Effect of tantalum and tungsten impurity on the phonon spectrum of vanadium

G. F. Syrykh, A. P. Zhernov, M. G. Zemlyanov, S. P. Mironov, N. A. Chernoplekov, and Yu. L. Shitikov

(Submitted September 13, 1975)
Zh. Eksp. Teor. Fiz. 70, 353–359 (January 1976)

It is shown by using the method of inelastic incoherent scattering of cold neutrons by samples of V and its alloys with Ta and W that singularities appear in the spectra of one-phonon neutron scattering by the impurity-containing crystals. These singularities are due to the onset of quasilocal oscillations (QLO) when the heavy Ta and W atoms are introduced into the V lattice. The character of the manifestation of the QLO in the doubly-differential cross section for neutron scattering by impurity crystals depends on the concrete ratio of the scattering amplitudes.

PACS numbers: 63.20.Dj, 61.12.Fy, 61.70.Rj

INTRODUCTION

It is known that quasilocal oscillations (QLO) are produced in the phonon spectrum of a crystal if it contains heavy impurity atoms. The possibility of the existence of such specific oscillation modes was predicted theoretically by Kagan and Iosilevskiĭ.[1] They were first revealed experimentally by the inelastic scattering of cold neutrons by an alloy of Mg with 2.8 at.% Pb,[2] and by the anomaly of the low-temperature heat capacity of the same alloy.[3] In subsequent experiments, the appearance of impurity phonon states in the physical properties of the crystals was investigated by various methods (see, e.g.,[4]), but the most direct and unambiguous method of determining the deformation of the phonon spectrum by the impurity is still the method of inelastic neutron scattering.

Among the impurity systems investigated with the aid of inelastic incoherent neutron scattering, a special space is occupied by alloys based on vanadium. The cross section for the scattering of neutrons by vanadium is practically fully incoherent. The coherent-scattering amplitude is negative and is small. Introduction of impurities that are characterized as a rule by a positive neutron-scattering amplitude makes the alloy a more fully incoherently scattering system. From data on the doubly differential cross section $\sigma_{in}(\omega)$ for neutron scattering by such a system it is possible, in principle, to reconstruct uniquely the phonon-state density function $g(\omega)$ and to determine quantitatively the energy position and the spectral characteristics of the impurity modes.

Inelastic incoherent scattering of neutrons by alloys based on vanadium with tantalum and tungsten impurities was investigated earlier in[5,6]. The results of these investigations were unexpected. Despite the relatively large difference between the masses of the host lattice and impurity atoms, only a slight change of $\sigma_{in}(\omega)$ was observed in[5] for alloys containing up to 5 at.% of the heavy impurity, compared with $\sigma_{in}(\omega)$ of the pure vanadium, and no changes were observed in[6] (as against the expected doubling of $\sigma_{in}(\omega)$ at low frequencies within the framework of the isotopic approximation). Thus, either no QLO are produced in the investigated systems at all, or else some mechanisms smear out the QLO and deprive them in fact of their resonant characters.

Experiments[7,8] have revealed an anomalous temperature dependence of the lattice component of the heat capacity of vanadium alloys with ~ 5 at.% Ta and W, thus evidencing the presence of QLO in these impurity-containing systems. To obtain more detailed information on the singularities observed earlier in[5], new measurements with higher resolution and with better statistical accuracy than in the preceding studies[5,6] were made of the inelastic incoherent scattering of neutrons by samples of the original vanadium, $V_{0.943}Ta_{0.057}$, and $V_{0.945}W_{0.055}$.

MEASUREMENTS AND DISCUSSION OF RESULTS

The measurements were performed with a time-of-flight spectrometer with a propane source of cold neutrons. A cold-neutron flux ~ 6×10^6 neut/cm^2 min was incident on a sample measuring $100\times60\times4$ mm. The average energy of the incident neutrons was $E_0 = 4.97$ MeV, with $\Delta E_0/E_0 \approx 10\%$. The neutrons scattered by the sample were registered simultaneously by three detectors placed at angles 90, 75, and 60° relative to the incident beam.

