Band Modes of Hydrogen in the bcc Metals Nb, V, and Ta

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A calculation of the frequency spectrum of the band modes of hydrogen located at a tetrahedral interstitial site shows a strong resonantlike peak with very little isotope effect. This mode was observed by neutron scattering in $NbH_{0.05}$ at 3.8 THz. The band modes provide a mechanism for classical diffusion with low activation energies.

In recent years the dynamics of H in the bcc transition metals Nb, Ta, and V have been studied extensively by means of neutron-scattering experiments.[1] These experiments have been concerned mainly with the high diffusivity of H, its high-frequency localized modes, and its influence on the acoustic-phonon spectrum of the host lattice. Only little attention was paid to the vibrations of the H atom itself within the range of the acoustic-phonon frequencies (band modes). Previous neutron-scattering experiments[2] could not show whether the spectrum of the band modes merely mirrors the phonon density of states of the metal or if there are some favored vibration modes with an H amplitude different from that of the metal atoms. Theoretical calculations of the H vibrations have been restricted to the localized modes.[3] The purpose of this Letter is to report the results of both theoretical and experimental investigations of the frequency spectrum of the band modes which give an important contribution to the thermal mean-square displacement of the H and lead to activation energies for a classical jump diffusion process distinctly smaller than the excitation energies of the localized modes.

We have calculated the local vibrational spectrum of the single H atom by standard Green's-function techniques for interstitials.[4] These methods have the advantage that all properties are expressed in terms of the ideal lattice Green's function, $g(\omega)$, and the coupling changes, φ, with respect to the ideal host lattice. The Green's function g was calculated by a modified Gilat-Raubenheimer method from Born-von Kármán fits to the ideal phonon spectra. The local spectrum, $Z_i^{\mathrm{H}}(\omega)$, of the vibrations of the H in direction i is given in terms of the hydrogen Green's function $G_{ii}^{\mathrm{HH}}(\omega)$ as

$$Z_i^{\mathrm{H}}(\nu) = 2\pi Z_i^{\mathrm{H}}(\omega) = 4m^{\mathrm{H}}\omega \,\mathrm{Im}\, G_{ii}^{\mathrm{HH}}(\omega) \tag{1}$$

with

$$G_{ii}^{\mathrm{HH}}(\omega) = \{m^{\mathrm{H}}\omega^2 - \varphi^{\mathrm{HH}} - \varphi^{\mathrm{HL}}[1 - g^{\mathrm{LL}}(\omega)\varphi^{\mathrm{LL}}]^{-1} g^{\mathrm{LL}}\varphi^{\mathrm{LH}}\}_{ii}^{-1}, \tag{2}$$

where the superscripts H and L denote the hydrogen and host lattice subspaces, respectively, and m^{H} is the hydrogen mass.

The dimensions of the matrices in Eq. (2) are reduced by decomposing them into their irreducible parts. The tetrahedral site has D_{2d} symmetry with subspaces A_1, A_2, B_1, B_2, and E. For the evaluation of the H vibration one has to consider only the subspaces B_1 (for the z vibration) and E (for the degenerate x and y vibrations).

In the simplest model which can be treated analytically and which is consistent with the observed frequencies of the localized modes the H atom is coupled only to its nearest-neighbor metal atoms by a purely longitudinal spring f. In this model the matrices in Eq. (2) are reduced to scalars for each direction:

$$\varphi_z^{\mathrm{HH}} = \tfrac{4}{5}f, \quad \varphi_z^{\mathrm{HL}} = -(2/\sqrt{5})f, \quad \varphi_z^{\mathrm{LL}} = f,$$

$$g_z^{\mathrm{LL}} = g_{xx}^{000} + \tfrac{2}{5}g_{xx}^{111} + \tfrac{16}{5}g_{xy}^{111} - \tfrac{4}{5}g_{xx}^{200} - \tfrac{1}{5}g_{zz}^{200}$$

for z vibrations and

$$\varphi_x^{\mathrm{HH}} = \tfrac{8}{5}f, \quad \varphi_x^{\mathrm{HL}} = -(\tfrac{8}{5})^{1/2}f, \quad \varphi_x^{\mathrm{LL}} = f,$$

$$g_x^{\mathrm{LL}} = g_{xx}^{000} + \tfrac{4}{5}g_{xx}^{200} - \tfrac{1}{5}g_{zz}^{200}$$

for x and y vibrations. Equation (2) then reduces to

$$Z_i^{\mathrm{H}}(\nu) = 4m^{\mathrm{H}}\omega \,\mathrm{Im}[m^{\mathrm{H}}\omega^2 - \varphi_i^{\mathrm{HH}}/(1 - g_i^{\mathrm{LL}}f)]^{-1}. \tag{3}$$

