon interaction constant does not change.

The character of the change of T_c in superconductors with impurity atoms was analyzed in detail in^[12] and the dependence of T_c on parameters describing the phonon spectrum of the impurity system was investigated. An expression for T_c was obtained with account of the frequency dependence of the parameter of the energy gap Δ . We turn our attention to the fact that McMillan,^[1] in the derivation of his well-known expression for T_c , neglected the frequency dependence of Δ . We note that Δ as a function of frequency generally has the same singularities as the function of the density of phonon states of the non-regular lattice. When account is taken in the expression for T_c of the singularities of $\Delta(\omega)$ that are due to the presence of impurity atoms, of the factor preceding the exponential is re-determined. (In most superconductors, the effective electron-phonon coupling constant is not small, and the value of T_c is determined to an equal degree by the values of the exponential and pre-exponential factors.) The indicated change turns out to be especially important in the presence of specific impurity modes in the vibrational spectrum. It was shown in^[12] that if the effective force constants change simultaneously when quasilocal and local modes appear, then this causes a perceptible renormalization of λ , too.

We have undertaken a systematic study of the connection between the restructuring of the phonon spectrum and the temperature of the T_c transition to the superconducting state. The effect of deformation of the phonon spectrum on T_c upon introduction of Ta, W and Hf impurity atoms into V was studied in^[13,14]. According to^[14], quasilocal oscillations in the phonon spectrum of the alloy $V_{94.3}Ta_{5.7}$ were revealed by the inelastic scattering of cold neutrons. The anomalous behavior of the phonon specific heat in the range of low temperatures of alloys of V with Ta also indicates a restructuring of the phonon spectrum in the region of low frequencies. Similar anomalies in the phonon specific heat were observed in alloys of V with Hf and W. In these systems, the softening of the phonon spectrum

led to a decrease in T_c .

In the present work, the results are given of the measurement of the specific heat of the alloys $V_{97.2}U_{2.8}$ and $V_{96.9}Be_{3.1}$ in the range 1.2–40°K. We note that, from estimates in the alloy of V with U, the characteristic frequency of the quasilocal mode should be considerably lower on the frequency scale than in alloys of V with Ta, W and Hf. Therefore, all the anomalies in the behavior of thermodynamic characteristics in the V–U system because of the quasilocal modes should be especially clearly pronounced.

In the V–Be system, the local modes were observed directly in the study of inelastic neutron scattering.^[15] Consequently, it was interesting to see how the hardening of the phonon spectrum because of the light impurities affects the value of T_c .

2. CHARACTERISTICS OF SAMPLES, RESULTS OF MEASUREMENTS AND THEIR DISCUSSION

The measurements of the low-temperature specific heat of the alloys $V_{97.2}U_{2.8}$ and $V_{96.9}Be_{3.1}$ were carried out in a vacuum adiabatic calorimeter with a superconducting solenoid^[13] in the temperature range 1.2–40°K in the absence of a field and at fields of 18 and 40 kOe in the temperature range 1.2–6°K.

The samples of the alloys $V_{97.2}U_{2.8}$ and $V_{96.9}Be_{3.1}$ were prepared from vanadium of type VEL-2, subjected to additional zone purification in a vacuum of 10^{-6} mm Hg in an electron-beam furnace. The alloy of V with U was smelted in the electron-beam furnace on a water-cooled copper pan in an argon atmosphere. For a uniform distribution of the U, the sample was turned over several times and remelted, after which it was quenched. The alloy $V_{96.9}Be_{3.1}$ was prepared in an induction oven in a vacuum of 10^{-5} mm Hg. For homogenization, the sample was subjected to annealing at a temperature of 1650° for a period of 10 hr with subsequent rapid cooling.

Data of x-ray and metallographic analyses showed that the investigated samples are single-phase and represent solid solutions. The content of U, Be, and foreign impurities in the vanadium was determined by chemical and spectral analyses. According to these analyses, the total content of foreign impurities did not exceed 0.03%.

The results of measurements of the temperature dependence of the specific heat of the pure vanadium and its alloys with U and Be, without field and in fields of 18 and 40 kOe, in the temperature range 1.2–8°K, are shown in Figs. 1–3 in the coordinates C/T and T^2 . The temperature of the superconducting transition T_c , the width of the transition ΔT_c , and the value of the jump $\Delta C/\gamma T_c$ were determined from the jump in the specific heat in measurements in the absence of field. To calculate the coefficient of the electronic specific heat γ and the Debye temperature Θ , it was necessary to destroy the superconductivity of the samples and carry out measurements of the specific heat in the normal state down to 1.2°K. It turned out here that the fields