The alloy samples were prepared on the basis of 99.98% pure vanadium with a resistance ratio $R(300\ K)/R(T_c) = 24$, obtained from VÉL-2 vanadium subjected to additional zone purification in a vacuum of 10^{-6} mm Hg. The x-ray structure and meallographic analysis data give grounds for assuming that the investigated alloys are single-phase and are substitutional solid solutions based on the bcc lattice of vanadium. Samples made from the same melts were used also for low-temperature measurements of the heat capacity.[7,8] The statistical error of the measurements in the region of low energy transfers by scattering amounted to ~ 3%. This required about 300 hours of measurements on each sample.

Figure 1 shows the phonon spectrum $g_0(\omega)$ of pure vanadium, reconstructed from the experimental doubly-differential neutron-scattering cross section. The spectrum duplicates the main singularities established in the earlier studies.[10] A weak singularity, usually attributed to the Kohn anomaly,[11] is clearly seen in the energy region close to 10 meV. The main peaks of the spectrum are less smeared out, probably because of

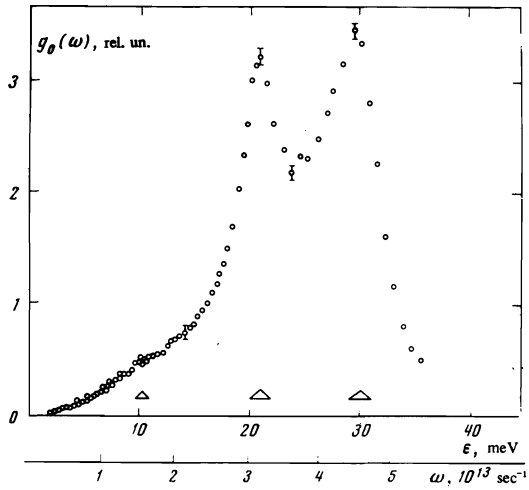

FIG. 1. Phonon spectrum of vanadium. The triangles indicate the resolution of the apparatus.

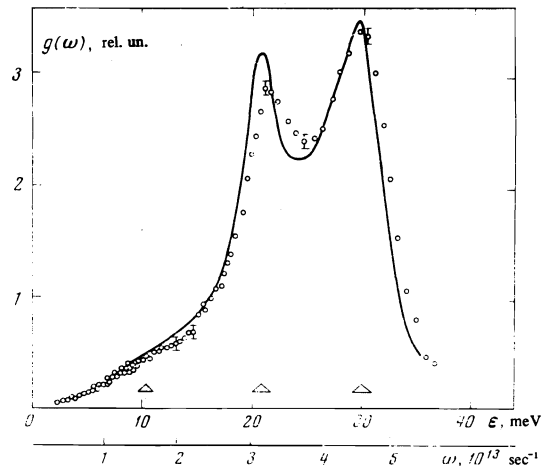

FIG. 3. Spectrum of vibrational excitations of the alloy $V_{0.945}W_{0.055}$. Points—VW spectrum, solid curve—V spectrum.

the higher purity of the investigated vanadium. In addition in this experiment it was possible to obtain for the first time information on the low-frequency part of the spectrum, down to 0.3×10^{13} sec^{-1} (~ 2 meV).

The results of the experimental determination of the probability of the single-phonon scattering by the samples $V_{0.943}Ta_{0.057}$ and $V_{0.945}W_{0.055}$, represented in a form analogous to the frequency distribution function, are shown in Figs. 2 and 3. The main singularities of the initial spectrum become somewhat smeared out for both systems. At low frequencies, $\sigma_{in}(\omega)$ for pure vanadium and for vanadium with impurities practically coincide, and at $\omega\approx 14$ meV, i.e., at $\omega=\omega_*$(QLO), a noticeable deviation of $\sigma_{in}(\omega)$ from monotonic behavior is observed on the curves for the alloys. The probability of the one-phonon scattering increases for the VTa alloy and decreases for the VW alloy. At higher frequencies, the spectra obtained for V and VTa coincide. In the case of VW, a shift of the spectrum boundary towards higher frequencies is observed.

