Vibrational spectra of the alloys $V_{0.75}Ti_{0.25}$ and $V_{0.75}Cr_{0125}$

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The changes in the phonon and electron subsystems of metallic V following introduction of impurity atoms Ti and Cr, whose masses are close to those of V, were determined by measuring the inelastic neutron scattering and the magnetic susceptibility. A correlation was established between the change of the density $N(0)$ of the electron state and the average frequency of the phonon spectrum of the alloy, namely, a decrease of $N(0)$ is accompanied by an increase of the level of the phonon frequencies, and vice versa.

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INTRODUCTION

The investigation of the dynamic properties of impurity-containing metallic crystals based on vanadium[1-3] has shown that introduction of heavy impurity atoms leads to a complicated deformation of the initial phonon spectrum of V. This cannot be fully described within the framework of the traditional concepts[4,5] that take into account the disorder with respect to the mass and force-interaction constant and neglect the changes in the electron subsystem of the alloys. Thus, e.g., in systems based on V and alloyed with U Pr atoms one observes not only the expected formation of a quasilocal state, but also a shift of the entire vibrational spectrum towards higher frequencies.[2,3] This shift cannot be attributed to the change in the volume of the unit cell in the alloys. The hypothesis was therefore advanced[3] that the substantial deformation of the entire spectrum is due to changes in the electron subsystem. The restructuring of the electron spectra in a number of alloys based on V was indicated in Refs. 6 and 7.

The correlation between the changes in the phonon and electron subsystems has, however, not been established. To do so, it was of interest to investigate the excitation spectra of alloys in which the main source of the deformation of the phonon spectra would be the difference between the electronic properties of the initial elements. We have therefore undertaken an investigation of the integral characteristics of the phonon and electron spectra, namely the density $g(\omega)$ of the phonon states and the density $N(0)$ of the electron states on the Fermi level for the alloys $V_{0.75}Ti_{0.25}$ and $V_{0.75}Cr_{0.25}$.

The proximity of the places of the alloyed elements in the periodic table should not lead to substantial changes in the phonon spectrum connected with the difference between the masses of the atoms, namely to the appearance of local and quasilocal oscillations. Moreover, there is every reason for assuming that the possible disorder of the force constants in solid solutions with close masses of the atoms is small and does not lead to the appearance of impurity oscillations.[8] This manifests itself experimentally in the invariance of the widths of the phonon reflections of inelastic coherent scattering of neutrons by such alloys.[9]

PREPARATION OF SAMPLES AND MEASUREMENTS

The samples of the investigated alloys were made of V of brand VÉL-1 in an arc furnace in an atmosphere of purified argon. Neutron-diffraction, x-ray structure, and metallographic analyses have shown that the samples are disordered substitutional solid solutions based on the bbc lattice of V with lattice parameters 3.029 ± 0.003 Å, 3.035 ± 0.003 Å, and 2.992 ± 0.003 Å for V, $V_{0.75}Ti_{0.25}$, and $V_{0.75}Cr_{0.25}$, respectively.

It is known that direct information on the density of the phonon states is obtained by using data on incoherent inelastic neutron scattering. In view of the proximity of the component masses and of the forces of interaction between the ions, the disordered alloys $V_{0.75}TI_{0.25}$ and $V_{0.75}Cr_{0.25}$ can be regarded as quasimonatomic crystals. The cubic lattice of these crystals makes it possible to use in the reduction of the experimental data an approach in which the phonon spectrum of the alloy is directly proportional to the doubly differential cross section for the incoherent scattering of the neutrons. The influence of the coherent scattering of the neutrons on the spectral distribution should be negligible (see Table I). Neutron structure measurements indeed confirm that the investigated alloys, just as pure V, scatter the neutrons predominantly incoherently.

Measurement of the doubly differential cross section of neutron scattering by the samples was performed with a time-of-flight spectrometer with a cold-neutron source.[10] The samples were placed in an evacuated chamber to exclude neutron scattering by air. The energy of the neutrons incident on the sample (E_0) was ~5 meV. An energy analysis of the inelastically scattered neutrons was carried out simultaneously at angles 90, 75, 60 and 45°. The measurement results obtained for different angles were reduced independently, with account taken of the corrections for the

TABLE I.

Cross section	Sample		
	V	$V_{0.75}Ti_{0.25}$	$V_{0.75}Cr_{0.25}$
$\sigma_{inc} \cdot 10^{24}$ cm^2	5.1	4.5	4.6
$\sigma_c \cdot 10^{24}$ cm^2	0.018	0.16	0.048

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double and two-phonon scattering, and were then summed. The energy resolution in the investigated energy interval was 5–7%.