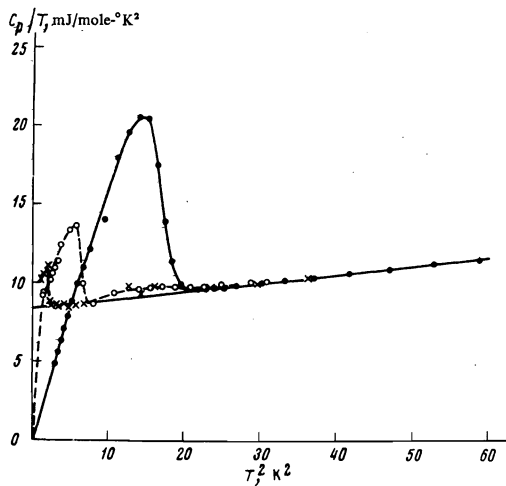


FIG. 2. Specific heat of the alloy $V_{97.2}U_{2.8}$: ●— $H=0$, ○— $H=18$ kOe, — $H=40$ kOe.

of 18 and 40 kOe were insufficient to destroy the superconductivity of the alloy of V with U. The alloy of V with U remained a hard superconductor.

From the location of the jumps in the specific heat without field and in fields of 18 and 40 kOe, the critical field of this alloy was calculated. It turned out that $H_{c2} \sim 50$ kOe. The dependence $H_{c2}(T)$ for the alloy of V with U is shown in Fig. 4.

Figure 5 shows the results of measurements of the specific heat of pure V and its alloys with U in the range 1.2–30° K and with Be in the range 1.2–40° K in the normal state. As is seen from this drawing, the introduction of 2.8 at. % U into the V lattice leads to a sharp increase in the specific heat in all temperature ranges studied, with the exception of the low-temperature region. In the region of low temperatures, the specific heat of the V–U system is substantially smaller than the specific heat of V because of the decrease in the electron specific heat. In the case of V–Be, the picture turns out to be qualitatively different. The introduction of 3.1 at. % Be into the lattice of vanadium leads to a decrease in the total specific heat over the entire

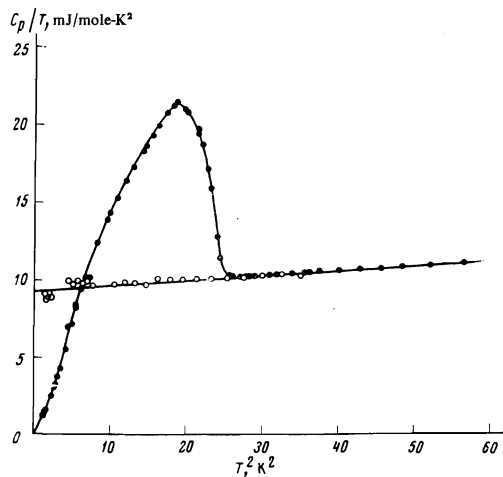


FIG. 3. Specific heat of the alloy $V_{96.9}Be_{3.1}$: ●— $H=0$, ○— $H=18$ kOe.

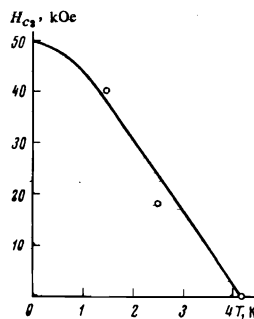


FIG. 4. Dependence of H_{c2} on T for the alloy $V_{97.2}U_{2.8}$.

range of temperatures studied.

The effect of the impurity atoms on the restructuring of the phonon spectrum appears most graphically in the temperature dependence of the relative change of the phonon specific heat

$$\Delta C_{ph}(T)/\eta C_{ph}^{(0)}(T), \quad \Delta C_{ph} = C_{ph}(\eta) - C_{ph}^{(0)}(0)$$

(where $C_{ph}^{(0)}$ is the phonon component of the specific heat of the lattice, and η the concentration of the impurity). As is well known (see, for example,^[16]) if specific impurity modes develop in the phonon spectrum, then this leads to singularities of the low-temperature behavior of the specific heat ΔC_{ph} . The presence of a sharp maximum in the curve $\Delta C_{ph}(T)/\eta C_{ph}^{(0)}(T)$ for $T \sim 12^\circ$ K for the alloy of V with U indicates the appearance of a quasi-local mode in the phonon spectrum of this system.^[16,17] In the case of the V–Be system, the observed behavior of ΔC_{ph} is connected with the decrease in the density of phonon states in the long-wavelength portion of the spectrum; these data enable us to assume the presence of local modes in the V–Be spectrum in agreement with the results of the work of Mozer.^[15]

Theoretical calculations, carried out for the systems V–U and V–Be show that the restructuring of the phonon spectrum is connected not only with the difference in