The results can be explained within the framework of the existing theory (see, e.g., [12]). Indeed, assuming

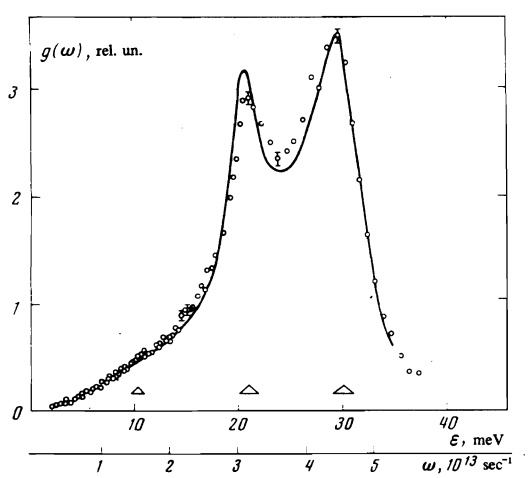

FIG. 2. Spectrum of the vibrational excitations of the alloy $V_{0.943}Ta_{0.057}$. Points—VTa spectrum, solid curve—V spectrum.

that all the atoms of a polycrystal scatter neutrons independently, and confining ourselves only to terms of first-order in the ratio of the recoil energy R from a single nucleus to the characteristic phonon frequency, we have

$$\Delta\sigma(\omega)/cRN_T\approx a_0^2\Delta K_{latt}(\omega)+(a_1^2-a_0^2)K_{imp}(\omega), \tag{1}$$

where $\Delta\sigma=\sigma(c)-\sigma(c=0)$ is the impurity correction to the one-phonon neutron-scattering spectrum; $N_T=(e^{\omega/T}-1)^{-1}$; c is the concentration of the impurity atoms; a_0 and a_1 are the total amplitudes of neutron scattering by atoms of the initial lattice and the impurity; $\Delta K_{latt}=(K_{latt}(c)-K_{latt}(c=0))/c$, and K_{imp} are the frequency Fourier components of the pair correlation functions constructed of the displacement operators of an arbitrary solution atom and an impurity atom, respectively. Explicit expressions for the functions ΔK_{latt} and K_{imp} were obtained by Kagan and Zhernov for the case when the defects can be regarded as isotopic.[13] A situation wherein the presence of impurities alters noticeably the effective local force constants was considered by Zhernov and August.[14]

Let us analyze the character of the behavior of the functions ΔK_{latt} and K_{imp} as functions of ω in the presence in the lattice of heavy impurity atoms. We confine ourselves to the qualitative aspect of the phenomenon. We neglect the change of the force constants. According to[13]

$$K_{imp}(\omega)=\frac{g_0(\omega)}{[1-\varepsilon\omega^2J(\omega)]^2+[\pi\varepsilon\omega^2g_0(\omega)]^2}, \tag{2}$$

$$\Delta K_{latt}(\omega)=\Delta g(\omega)+\varepsilon K_{imp}(\omega), \tag{3}$$

$$\Delta g(\omega)=\frac{1}{\pi}\operatorname{Im}\left\{\left[\frac{d}{d\omega^2}\varepsilon\omega^2\int_0^\infty\frac{dz^2\,g_0(z^2)}{\omega^2-z^2+i\delta}\right]\left[1-\varepsilon\omega^2\int_0^\infty\frac{dz^2\,g_0(z^2)}{\omega^2-z^2+i\delta}\right]^{-1}\right\}, \tag{4}$$

where $\varepsilon=1-M_1/M_0$; M_0 and M_1 are the masses of the atoms of the matrix and of the impurity. The function $\Delta g(\omega)$ is by definition the correction, due to the presence of impurity atoms, to the phonon state density function $g_0(\omega)$. The impurity component of the phonon heat capacity is expressed directly in terms of $\Delta g(\omega)$.

We note that as $\omega \to 0$ the correction to the phonon-state density function[12] is

$$\Delta g \approx -\tfrac{3}{2}\varepsilon c. \tag{5}$$

At the same time, as follows from (1)–(4), at $a_1 \approx a_0$ we have

$$\Delta\sigma \approx -\tfrac{1}{2}\varepsilon c.$$

Since $\varepsilon = -2.6$ for the alloys VTa and VW, and the correction due to the change of the force constants only decreases here the value of $\Delta\sigma$, it follows that the weak deformation of $\Delta\sigma$ could not be detected in the acoustic limit.

