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CHANGE OF THE VANADIUM PHONON SPECTRUM FOLLOWING INTRODUCTION OF TANTALUM ADMIXTURES

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The specific heats of pure V and its alloys containing Ta($V_{99.18}Ta_{0.82}$, $V_{96.45}Ta_{3.55}$, $V_{94.32}Ta_{5.68}$) are measured between 1.5 and 40°K. The electron specific heat coefficient γ and the Debye temperature Θ are determined from measurements of the specific heat in a magnetic field of ~ 18 kOe and at temperatures 1.5–6°K. Maxima at ~ 20°K are observed in the relative variation $\Delta C(T)/C_0(T)$ of the alloy and pure vanadium phonon specific heats. The maxima are related to the appearance, in the alloy phonon spectrum, of quasilocal oscillations due to the introduction of heavy Ta impurity atoms into the V lattice. The experimental values of $\Delta C(T)/C_0(T)$ are compared with those calculated by employing various vanadium phonon spectra in the isotopic approximation as well as by taking into account variation of the force constants. The experimental data can satisfactorily be described by a V phonon spectrum determined from inelastic neutron scattering data on the assumption that the force constants for interaction between the impurity atom and its closest neighbors exceed the atomic interaction constants in the initial lattice by ~ 30%.

1. INTRODUCTION

FOLLOWING publication of McMillan's paper[1], interest has increased in the connection between a change of the phonon spectrum of a metal and the temperature of its transition to the superconducting state. This connection is of particular interest for transition metals and alloys on their basis, since the mechanism of the interaction between the electrons, which is responsible for the onset of superconductivity[2], has not yet been fully explained.

One of the simplest ways of obtaining the predicted deformation of the phonon spectrum of the crystal is by introducing in it substitution impurity atoms with mass m′ greatly different from the mass m of the atoms in the initial lattice. If an impurity with $m' \ll m$ is introduced into the crystal, then the density of states in the low-frequency region decreases in the phonon spectrum of the crystal with the impurity, and a local oscillation (LO) is produced in the forbidden region above the maximum frequency of the allowed spectrum of the normal vibrations[3]. The frequency of the local oscillation is farther from the end point of the unperturbed phonon spectrum of the initial lattice the larger the difference between the masses of the impurity and matrix atoms, and the stronger the impurity atom is bound in the real crystal. The atom displacements in the local oscillation decrease exponentially with increasing distance from the impurity site.

If a heavy impurity atom with $m' \gg m$ is introduced into the crystal, the density of states in the phonon spectrum of the real crystal decreases in the high-frequency region, and a quasilocal oscillation (QLO) is produced in the allowed low-frequency region of the spectrum[4,5]. The QLO is lower the heavier the impurity atoms and the weaker its binding in the crystal. As shown by Kagan and Zhernov[6], the QLO play a more noticeable role in the change of the physical properties of the crystals with impurities than the LO.

Among the possible experimental methods of investigating LO and QLO (coherent and incoherent inelastic neutron scattering, the Mössbauer effect, scattering and absorption of light, tunnel spectroscopy of superconductors, measurements of the low-temperature specific heat, of the electric conductivity, of the thermal conductivity, etc.), special mention should be made of two methods, inelastic scattering of neutrons and measurement of the low-temperature specific heat. They are applicable to any crystal, be it a metal or nonmetal, and taken together they make it possible to determine uniquely the changes of the phonon and electron spectra of the crystal following the introduction of impurity atoms. The first direct experimental observations of QLO in crystals with heavy impurity atoms[7-10] were made by these methods.

To study the connection between the deformation of the phonon spectrum of a metal and its superconducting transition temperature T_c, it is natural to use the simplest impurity systems, namely, dilute substitutional solid solutions in which the mass of the atom of the dissolved matter differs greatly from the mass of the solvent atom. The changes of the metal phonon and electron spectra, accompanying the introduction of the impurity atoms, can be investigated by one or several of the already mentioned experimental methods.

In the present paper, to determine the changes of the phonon and electron spectra of vanadium following the introduction of heavy isoelectronic Ta impurity atoms, we measured the low-temperature specific heat of pure vanadium and its dilute alloys with Ta at concentrations 0.82, 3.55, and 5.68 at.% Ta. The choice of vanadium as the initial matrix was dictated by a number of considerations. Vanadium itself and many of its alloys and compounds are characterized by high values of T_c. The phonon spectrum of vanadium was rigorously reconstructed, without the use of a model, from the measurements of inelastic incoherent scattering of cold neutrons[11].