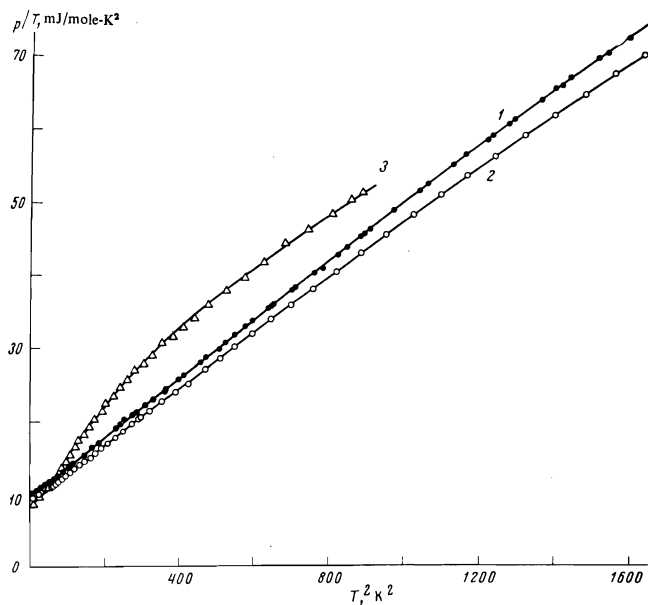


FIG. 5. V and its alloys with U and Be in the normal state in the region of 1.2–40° K: 1—V, 2— $V_{96.9}Be_{3.1}$; 3— $V_{97.2}U_{2.8}$.

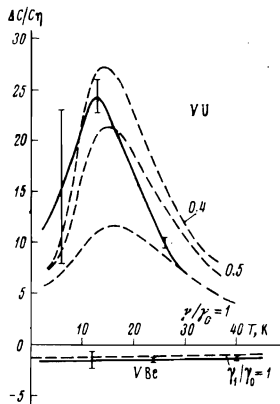


FIG. 6. Temperature dependence of the relative change in the phonon specific heat of the alloys $V_{97.2}U_{2.8}$ and $V_{96.5}Be_{3.5}$, normalized to the concentration: continuous curves—experimental; dashed curves—theory with account of the change in the effective force constants.

the masses of the impurity atoms and the atoms of the matrix, but also with the change in the effective force constants. The results of the calculations are given in Fig. 6 by the dashed lines. The anomalously large increase in the phonon specific heat for the alloy of V with U is connected with the difference in the masses of the atoms and with the sharp decrease in the force constants ($\gamma_1/\gamma_0 \sim 0.45$). In the alloy of V with Be, the force constants change comparatively little ($\gamma_1/\gamma_0 \approx 0.8$). (By γ_1 and γ_0 , we mean the effective force constants for the impurity atom and the atom of the matrix.)

We now proceed directly to the discussion of the effect on the value of T_c of vanadium atoms for the impurity atoms U and Be. The experimental results are given in Table 1. In this table we also show the values of T_c obtained from measurements of the electrical conductivity. As is seen, the introduction of the impurity atoms of U and Be in V leads to a decrease in T_c that is significant for the V-U system and insignificant for V-Be. The coefficient of the electron specific heat γ falls off, the Debye temperature Θ falls off significantly for V-U and insignificantly for V-Be.

In order to represent the scale of the change of T_c due to the appearance of quasilocal modes in the phonon spectrum of V-U and of local modes in V-Be, we have estimated this contribution on the basis of the results

TABLE 1.

	V	$V_{97.2}U_{2.8}$	$V_{96.5}Be_{3.5}$
$\rho(300\text{ K})/\rho(T_c)$	24	2.2	9.7
$T_c, \text{ K}^*$	I 5.24	4.16	4.86
	II 5.21	4.30	4.89
$\Delta T_c, \text{ K}^{**}$	0.2	0.6	0.5
$\gamma, \text{ mJ/mole-K}^2$	9.80	8.30	9.10
$\Theta, \text{ K}$	373	323	378
$\Delta C/\gamma T_c$	1.40	1.04	0.95
$(C_{es}/C_{em})_{T_c}$	2.52	2.25	2.22

*Here I— T_c obtained from measurements of the specific heat; II—from measurements of the electrical conductivity.

** ΔT_c is the width of the superconducting transition.

TABLE 2.

