AN INVESTIGATION OF INELASTIC NEUTRON SCATTERING BY A CRYSTAL DOPED WITH LIGHT IMPURITY ATOMS

M. G. Zemlyanov, V. A. SOMENKOV, and N. A. CHERNOPLEKOV

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The deformation of the phonon spectrum of the Ni lattice due to the injection of light Be atoms is investigated experimentally using the inelastic scattering of cold neutrons. The localized vibrational level of a Be light impurity atom in the Ni lattice is displaced considerably relative to the position calculated theoretically in the isotopic impurity approximation. The width of the localized level is accounted for by anharmonicity and concentration broadening.

WE know [1] that when an atom of a perfect crystal is replaced with a light atom the phonon spectrum of the now impure crystal can contain a localized vibration having a frequency $\omega_D > \omega_{max}$, where ω_{max} is the phonon frequency limit of the original crystal. For an isolated impurity, provided that the force constants of the interatomic interactions remain unchanged, ω_D is given by

$$\varepsilon\omega_D \int_0^{\omega^2_{max}} \frac{g(\omega^2)\,d\omega^2}{\omega_D^2 - \omega^2} = 1. \qquad (1)$$

Here $\epsilon = 1 - m'/m$, where m' and m are the masses of the impurity atom and an atom of the original nucleus; $g(\omega^2)$ is the distribution function of the squared phonon frequencies in the original lattice. A frequency is split only if

$$\varepsilon > \left[\int_0^{\omega^2_{max}} \frac{g(\omega^2)\,d\omega^2}{1-(\omega/\omega_D)^2} \right]^{-1}. \qquad (2)$$

For a cubic crystal ω_D is triply degenerate; for a crystal having any other type of symmetry this degeneracy is either partially or entirely removed. In dielectric crystals the appearance of localized or quasi-localized vibrations accompanying impurity atoms is investigated using optical methods. [2] For metals this investigation can be performed only by using inelastic neutron scattering.

The theory of inelastic interactions between neutrons and crystals containing substitutional defects has been developed in [3-5], and most thoroughly of all in [4]. In the latter work it was shown that by measuring the cross section for inelastic neutron scattering on an impure crystal we can obtain information about both the changes in the phonon spectrum that follow the introduction of an impurity atom, and the spectrum of the original undisturbed crystal.

Mozer et al. were the first to attempt an investigation of the localized vibrational level of a light impurity atom by means of inelastic neutron scattering. [6] They studied solid substitutional solutions of Ni in Pd with Ni concentrations varying from 5 to 20%. However, the relatively small mass difference between the original lattice atoms and the impurity, as well as the inadequate energy resolution of the measuring spectrometer, prevented a reliable quantitative determination of the properties exhibited by the localized vibrational level of Ni impurity atoms in a Pd lattice.

In [7] inelastic neutron scattering on samples of the interstial system $VH_{0.04}$ was studied. Unfortunately, for interstital solutions no rigorous theoretical relation has been established between the cross section for inelastic neutron scattering and the characteristics of impurity-atom vibrations. Moreover, in the hydrides of such transition metals as V, Ta, and B the mobility of hydrogen is high at elevated temperatures, while at low temperatures, even for low concentrations, a strong interaction is observed in the hydrogen sublattice. This hinders the study of the samples as systems with isolated impurities. [8] It was therefore possible to have as the width of the "localized" vibrational level of hydrogen in $VH_{0,04}$, $\Delta\omega_D/\omega_D \gtrsim 50\%$, where $\omega_D > 2\omega_{max}$ and the level is not greatly broadened as a result of anharmonicity. It appears that the responsibility for the broadening of the level lies either in the mobility of the hydrogen or the existence of a band of vibrational proton states in the lattice of the hydride even at low hydrogen concentrations.

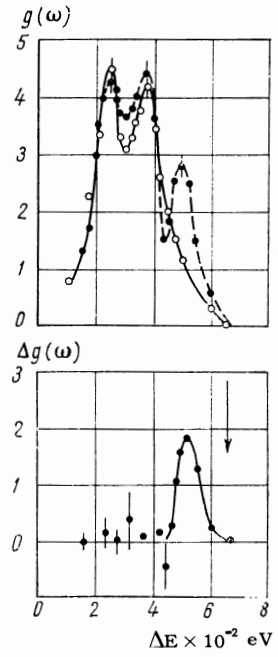
Using the inelastic scattering of cold neutrons we investigated local vibrational levels in the

phonon spectrum of Ni into which Be atoms had been introduced as an impurity. This system was selected for several reasons. The mass ratio of the impurity and host atoms is small. This ratio is $\epsilon = 0.85$; therefore, according to (1), the localized level should be quite distant from the phonon spectral limit of Ni. A calculation performed in the isotopic approximation using the Debye spectrum of Ni with $\Theta = 400°K$ gave $\omega_D = 2\omega_{max}$. This indicates that the localized level in the spectrum of inelastic neutron scattering will lie in a region containing only a weak background due to two-phonon processes, and that the energy resolution of the apparatus, $\Delta E/E \lesssim 10\%$, is quite satisfactory for detection of the localized level.