Attempts were made to determine experimentally the phonon-spectrum deformation, due to the introduction of the impurity, for several dilute substitution solutions based on vanadium, including diluted alloys with Ta, using inelastic incoherent neutron scattering. Unfortunately, the results did not yield definite quantitative data on the QLO in the crystal with impurities, but a weak change in the low-frequency region of the phonon spectrum was observed. Thus, measurements of the low-temperature specific heat of the investigated alloys, in conjunction with data on the inelastic scattering of neutrons, permit a quantitative determination of the changes produced in the phonon and electron spectra of vanadium by introducing Ta impurity atoms.

2. EXPERIMENT AND DESCRIPTION OF SAMPLES

To measure the specific heat we used an adiabatic calorimetric setup, with which we could perform measurements in the temperature interval 1.2—40°K in magnetic fields up to 18 kOe. The calorimeter was equipped with two vacuum jackets, from which the heat-exchange gas was evacuated with adsorption pumps. The outer jacket with outside diameter 60 mm was placed in the cavity of a superconducting solenoid operating at 4.2°K; the inner jacket contained an additional volume with liquid helium, the pumping of which has made it possible to lower the temperature of the sample to ~ 1.2°K. The sample was suspended on capron filaments inside heat screens. The outer screen was fused to the evacuated helium volume, and the inner screen was suspended on capron filaments and was equipped with a heater, so that measurements could be performed under good adiabatic conditions at temperatures much higher than the bath temperature.

The sample temperatures were measured with thoroughly calibrated germanium (2.5—20°K) or platinum (1.5—40°K) resistance thermometers[1]. At the lowest temperatures, we used a carbon resistor made by the Speer Resistor Company. For measurements in a magnetic field, we used a calibration obtained in special experiments, in which the resistances of both thermometers before and after turning on the field were measured at constant temperature. The calibration of the Speer Resistor thermometer, in which the value of the temperature was determined either from measurements with a germanium thermometer or from measurements of the vapor pressure, was used to determine the coefficients a and b in the expansion in accordance with the Klemens formula:

$$(T^{-1}\lg R)^{1/2} = a + b \lg R.$$

The use of germanium and platinum thermometers, of a null measuring circuit with an R-308 potentiometer, and of a reliable adiabatic setup has ensured sufficiently high accuracy in the measurement of the specific heat. The error connected with the evaluation of the temperature drift before and after heating to determine ΔT, and with the determination of the supply power ΔQ, did not exceed 0.3%. A systematic error resulted from the inaccuracies in the determination of the extraneous specific heat (the specific heat of the thermometers, of the heater, of the BF-2 adhesive, and of the copper foil) and from the error in the determination of the number of moles in the sample, which was calculated from the chemical analysis of the alloys. The error in the determination of the molar specific heat was estimated by us at 0.5% in the regions 1.2—5 and 20—40°K and at 2% in the interval 2—20°K. It should be noted that the influence of the systematic error on the relative change of the phonon specific heat of the alloy and of pure vanadium is small in practically the entire temperature interval, because the error enters in the measured quantities in like fashion.

The samples were made of brand VEL-2 vanadium subjected to additional zone purification in a vacuum of 10^{-6} mm Hg. The VTa alloys were prepared in the same electron-beam furnace. Samples of 18—20 mm diameter and 50 mm length were cut from the obtained ingots. To remove the mechanical surface stresses, the samples were annealed in a stream of evaporating helium for six hours at a temperature of 1000°C, and were then slowly cooled.

The contents of the Ta in the vanadium and of the extraneous impurities were determined by chemical and spectral analysis. The spectral analysis has shown that the content of extraneous metallic impurities (W, Mo, Zr, Nb, Ni, Fe, Cr, Ca, Co, Mn, Al, B) is less than 0.3%. The resistance ratios $R_{300°K}/R_{T_c}$ for pure V, $V_{99.18}Ta_{0.82}$, $V_{96.4}Ta_{3.55}$, and $V_{94.32}Ta_{5.68}$ were respectively 24, 9.6, 5.6, and 4.8.

The x-ray structure analysis data indicate that the investigated alloys are single-phase and constitute a solid solution on the basis of the BCC lattice of V; the lattice constants a for V and its alloys were 3.029 ± 0.003, 3.031 ± 0.003, 3.037 ± 0.003, and 3.049 ± 0.005 Å, respectively.

The single-phase character of the samples was confirmed by a metallographic analysis.

