Calorimetric investigation of the changes in the electron and phonon spectra of the V-Pt system

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The temperature dependence of magnetic susceptibility and low-temperature specific heat of pure vanadium and of vanadium with 5 and 7 at.% Pt impurity have been measured. It is shown on the basis of the results obtained and of results of previous measurements of deformation of the vanadium phonon spectrum on introduction of Pt impurity [G. F. Syrikh *et al.*, Sov. Phys. JETP **46**, 162 (1977)] that the cause of the anomalous impurity deformation of the phonon spectrum of vanadium is the alteration of the electronic subsystem of the metal. This is manifest, in particular, in the considerable decrease of the electron density of states at the Fermi level which grows with increasing impurity concentration and is accompanied by a stiffening of the phonon spectrum.

1. INTRODUCTION

Analysis of the deformation of the phonon spectrum of a metal into which an impurity of very different mass has been introduced, is usually carried out within the framework of a theoretical approach with a model Hamiltonian which does not take account of a change in the electronic spectrum, the so-called isotopic approximation.[1,2] The possible adjustment of the electron density near the impurity is taken into account phenomenologically by a change in the local force constants (FC) for the interaction of impurity atoms with matrix atoms.[3] Such a description of the observed deformation of the phonon spectrum of the impure crystal and all the properties associated with it seem, in many cases, to be perfectly satisfactory.[4,5]

However, Syrykh *et al.*[6,7] appear to have been the first to observe an unusual impurity deformation of a phonon spectrum. It was established from results of inelastic neutron scattering and of low-temperature lattice specific heat of weak solutions of *W* and *U* in vanadium that at low frequencies the introduction of small quantities of heavy impurities is accompanied by a resonant readjustment of the vanadium phonon spectrum; quasilocalized modes (QLM) arise. However, contrary to the expected lowering of the limiting frequency of the crystal containing a heavy impurity, an increase was observed. The integral characteristic of the electron spectrum—the electron density of states at the Fermi level $N(\varepsilon_F)$ for the impure crystals was then $\sim 10\%$ less than in the starting vanadium. Nevertheless, it turns out to be possible, by ignoring the small shift in the phonon limiting frequency, strictly the low-frequency adjustment of the phonon spectrum, to describe satisfactorily the position and spectral distribution of the QLM, by taking account only of the change in the local FC of the interaction between the impurity and matrix.

The most unusual impurity deformation of the phonon spectrum of the starting metal appeared on introducing heavy Pt atoms into V.[8] It followed from results of ineleastic incoherent neutron scattering by specimens of V with 5 and 7 at.% Pt, compared with results on pure V, that an appreciable increase in the limiting frequency in the impure crystal ($> 10\%$) appeared besides the QLM which arises in this system.

Since only the deformation of the phonon spectrum of the V-Pt system was studied,[8] the aim of the present work was: to determine from measurements of the temperature dependence of magnetic susceptibility and low-temperature specific heat, the integral characteristics of the changes in the electron spectrum, to determine more accurately the effect of the QLM on the temperature dependence of the lattice specific heat and from all the results obtained to explain the reasons for the anomalous deformation of the phonon spectrum of V on introducing heavy nonisoelectronic Pt atoms, as had been done for a system with atoms close in mass.[9]

2. EXPERIMENTAL SECTION

The specific heat of a $V_{0.93}Pt_{0.07}$ specimen was measured in a vacuum adiabatic calorimeter over the temperature range 2–40 K. Random errors in determining the molar heat capacity were not more than 1%. A detailed account of the apparatus and method of measurement has been given before.[10]

The magnetic susceptibility of $V_{0.95}Pt_{0.05}$ and of $V_{0.93}Pt_{0.07}$ specimens was measured over the temperature range 2–300 K using a string magnetometer in a field ~ 7 T produced by a superconducting solenoid. The design of the apparatus is similar to that described by Alekseevskiĭ *et al.*[11] The systematic error in the measurements was $\sim 3\%$ and the random error not more than 0.5%.