Large neutron scattering amplitudes coming from both Be and Ni atoms facilitate distinctness of the experimental localized level, because a contribution to the scattering comes both from the impurity atoms and from atoms of the host lattice that are located in disturbed regions close to the impurity atoms, although the amplitude of the perturbation falls off rapidly. In the measurements using cold neutrons this was especially important, because the localized level has a small population at ordinary temperatures, yielding a small cross section for inelastic neutron scattering. The fact that we investigated the alloy $Ni_{0.94}Be_{0.06}$, which is a decomposing solid solution, imposed specific requirements on the sample, a freshly prepared alloy, whose homogeneity was checked by x-rays both before and after the measurements...

The spectra of protons inelastically scattered by polycrystalline samples of the host Ni and the alloy $Ni_{0.94}Be_{0.06}$ were measured at room temperature with the apparatus described in [9]. The measurements were subjected to necessary experimental corrections; they were normalized to the same initial cold neutron flux and to an identical number of Ni atoms in the samples. The phonon spectra of the test materials were then established in the incoherent approximation; the results of this procedure are shown in the accompanying figure. The Ni phonon spectrum obtained here agrees satisfactorily with earlier measurements in [10,11].

The "phonon" spectrum of $Ni_{0.94}Be_{0.06}$ reveals, in actuality beyond the spectrum of the original Ni lattice, a clear additional peak with $\Delta E \approx 5 \times 10^{-2}$ eV that is associated with the localized vibrations of Be impurity atoms in the Ni lattice. The position of this peak is not what we would expect from the assumed isotopic character of the impurity.



(Above) Phonon spectra g(w) of Ni latice (solid curve) and Ni lattice containing Be impurity (dashed curve). (Below) Difference Δg(w) between phonon spectra of pure Ni, and Ni with Be impurity. The arrow indicates the position of the localized level calculated in the isotopic impurity approximation.

While the calculation yields $\omega_D/\omega_{max} \approx 2$, the experimental result is ≈ 1.5. The observed shift of the impurity level relative to the calculated value in the isotopic impurity approximation is obviously associated, in the first place, with a considerable change of the interaction constant for impurity and host atoms. The results given in [12] permit a rough estimate of the change in the interaction constant on the central-force model. We find that the Ni-Be interaction constant is more than 20% smaller than the Ni-Ni interaction constant.

This is, to our knowledge, the first experimental result that demonstrates directly the change of the force constant for impurity atoms and a metal (the deviation from the isotopic case). Mainly on the basis of Mössbauer effect measurements for impurity atoms in metals, it was previously assumed that by means of the electron component of the metal a "fine adjustment" of the force constants for impurity-host interactions and for host-atom interactions takes place. We cannot exclude the possibility that the destruction of this adjustment is characteristic of decomposing solid solutions.

Besides the shift of the localized frequency with respect to the frequency calculated for an isotopic impurity, the investigated system is notable for the relatively great width of the localized level. Taking into account the total resolution of the apparatus, we find $\Delta\omega_D/\omega_D \approx 18\%$ for the intrinsic width of the localized level.

We can expect that the main reasons for the broadening are: a) the finite lifetime of the localized level, depending on the probability of its decay because of anharmonicity and the electron-phonon interaction; b) concentration broadening of the localized level, since a finite concentration of impurity atoms is accompanied by a substantial interaction among them, which splits the localized level; c) splitting of the localized level, resulting from the possible destruction of cubic lattice symmetry by deformation fields arising near impurity atoms when the sample is quenched. Unfortunately, the broadening of the localized level is an extremely complex question that is not easily resolved quantitatively; we must therefore limit ourselves to certain very crude estimates.

Since in the present case $\omega_D \approx 1.5\,\omega_{max}$, the lifetime of the localized level is apparently governed by three-phonon anharmonicity. An estimate of the lower limit of localized level width resulting from anharmonicity at $T = 0$, based on several investigations,[13] is $\Delta\omega_D/\omega_D \approx 5 \times 10^{-2}$. At high temperatures the broadening can increase by a factor of 3—10. A portion of the observed localized vibration width is associated with the electron-phonon interaction, which is of considerable magnitude in the case of Ni, as could be expected, and can be the main term at low temperatures.[14] The range of broadening due to the electron-phonon interaction is 10^{-3}—10^{-2}.

Additional broadening of the localized level, resulting from a disordered distribution of the isotopes in the original Ni lattice and also from interactions between impurity atoms, has been evaluated in accordance with[15]; the result is $\Delta\omega_D/\omega_D \approx 3 \times 10^{-2}$. It is not possible to evaluate the third of the aforementioned factors.

From our investigation of the inelastic scattering of cold neutrons on Ni samples and the $Ni_{0.94}Be_{0.06}$ alloy we have thus established that when Be atoms are added as an impurity in Ni the phonon spectrum of Ni contains a localized vibrational level of the light impurity atoms. The location of this level is not consistent with the calculated value in the isotopic approximation and the level itself is very broad. Investigations of the temperature and concentration dependences of the position and width of a localized vibrational level belonging to Be atoms in a Ni lattice will obviously enable us to establish more firmly the causes of the shift and broadening of this level. Moreover, as can be expected, such investigations will permit a better understanding of the nature of decomposing solid solutions.

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