Information on the change of the density of the electron states on the Fermi level upon introduction of impurity atoms in a metal is usually extracted from data on the low-temperature heat capacity of the initial metal and of the alloys. In the present study, the phonon spectra were measured at room temperature. This made it possible to obtain information on the electron-state density $N(0)$ at room temperature from measurements of the temperature dependence of the magnetic susceptibility. The magnetic susceptibility of the samples was measured with a string magnetometer[11] in the temperature interval 4—300 K. We used in the installation a superconducting magnet with induction up to 8 T.

DISCUSSION OF RESULTS

Figures 1 and 2 shows the phonon spectra of the alloys $V_{0.75}Ti_{0.25}$ and $V_{0.75}Cr_{0.25}$. For comparison, the same figures show the previously obtained[1] phonon spectrum of pure V. Introduction into V of the atoms Ti and Cr, which are close to it in mass, leads to a substantial change in the intial phonon spectrum of V. For the $V_{0.75}Cr_{0.25}$ alloy, the phonon spectrum becomes much harder: the end-point frequency is increased by 5.6 meV, and the mean square of the frequency over the spectrum $\langle\omega^2\rangle$ is increased by 22.0%. In the case of $V_{0.75}Ti_{0.25}$ the end-point frequency of the spectrum remains practically unchanged, but the density of the phonon states in the low-frequency region of the spectrum increases greatly, and this leads to a decrease of the mean squared frequency $\langle\omega^2\rangle$ by 9.0%.

Figure 3 shows the temperature dependence of the magnetic susceptibility χ of pure V and of the alloys $_{0.75}Ti_{0.25}$ and $V_{0.75}Cr_{0.25}$. The measurements were made on the same samples that were previously used to obtain data on the phonon spectra. The results are in satisfactory agreement with the data of Ref. 12, where the temperature dependence of the susceptibility was investigated for V-Ti alloys of close composition, and with the data of Ref. 13, in which measurements were made on the alloy $V_{0.75}Cr_{0.25}$, but only at room temperature. The temperature dependence of χ is similar for V and for the alloys, and this may be evidence of invariance of the band structure. The absolute values of χ do vary: the value of χ is increased by 6% in $V_{0.75}Ti_{0.25}$ and decreased by 14% in $V_{0.75}Cr_{0.25}$.

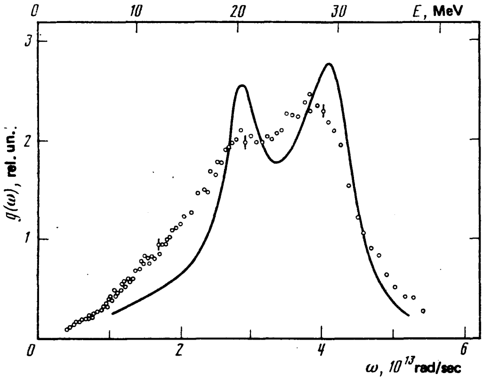

FIG. 1. Phonon spectra of the alloy $V_{0.75}Ti_{0.25}$ (points) and pure V (solid line).

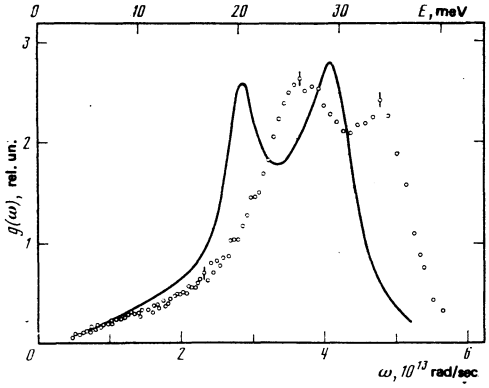

FIG. 2. Phonon spectra of the alloy $V_{0.75}Cr_{0.25}$ (points) and of pure V (solid line).

To determine the changes that occur in the electron subsystem in transition-metal alloys by using data on the magnetic susceptibility it is necessary to separate correctly the various components; viz., the spin and orbital paramagnetism and diamagnetism of the conduction electrons, and the diamagnetism of the ion cores.[14] To this end it is necessary to resort to other experimental data, such as information on the electronic heat capacity.

If the traditional approach is used then, neglecting the diamagnetism of the conduction electrons and ion cores because of their smallness, it can be assumed that the magnetic susceptibility consists in the main of two contributions: spin and orbital paramagnetism of the conduction electrons.