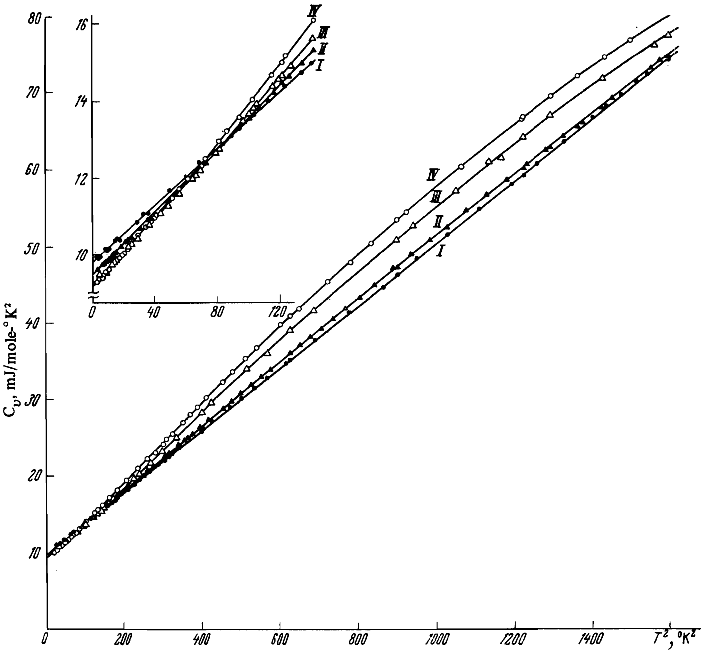

FIG. 1. Specific heat of V and of its alloys with Ta (I—V; II—$V_{99.18}Ta_{0.82}$; III—$V_{96.45}Ta_{3.55}$; IV—$V_{94.32}Ta_{5.68}$) in the normal state.

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3. MEASUREMENT RESULTS AND DISCUSSION

We have measured the specific heat of pure vanadium and of its alloys with Ta ($V_{99.18}Ta_{0.82}$; $V_{96.45}Ta_{3.55}$; $V_{94.32}Ta_{5.68}$) without the magnetic field in the temperature interval from 1.5 to 40°K and in a field ~ 18 kOe in the interval 1.5—6°K. The superconducting transition temperature T_c was determined from the jump in the specific heat when the sample became superconducting. The electronic specific-heat coefficient γ and the Debye temperature Θ were calculated from measurements of the specific heat in the magnetic field. The results of the measurements of the specific heat of pure vanadium and its alloys with Ta in the normal state in the interval 1.5—40°K, plotted in coordinates C/T and T^2 are shown in Fig. 1 and in the table. As seen from the table, T_c varies strongly in these systems with increasing Ta content. These data are in satisfactory agreement with measurements of the low-temperature specific heat of V alloys with high Ta content, performed by others[14,15] and extrapolated to the low-concentration region. A decrease of T_c, Θ, and γ with increasing Ta concentration was observed on going from pure vanadium to vanadium alloyed with Ta.

Attention is called to the following peculiarity of the experimental curves (see Fig. 1). With increasing Ta concentration in the alloys, the dependence of C_V/T and T^2 deviates more and more from a straight line and turns into a curve with positive curvature. This is a manifestation of the ever increasing influence of the QLO on the specific heat of the alloy. It is appropriate to note here that, as seen from Fig. 1, when $\Theta(T = 0)$ and γ in systems with heavy impurity atoms, similar to the investigated system, are determined by extrapolation from the temperature region 5—10°K the errors can be appreciable.

The influence of the QLO on the specific heat of a crystal with heavy impurity atoms is seen most clearly in the temperature dependence of the quantity $\Delta C_V(T)/C_V^0(T)$, where $\Delta C_V(T)$ is the difference between the phonon specific heats of the alloy and of the initial vanadium, and $C_V^0(T)$ is the phonon specific heat of the initial vanadium. For the impurity atom and its nearest perturbing neighbors, which oscillate in a relatively narrow interval of frequencies about the QLO, the transition to the classical limit of the specific heat occurs at a lower temperature. Therefore the quantity $\Delta C_V(T)/C_V^0(T)$ has in the presence of QLO a maximum whose position and amplitude are determined completely by the change induced in the phonon spectrum by the introduction of the heavy impurity into the crystal.

The temperature dependence of $\Delta C_V(T)/C_V^0(T)$, determined for different alloys from the experimental data and normalized to the impurity concentration, is shown in Fig. 2. It is the same for all three alloys within the limits of experimental accuracy, and has a clearly pronounced gently sloping maximum at T ≈ 20°K. Thus, the introduction of heavy Ta impurity atoms into the V lattice leads to the appearance of QLO in the phonon spectrum of the alloy, a fact manifest by an appreciable deviation of the specific heat of the alloy from the specific heat of the pure vanadium.