In the frequency interval near ω_* the functions K_{imp} and Δg take the form

$$K_{imp}(\omega) \approx R(\omega)/|\varepsilon|. \tag{6}$$

$$\Delta g(\omega) \approx R(\omega)(1-\beta|\varepsilon|), \quad \beta \leqslant 1. \tag{7}$$

$$R(\omega) \approx \frac{1}{\pi}\frac{\Gamma}{(\omega^2-\omega_*^2)^2+\Gamma^2}, \quad \Gamma \approx \frac{1}{3}\frac{1}{|\varepsilon|^{1/2}}. \tag{8}$$

It follows from (6)–(8) that near the frequency ω_* the functions $K_{imp}(\omega)$ and $\Delta g(\omega)$ go through a clearly pronounced maximum. To the contrary, $\Delta K_{latt}(\omega)$ is negative at $\omega \approx \omega_*$ and goes through a minimum. As a result, $\Delta\sigma/cRN_T$ is determined essentially by the ratio of the total amplitudes of the neutron scattering by the impurity and matrix atoms. Namely, if $a_1^2 \gg a_0^2$, then the function $\Delta\sigma/cRN_T$ goes through a sharp maximum (the situation realized in MgPb[2] and TiU[15]). At $a_1^2 \ll a_0^2$ the picture is reversed: the function $\Delta\sigma/cRN_T$ goes through a sharp minimum. When $a_1^2 \approx a_0^2$, and this is precisely the relation between the total amplitudes of neutron scattering in solutions of Ta and W in V, the singularities on the plots of σ against ω are less pronounced.

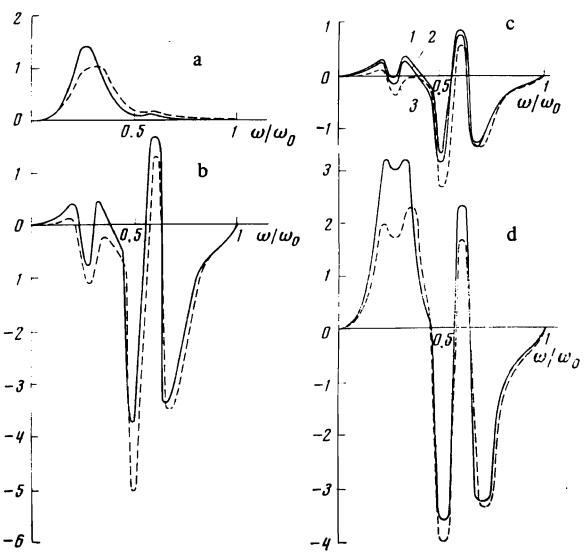

FIG. 4. Calculated values of the functions of the impurity crystals: a) K_{imp}; b) ΔK_{latt}; d) Δg for VW (solid curve—$\gamma_0 = \gamma_1$; dashed—$\gamma_0 = 1.4\gamma_1$); c) $\Delta\sigma/cRN_T$; 1—VTa ($\gamma_0 = \gamma_1$), 2—VW ($\gamma_0 = \gamma_1$), 3—VW ($\gamma_0 = 1.4\gamma_1$).

To illustrate the foregoing, Fig. 4 shows the form of the correlators of K_{imp} and ΔK_{latt}, and also the factors Δg and $\Delta\sigma/cRN_T$ ($a_1^2 \approx a_0^2$). The curves were obtained in the isotopic approximation and with allowance for the change of the effective local force constants γ_1/γ_0. Figure 4c shows the curves for the cross section $\Delta\sigma/cRN_T$, calculated for concrete values of the total scattering amplitudes of V, Ta, and W. If it is assumed that the local force constants remain practically unchanged in VTa but change noticeably in VW, then a qualitative agreement is observed between the experimental and the calculated values: at $\omega \approx \omega_*$ the cross section $\Delta\sigma/cRN_T$ is positive for VTa and negative for VW. An analogous conclusion concerning the character of the change of γ_1/γ_0 was drawn in[7-8] on the basis of data on the measurement of the low-temperature heat capacity V with impurity atoms Ta and W.