The calorimetric and magnetic measurements were made on specimens which had been used before for studying the phonon spectra by neutron scattering.[8] From results of metallographic, x-ray and neutron structural analysis, they were disordered substitutional solid solutions based on the bcc V lattice. The lattice parameter of V did not change to within an accuracy of $\pm 0.15\%$ on introducing the amounts of Pt indicated.

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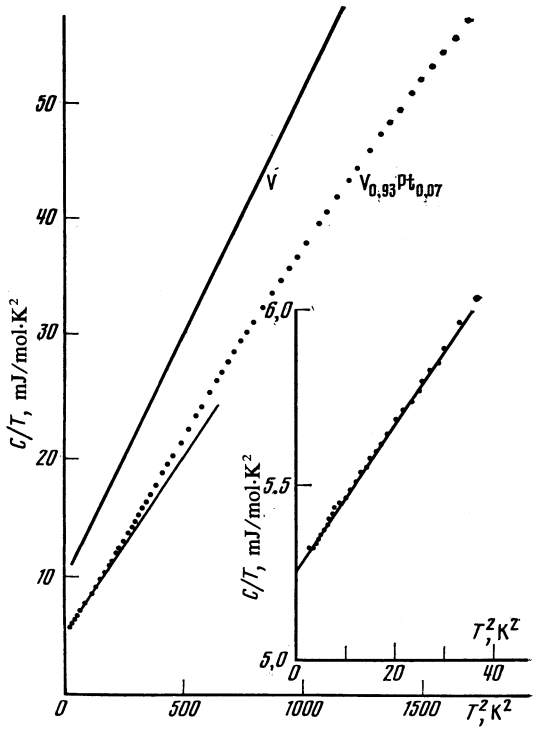

FIG. 1. Specific heat of the alloy $V_{0.93}Pt_{0.07}$ -points and of pure V—solid line.

3. THE RESULTS OF THE MEASUREMENTS AND DISCUSSION

The results of measuring the specific heat of the $V_{0.93}Pt_{0.07}$ specimen over the temperature range 2–40 K are shown in Fig. 1 as the dependence of C/T on T^2. The results for the specific heat of the original V, obtained earlier[10] are shown in the same figure for comparison. The results in the range 2–8 K are shown separately on a larger scale and by extrapolation of these to 0 K, the values of the coefficient of the electronic specific heat and of the Debye characteristic temperature $\Theta_D(0)$ are obtained (Table I). The results of measuring the magnetic susceptibility of V, $V_{0.95}Pt_{0.05}$ and $V_{0.93}Pt_{0.07}$ specimens in the temperature range 2–300 K are shown in Fig. 2 and demonstrate the weak temperature dependence.

By comparing results for the coefficient of the electronic specific heat with the spin component of the magnetic susceptibility, which are determined by the expressions

$$\gamma(0)=^2/_3\pi^2k_B^2N(\varepsilon_F)(1+\lambda_0), \quad \chi_{sp}=2\mu_B^2N(\varepsilon_F)$$

(k_B is Boltzmann's constant and μ_B is the Bohr magneton), an estimate was made of the electron-phonon interaction constant λ_0 for $V_{0.93}Pt_{0.07}$ [1)] and of the change in the electron density of states at the Fermi level $N(\varepsilon_F)$ on introducing 5 and 7 at.% Pt into V (Table I). Separation of the spin component out of the paramagnetic susceptibility was carried out by Miedema's rule,[12] using literature data on the orbital and diamagnetic components for V (Ref.13) and Pt (Ref. 14) and making the assumption that they are independent of temperature.

It was established, from the analysis carried out, that the introduction of 5 and 7 at.% Pt into V leads to a considerable readjustment of the electron spectrum, the lowering of the electron density of states at the Fermi level being ~30 and ~40% respectively. An increase in the Debye characteristic temperature Θ_D from 373 K for the initial V to 427 K for $V_{0.93}Pt_{0.07}$ was also found.