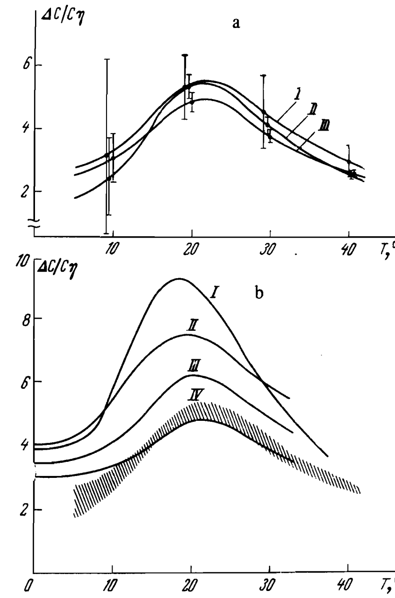

FIG. 2. Temperature dependence of the relative change of the phonon specific heat of V-T alloys and of V, normalized to the impurity concentration. a—Experimental data; I—$V_{99.18}Ta_{0.82}$; II—$V_{96.45}Ta_{3.55}$; III—$V_{94.32}Ta_{5.68}$. b—Theoretical curves: I—Debye approximation; II—calculation from the spectrum of V without a change in the force constants, $\tau = 0$; III—$\tau = 1.2$; IV—$\tau = 1.3$. The region of the experimental values obtained for V-Ta alloys is shown shaded.

It is natural to inquire as to the degree to which the observed change in the specific heat can be quantitatively described within the framework of the existing theoretical concepts. Figure 2b shows a comparison of the experimentally determined $\Delta C_V(T)/C_V^0(T)$ with the values calculated using different vanadium phonon spectra, both in the isotopic approximation and with allowance for the change in the force constants of the interaction between the impurity and the matrix atom in comparison with the interaction in the initial matrix. A consistent theory that takes into account the change in the force constants of the interaction was developed by Zhernov and Augst[16]. According to their results, the deformation of the phonon spectrum of the crystal with impurity is influenced not only by the mass difference, a fact accounted for in the isotopic approximation[4,5], but also by the change in the force constants of the interaction. The weaker the heavy impurity atoms is bound in the crystal, the lower the energy and the sharper the distribution of the QLO.

If the force constants are very abruptly decreased, then QLO can occur also for a light impurity. If, following[16], we consider only the interaction between nearest neighbors, we can assume that the constants of the central and noncentral interactions are equal and characterize the change of the force constants by the quantity $\tau = 1 - \gamma_1/\gamma_0$ (γ_1 is the force constant of the interaction between the impurity atom and the nearest

Composition	T_c ±0,1%, °K	γ ± 0,5%, $\frac{\text{mJ}}{\text{mole-°K}^2}$	Θ_{exp} ± 3%, °K	Θ_{calc}, °K
V	5.24	9.80	373	373
$V_{99,18}Ta_{0,82}$	4.90	9.50	370	369
$V_{96,45}Ta_{3,55}$	4.55	9.25	359	359
$V_{94,32}Ta_{5,68}$	4.46	9.16	350	351

neighbors, while γ_0 is the same for the matrix atom) then, according to[16], the QLO distribution has a maximum at the frequency ω_k:

$$\omega_k = \omega_0 \left\{ |\varepsilon| \left\langle \left(\frac{\omega_0}{\omega}\right)^2 \right\rangle \left[1 - \frac{2\tau}{1-\tau} \frac{1-\varepsilon}{\varepsilon} \left\langle \left(\frac{\omega}{\omega_0}\right)^2 \right\rangle \right] \right\}^{-1/2}. \quad (1)$$

Here $\epsilon = 1 - m'/m$ and ω_0 is the end-point frequency of the phonon spectrum of the crystal without the impurity. For the investigated alloys, $\omega_k \approx 150°\,K$.

In the case of extremely low temperatures, theory[16] yields for the relative change of the phonon specific heat of a BCC lattice

$$\left.\frac{\Delta C_v(T)}{C_v^0(T)}\right|_{T\to 0} = \eta \left[\frac{3}{2}|\varepsilon| + \frac{3\tau}{1-0.16\tau} \right], \quad (2)$$

where η is the concentration of the impurity atoms. At $\tau = 0$, expressions (1) and (2) go over into the expressions obtained in the isotopic approximation[4].

As follows from a comparison given in Fig. 2b, the calculation of the temperature dependence of $\Delta C_V(T)/C_V^0(T)$ using the Debye phonon spectrum of vanadium with $\Theta = 373°\,K$, in the isotopic approximation, does not describe the experimentally observed temperature dependence of the relative change of the specific heat. A somewhat better agreement between calculation and experiment, in the same isotopic approximation, is obtained by using in the calculation the vanadium phonon spectrum, determined with the aid of inelastic neutron scattering[11]. Even in this case, however, the discrepancy is still quite large.