Attention is called also to the following circumstance. The end-point frequency of the phonon spectrum in the alloy of V with W turns out, as already noted, to be shifted towards higher energies. This indicates that in the VW system there is apparently a substantial restructuring of not only the phonon spectrum but also of the electron spectrum. Therefore the usual approach, based on smallness of the perturbing influence of the impurity at concentrations up to ~ 5 at.%, turns out, strictly speaking, to be unjustified in the case of VW, and in similar cases it is necessary to carry out a special analysis that takes into account the more appreciable restructuring of the excitation of the spectra of a system with impurities.

Thus, the results of more careful measurements of the inelastic incoherent scattering of neutrons by pure vanadium and by vanadium with ~ 5% Ta and W impurities, and a more detailed analysis of the results, have shown that the introduction of the heavy impurity atoms Ta and W into the V lattice is accompanied by the onset of QLO in the phonon spectrum. The characteristics of the QLO in these systems coincide with those estimated from measurements of the temperature dependence of the heat capacity[7,8] and confirm the latter. The difficulties in the observation of the manifestations of the QLO in the investigated systems with the aid of neutrons are due to a fortuitous circumstance—that the amplitudes for the scattering of the neutrons by the matrix and impurity nuclei are close to each other.

In conclusion, the authors thank A. V. Elyutin and L. I. Voronenko for preparing the samples, and P. S. Mamonov, Yu. V. Sereda, V. G. Fedorov, Yu. I. Zaĭtsev, and V. V. Gavrilin for help with the measurements.

[1]Yu. Kagan and Ya. Iosilevskiĭ, Zh. Eksp. Teor. Fiz. 42, 259 (1962) [Sov. Phys. -JETP 15, 182 (1962)].
[2]N. A. Chernoplekov and M. G. Zemlyanov, *ibid.* 49, 449 (1965) [22, 315 (1966)].
[3]G. Kh. Panova and B. N. Samoilov, *ibid.* 49, 456, 1965 [22, 320 (1966)].
[4]A. A. Maradudin, Defects and Vibrational Spectrum of Crystals, (Russ. transl.), Mir, 1968.
[5]M. G. Zemlyanov, S. P. Mironov, and G. F. Syrykh, Neutron Inel. Scatt., IAEA, Vienna, 1968.

[6]B. Mozer, *ibid.*
[7]N. A. Chernoplekov, G. Kh. Panova, B. N. Samoilov, and A. A. Shikov, Zh. Eksp. Teor. Fiz. **63**, 1381 (1972) [Sov. Phys. -JETP **36**, 731 (1973)].
[8]A. A. Shikov, N. A. Chernoplekov, G. Kh. Panova, B. N. Samoilov, and A. P. Zhernov, *ibid.* **69**, 1825 (1975) [**42**, 000 (1973)].
[9]M. G. Zemlyanov, A. E. Golovin, S. P. Mironov, G. F. Syrykh, N. A. Chernoplekov, and Yu. L. Shitikov, Prib. Tekh. Éksp. No. 5, 34 (1973).
[10]N. A. Chernoplekov, M. G. Zemlyanov, and A. G. Chicherin, Zh. Eksp. Teor. Fiz. **43**, 2080 (1962) [Sov. Phys. -JETP **16**, 1472 (1963)].
[11]J. Pelach, R. Haas, W. Kley, K. H. Krebs, J. Peretti, R. Rubin, Inel. Scatt. Nuetron, IAEA, Vienna, 1963.
[12]Yu. Kagan. A Materialy shkoly po teorii defektov v kristallakh i radiatsionnykh narushenii, Telavi 1965) Proceedings of School on Defects in Crystals and Radiation Damage, Telavi, 1965), Tbilisi, 1966.
[13]Yu. Kagan and A. P. Zhernov, Zh. Eksp. Teor. Fix. **50**, 1107 (1966) [Sov. Phys. -JETP **23**, 737 (1966).
[14]A. P. Zhernov and G. R. August, Fiz. Tverd. Tela **9**, 2196 (1967) [Sov. Phys. -Solid State **9**, 1724 (1968)].
[15]N. A. Chernoplekov, G. Kh. Panova, M. G. Zemlyanov, B. N. Samoilov, and V. I. Kutaitsev, Phys. Stat. Sol. **20**, 767 (1967).

Translated by J. G. Adashko