Traditionally, the information of impurity vibrational modes is established in calorimetric studies from an increase in the phonon specific heat of the crystal with the heavy impurity, C_{ph}^{imp}, above the matrix specific heat, C_{ph}^{0}. However, as can be seen from Fig. 1, the specific heat of the $V_{0.93}Pt_{0.07}$ specimen over the temperature range measured turned out to be less than that of the initial V. The usual analysis of the experimental results leads to the change in lattice specific heat having a negative value, although a resonance behavior appears, characteristic of a system in which QLM's are formed (Fig. 3a).

A different procedure was, therefore, used to analyse the calorimetric results, which consisted in a comparison of the experimental results on the low-temperature specific heat of the impure system with results of calculations of the specific heat of the "matrix," made by using the excitation spectrum of the matrix atoms in the alloy. It has been shown[8] that the limiting energy of the V phonon spectrum shifts appreciably in the direction of larger values on increasing the Pt impurity atom concentration. The introduction into V of the nonisoelectronic impurity Pt produces a change in the force constant of the interaction between atoms of the matrix. At the same time, Pt as a heavy impurity in the V matrix, deforms the low-frequency region of the phonon spectrum due to the formation of a QLM. However, it appeared that the energy position of the QLM depends on the concentration of Pt impurity atoms, and this change in the QLM position is proportional to the shift in the limiting energy of the phonon spectrum. The change in the position of the QLM for two compositions of dilute solid solutions cannot be explained by the concentration dependence of the behavior of the impurity vibrational states which can only lead[16] to a smearing of the spectral distribution of the QLM. It is known[1] that the QLM characteristics, position and spectral distribution, are determined by the phonon spectrum of the matrix and by a possible change in the local FC of theimpur-

TABLE I.

	χ_{pm}, emu/G-A ·10⁶	$\chi_{iorb}+\chi_{dm}$, emu/G-A ·10⁶	χ_{isp}, emu/G-A ·10⁶	$\gamma(0)$, mJ/mol-K	$\Theta_D(0)$, K	λ_0	$N(\varepsilon_F)$, states/eV-At
V	297	184	113	9,80	373	0,42	1.46
$V_{0,95}Pt_{0,05}$	256	175	81	–	–	–	1.05
$V_{0.93}Pt_{0,07}$	226	170	56	5,25	427	0,29	0,86

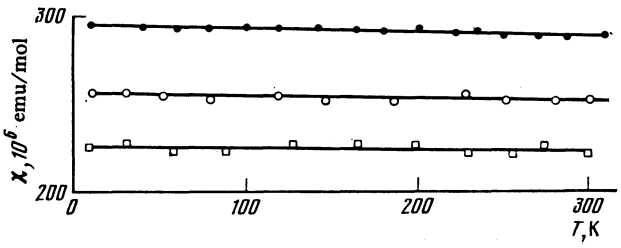

FIG. 2. Magnetic susceptibility of the alloys $V_{0.93}Pt_{0.07}$ (□), $V_{0.95}Pt_{0.05}$ (○) and of pure V (●).

ity-matrix interaction. Since a correlation is observed in the present case between the position of the QLM and the shift in the limiting energy of the phonon spectrum, it can be concluded that the introduction of nonisoelectronic Pt atoms into V leads to a readjustment of the initial V phonon spectrum, and the QLM which arises deforms the low-energy region of the already readjusted phonon spectrum, i.e., the heavy impurity atoms can be regarded as contained in a new "matrix." The phonon spectrum of such a matrix was established for the system containing 7 at.% Pt from neutron data. The low-energy part was approximated by a Debye spectrum with characteristic temperature $\Theta_D = 427$ K, obtained in the present work.

The results of comparing the measured and calculated temperature dependences of specific heat are shown in Fig. 3b. A calculation of the impurity contribution to the specific heat was also made, on the basis of the hypothetical matrix, in the isotopic approximation and taking account of the local interaction FC's. It can be seen from Fig. 3b that introduction of Pt impurity into V leads to a temperature dependence of the impurity lattice specific heat characteristic of the systems in which QLM's are formed. Comparison with theoretical curves indicates that the impurity-matrix and matrix-matrix interaction FC's in the V-Pt system are the same, although the matrix-matrix interaction depends on the concentration of Pt impurity atoms.