The impossibility of satisfactorily describing the observed relative change of the specific heat with temperature within the framework of the isotopic approximation, when the interaction between the impurities can certainly be neglected since the condition $(3/2)\eta|\epsilon| \ll 1$ is satisfied for all the samples[17], indicates that introduction of even an isoelectronic heavy impurity Ta atom into the V lattice is accompanied by a change in the force constants. It is seen from the curves of Fig. 2b that the experimental data on the temperature dependence of $\Delta C_V(T)/C_V^0(T)$ are satisfactorily described on the basis of the theory of[16] by using the experimentally determined phonon spectrum of vanadium[11] and assuming that the force constants of the interaction of the impurity atom with the nearest neighbors exceed the corresponding constants in the initial lattice by 30%. Thus, the impurity atom turns out to be more rigidly bound in the crystal, meaning that the QLO in the investigated alloys are located at a higher energy and the amplitude of the deformation of the phonon spectrum is smaller than in the case of a pure isotopic impurity. This explains primarily the difficulties of observing the QLO in VTa alloys with the aid of inelastic neutron scattering, which were encountered in[12,13].

It is usually assumed that in a simple metal with a low impurity concentration, local restructuring of the lattice and changes of the electron density occur near the impurity, such that the force constants of the interaction of the impurity atom either do not differ from the force constants of the interaction of the atoms in the initial matrix, or differ very little. As seen from the results and from their comparison with the calculations, this assumption is approximately valid for the investigated alloys of transition metals of the isoelectronic system VTa, the components of which form a continuous series of solid solutions. An obvious change in the force constants is observed. It should be noted that according to the model concepts used in[16] the change of the force constants pertains to the case when introduction of the impurity atom is not accompanied by a change in the parameters of the crystal lattice with impurity in comparison with the initial crystal. In our system the introduction of the impurity is accompanied by expansion of the lattice and it is possible that the compensating action of the lattice expansion causes τ to be small. Therefore the real ratio of the force constants of the interaction of the impurity with its neighbors to the interaction of the initial-matrix atom with its neighbors in a real alloy crystal differs from the ratio determined from a comparison of the experimental and calculated relative change of the specific heat with temperature and shown in Fig. 2. In this sense, τ is a model-dependent parameter; to calculate the thermodynamic properties of a crystal with an impurity within the framework of this model, it suffices to know the phonon spectrum of the initial crystal and the changes of the mass ϵ and of the force constants τ, which characterize the given impurity relative to the given matrix[16].

Using the QLO parameters obtained in the present paper for dilute VTa alloys, we calculate the concentration dependence of the characteristic temperature of the alloys. On the basis of the paper by Zhernov and Augst[16] as applied to a BCC lattice, we can write

$$\Theta(\eta)_{T\to 0} = \Theta(0)_{T\to 0} + 0.5\eta \left[\varepsilon - \frac{2\tau}{1-0.16\tau} \right]. \quad (3)$$

The notation here is the same as before, and $\Theta(0)$ is the characteristic temperature of pure vanadium. The results of the calculation by means of Eq. (3) and their comparison with the experimentally determined values of $\Theta(\eta)$ are given in the table. Both experiment and calculation give a linear dependence of the characteristic temperature on the concentration of the Ta in V, and the calculated and experimental values of Θ themselves agree well with one another.

In an earlier investigation of the QLO in an alloy of Ti with 5 at.% U[18], using elastic scattering of neutrons and measurements of the low-temperature specific heat, a deviation of the experimental results from the predictions of a theory based on the isotopic approximation was likewise observed. The hypothesis was then advanced[16], however, that the change of the force constants is typical of non-equilibrium metallic systems obtained by quenching. The results of the present paper, and also the results of an investigation of the inelastic scattering of neutrons in CuAu alloys at heavy-component concentrations from 1 to 19 at.%[19], and in CrW alloys with a W concentration from 0.3 to 3 at.%[20], show that the force constants are altered by introduction of heavy impurity atoms into the crystal, both in alloys of transition metals and of nontransition metals. A more accurate estimate of the scale of variation of the force constants than obtained in the framework of the model of[16], can be obtained, obviously, by taking into account the actual expansion or contraction of the metal lattice resulting from the introduction of the impurity.

A discussion of the connection between the deformation of the phonon spectrum and the change of T_c in dilute VTa alloys will be presented in a separate paper.

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148