	$V_{97.2}U_{2.8}$	$V_{96.5}Be_{3.5}$
γ_1/γ_0	0.45	0.80
$N(\epsilon_F), (\text{eV}^{-1} \text{at})^{-1}$	1.76	1.93
M_0/M_1^*	0.21	5.86
$\gamma_1 M_0/\gamma_0 M_1$	0.10	4.53
$\langle a_1^2 \rangle/\langle a_0^2 \rangle$	2.10	1.44
A_1	0.35	0.06
A_2	-0.40	-0.19
A_3	-0.22	-0.02
$(\delta T)_{\text{calc}}$	-0.27	-0.09
$(\delta T)_{\text{exp}}$	-0.21	-0.07

* M_0 and M_1 are the mass of the matrix atom and the impurity atom, respectively.

of the earlier work.^[12] Since the ratio $\rho(300\text{ K})/\rho(T_c) \approx 24$ for the initial samples of V, the contribution to T_c from the impurity isotropization of the energy gap was not taken into account. Then, in account with^[12,13] the relative change is determined by the contribution of three terms:

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

A few words are necessary on the coefficients A_i . The quantity A_1 is determined by the ratio of the effective scattering amplitudes of the electrons and the force constants of the atoms of the impurity and of the initial matrix, and A_2 reflects the role of the renormalized electron states on the Fermi surface. The coefficient A_3 describes the effect on T_c of the impurity modes. The analytic expressions for A_1 , A_2 and A_3 are given in^[18] (Eqs. P. 3–P. 5).

The value of the parameters entering into the expressions for A_i in^[18] and also the coefficients A_i for the investigated alloys are given in Table 2. We note that the values of γ_1/γ_0 and $N(\epsilon_F)$ are obtained from data on the measurement of the specific heat and the ratio $\langle\langle a_1^2 \rangle\rangle/\langle\langle a_0^2 \rangle\rangle$, where a_1 and a_2 are the scattering amplitudes of electrons on the impurity atom and the matrix atom, as estimated from results on the measurement of the electrical conductivity. As is seen from Table 2, excellent agreement is observed between the experimental and theoretical values of the relative change of T_c , both in sign and in order of magnitude.

In the V-U system, the contribution to T_c due to the difference in the scattering amplitudes and the force constants is positive ($A_1 > 0$) since $a_1 > a_0$ and $\gamma_1 < \gamma_0$. Decrease in the density of normal electron states on the Fermi surface $N(\epsilon_F)$ leads to the result that the coefficient A_2 becomes negative. Because of the radical restructuring of the frequency dependence of the parameter of the energy gap $\Delta(\omega)$ in the range of low frequencies, brought about by the presence of quasilocal modes, the coefficient A_3 is large in magnitude and negative in sign. In other words, the softening of the phonon spectrum leads to a decrease in T_c . We note that the coefficients A_1 , A_2 , and A_3 are similar in value. As a result of the above, it follows that the falling off of T_c in the V-U system can be explained if we take

simultaneously into account the deformations of the phonon and electron spectra.

In the V-Be system, the picture is as follows. Since $a_1 > a_0$ and $\gamma_1 < \gamma_0$, the coefficient A_4 is positive. The correction to T_c due to the restructuring of the electron spectrum (A_2) is negative. The presence of a local mode in the phonon spectrum is responsible for the substantial change in the form of the frequency dependence of the parameter of the energy gap in the high frequency region. The hardening of the phonon spectrum brought about by this leads to a positive contribution A_3 to δT_c . The coefficients A_1 and A_2 are close in value. It follows from the consideration given that the negative sign of δT_c in the V-Be system is connected with the decrease in the density of the normal electron states on the Fermi surface. Renormalization of the value of the effective scattering amplitudes and hardening of the phonon spectrum essentially cancel the contribution to δT_c from the renormalization of $N(e_F)$.

3. CONCLUSION

As a result of the study of the low-temperature specific heat of alloys of V with U and Be in this work, and alloys of V with Hf, Ta and W in^[13,14], we can draw the following conclusions.

1. The softening of the phonon spectrum because of the heavy impurity atoms leads to a significant drop in T_c . On the other hand, upon the introduction of light impurities, i. e., in a situation in which the spectrum is hardened, the corresponding contribution to T_c turns out to be positive.

2. In the considered systems, as it turns out, the effective force constants are considerably reduced. This change has a significant effect on the value of the effective electron-phonon interaction constant. The great weakening of the force constants, which is observed in the systems V-Hf and V-U, promote an increase in T_c . The increase in the force constants, as, for example, in the case of V-W, decreases T_c .

3. In alloys based on vanadium, the changes of T_c because of the appearance of specific impurity modes in the phonon spectrum and the redistribution of the density of normal electron states on the Fermi surface have the same order of magnitude.

4. As follows from the given analysis, in weak solutions, where the atoms of the second component are light and simultaneously the effective force constants are significantly weakened, the resultant deformation of the phonon spectrum leads to an increase in T_c .

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