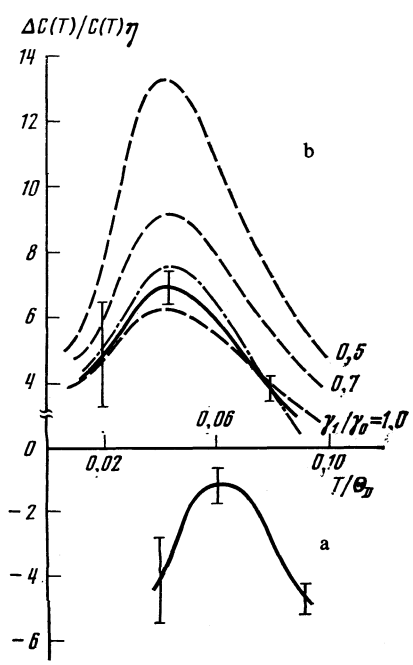

FIG. 3. Temperature dependence of the relative change in phonon specific heat of the alloy $V_{0.93}Pt_{0.07}$: a) $\Delta C = C^{exp}_{V\text{-}Pt} - C^{exp}_{V}$; b) full curve—$\Delta C = C^{exp}_{V\text{-}Pt} - C^{calc}_{matrix}$, dashed curves calculated using data from Ref. 8.

It should be noted that in this analysis the temperature dependence of the coefficient of the electronic specific heat $\gamma(T)$ was taken into account on separating the phonon component. This consideration has not usually been taken into account because it was assumed that the temperature dependence of $\gamma(T)$ for the initial matrix and for the impurity system differ insignificantly, and that on determining the impurity phonon specific heat from the difference of two experimental values, the contributions of $\gamma(T)$ would cancel out. In the present case the phonon specific heat of the "matrix" is obtained by calculation, so that in separating out the experimental phonon specific heat of the $V_{0.93}Pt_{0.07}$ specimen, the dependence of γ on T was taken into account within the framework of Kresin and Zaĭtsev's theoretical work,[17] using values obtained for λ_0 and $N(\varepsilon_F)$. Taking account of this contribution leads to a small ($\sim 10\%$) weakening of the resonance effect in the temperature dependence of the impurity specific heat.

The reason for the stiffening of the phonon spectrum of V on introducing nonisoelectronic Pt atoms now becomes understandable. As has already been remarked, the correlation between changes in electronic and phonon spectra, consisting in a fall in the electron density of states at the Fermi level being accompanied by a stiffening of the phonon spectrum, and vice versa, was confirmed for impurity systems with nearby masses. Since the lattice parameter of V practically does not change for the solutions of Pt in V studied, the stiffening of the phonon spectrum of V on introducing nonisoelectronic Pt atoms must be ascribed to a change in the electronic subsystem, namely the fall in the electron density of states at the Fermi level.

The following conclusions can be drawn as a result of our study:

1. A strong reduction in the electron density of states at the Fermi level on introducing Pt impurity atoms into V was established.

2. The formation of a QLM in the V-Pt system was confirmed by a calorimetric method. Use of the traditional method for separating the impurity phonon component turned out to be inappropriate under the conditions of an anomalous readjustment of the phonon spectrum of the impure matrix.

3. It was established by a combination of calorimetric and neutron data that the reason for the anomalous readjustment of the phonon spectrum is the reduction in the electron density of states at the Fermi level.

In conclusion we are glad to express our thanks to G. Kh. Panova and A. P. Zhernov for joining in the discussion of the results, and to A. M. Finogin for help with the preparation of the specimens.

[1]In the temperature interval studied a transition to the superconducting state for the alloy $V_{0.93}Pt_{0.07}$ was not found, so that it was not possible to determine λ_0 from the McMillan relation.[15] By calculation T_c is ~ 0.1 K.

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