Since the spin susceptibility χ_{sp}, just as the electronic heat capacity, is proportional to the electron-state density on the Fermi level, the change of χ_{sp} at low temperature should correlate with the change of the electronic heat capacity on going from the alloy $T_{0.75}Ti_{0.25}$ to the alloy $V_{0.75}Cr_{0.25}$. By using the published data[15,16] on the electronic heat capacity of the investigated systems, a quantitative agreement can be obtained between the change of the electronic heat capacity and χ_{sp}, provided that the orbital paramagnetic contribution does not change when 25 at.% of Ti or Cr is added to the V. In Refs. 17 and 18, the orbital paramagnetic susceptibility was theoretically and experimentally estimated for V, and amounted to (180—200)×10^6 emu/mole. Assum-

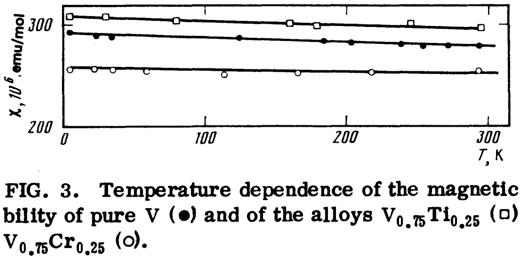

FIG. 3. Temperature dependence of the magnetic susceptibility of pure V (●) and of the alloys $V_{0.75}Ti_{0.25}$ (□) and $V_{0.75}$ $V_{0.75}Cr_{0.25}$ (○).

ing the average value for χ_{orb}, we estimate the relative change of the spin contribution to the total susceptibility, using the formula

$$\Delta\chi_{sp}=\frac{\chi_{all}-\chi_V}{\chi_V-\chi_{orb}},$$

where χ_{all} and χ_V are the magnetic susceptibilities of the alloys and of the pure V. We obtain a 16% increase of χ_{sp} for $V_{0.75}Ti_{0.25}$, and a 38% decrease for $V_{0.75}Cr_{0.25}$. The absence of a temperature dependence for the orbital susceptibility and the weak temperature dependence of the total susceptibility allow us to conclude that the change of χ_{sp} is in approximately the same ratio also at room temperature, as is consequently also the change in the density of the electronic states on the Fermi level in the investigated systems.

When analyzing the deformation of the phonon spectrum of V as a result of the introduction of the impurity atoms Ti and Cr, which are close to V in mass, it is necessary above all to take into account the contribution due to the change of unit-cell volume. Using the data of Ref. 19 on the Grüneisen constant for the initial components, we can estimate the value of the constant for the alloys. Estimates show that the constants of the investigated alloys lie in the range 1.3–1.5. The observed shift in the spectral distribution cannot be fully explained by taking into account the indicated values of the constants: it would be necessary for this purpose to assume for the constant a value of approximately 6, which is patently higher than the values determined for the metals. The additional shift of the frequencies in the metallic alloys is naturally due to changes in the electron subsystem.

The change of the level of the phonon frequencies as a function of the average number *e/a* of electrons per atom was investigated in a number of studies.[9,20-22] An attempt to establish a single correlation between the level of the phonon frequencies and the value of *e/a* led to contradictory conclusions. In some cases an increase of *e/a* is accompanied by an increase of the phonon frequencies, and in others by a decrease. Consequently, such a traditional characteristic of alloys as *e/a* is in the general case not adequate for the description of the changes in the phonon subsystem. It follows from the results of the present paper that an increase of the density of the electronic states on the Fermi level corresponds to a softening of the initial phonon spectrum of V when Ti is introduced into it. Conversely, the decrease of $N(0)$ following the introduction of the Cr impurity makes the phonon spectrum of V harder.

The cause of the dependence of $\langle\omega^2\rangle$ on $N(0)$ is the renormalization of the phonon frequencies on account of the electron-phonon interaction. Thus, e.g., it was established theoretically[23] that the mean squared phonon frequency of the pure metal can be expressed in in terms of the plasma frequency and of the contribution due to the electron-phonon interaction, the latter being proportional to $N(0)$. Extending this relation to alloys, the shift of the phonon frequencies upon introduction of the impurity can be qualitatively explained by the change of the ion-ion interaction on account of the change of the density of the electronic states on the Fermi level.

To obtain more detailed information on the connection between the electron and phonon subsystems, data are necessary on the changes of the Fermi surface and of the dispersion curves of the phonons.

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