Because of the large spring constant f (70 000 dyn/cm, approximately 3 times the nearest-neighbor host spring) and the small mass m^{H}, the term $m^{\mathrm{H}}\omega^2$ can be omitted to a good approximation for the band modes. The resulting expression is independent of the spring constant f, and the band part of the H spectrum is determined solely by geometry and host-crystal properties. In Fig. 1 the spectrum, in the z direction, for this model applied to H in Nb is shown together with the host spectrum for Nb. The spectra were divided by the respective masses in order to be proportional to the vibration amplitudes of the H and the metal atoms. Although only 1.4% (z component) of the total H spectrum appears in the band modes, the vibration amplitudes of H have the same order of magnitude as the metal atoms. A striking feature of the spectrum is the pronounced peak at 3.8 THz for the z vibration. The position of the peak coincides with that of the phonon density of states of the pure metal, emphasizing the importance of the coupling of the z vibration to the $[110]\mathrm{TA}_1$ zone-boundary phonons. The H atom vibrates with an enhanced amplitude in phase with the surrounding host-lattice atoms so that the strong coupling constant f is not strained; see inset Fig. 1. In order to be able to describe more experimental data (lattice parameter change, absence of Snoek effect, i.e., isotropy of the long-range displacement fields, and qualitatively the change of elastic constants[5]) the calculations were repeated for a more general model which included an additional transverse coupling of the H and longitudinal and transverse coupling changes between its four neighbors (six parameters). Such a model seems to be appropriate in order to take into account changes in the electronic structure[6] and in the dispersion curves[7] induced by the H. Qualitatively the structure of the spectra is unchanged; however, a change in peak position and intensity reflects the local coupling changes. In Fig. 1 the spectra for the x and z vibrations are shown for the best fit. Because of their strong coupling to the host-lattice vibrations the H band modes show only a very small isotope effect.

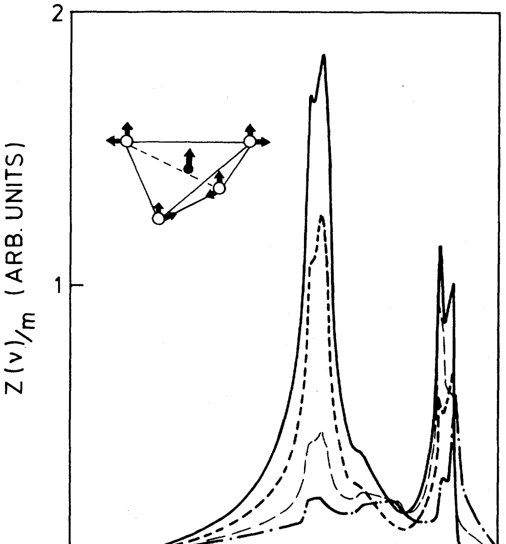

FIG. 1. Spectrum of the band modes divided by mass for H in Nb. Short-dashed line, $Z_z^{\mathrm{H}}(\nu)$ for simple model; solid line, $Z_z^{\mathrm{H}}(\nu)$ for general model; dash-dot, $Z_x^{\mathrm{H}}(\nu)$ for general model; long-dash, $Z(\nu)$ of pure Nb. Inset: coupling of the hydrogen z vibration to the host lattice (filled circle, H atom; empty circle, nearest-neighbor Nb atoms).

In order to confirm the existence of the resonantlike mode in the spectrum we carried out a neutron-scattering experiment with the triple-axis spectrometer IN2 at the Grenoble high-flux reactor. Measurements performed in $\mathrm{NbH}_{0.05}$ and $\mathrm{VH}_{0.05}$ single crystals at constant $\vec{Q}$ (scattering vector) and constant E_f (final energy) allow direct comparison of the calculated spectra with the measured intensities. The measurements were performed at 57°C and 101°C in the α phase of the metal hydrides. Several energy scans at different $\vec{Q}$ values with $E_f = 30$ meV and $E_f = 38$ meV were recorded.

Figure 2 shows a typical energy spectrum in $\mathrm{NbH}_{0.05}$ together with the curves obtained from the calculated spectra. There is clear evidence of a prominent mode at 3.8 THz. It should be noted that Nb itself has only negligible incoherent scattering. The energy spectra were analyzed in terms of a one-phonon approximation.[8] The quasielastic scattering was calculated for a model involving jumps between neighboring interstitial sites; for the one-phonon term we suppose the scattering law of a damped harmonic oscillator of mass m^{H},

$$S(\vec{Q},\omega) = \frac{\hbar}{\pi}\frac{Q^2}{1-\exp(-\hbar\omega/kT)} \times \int d\omega_0 \frac{\omega\Gamma Z^{\mathrm{H}}(\omega_0)}{m^{\mathrm{H}}[(\omega^2-\omega_0^{\,2})^2+(\omega\Gamma)^2]}, \tag{4}$$

where Z^{H} is the orientational average of Z_i^{H}. We assume that the damping constant Γ is equal

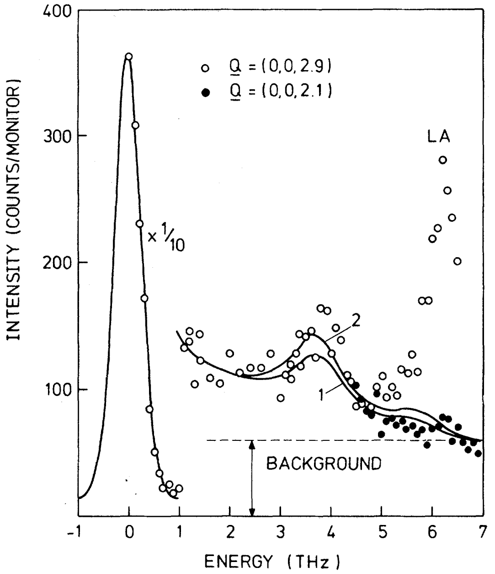

FIG. 2. Measured energy spectrum for $NbH_{0.05}$ at 57°C (curve 1, simplified model; curve 2, general model). The peak LA stems from a host-lattice phonon.

to the jump rate $1/\tau = 6D/d^2$ (D is the diffusion constant, $d = \sqrt{2}\, a/4$ = jump distance). The calculated spectra were convoluted with the energy resolution (Gaussian of full width at half maximum = 0.5 THz) and normalized in the frequency range between 1.0 and 3.0 THz. The measured spectra are well reproduced over the entire energy range. The general model shows a substantially better agreement.

Because of the higher mobility of H in V ($1/\tau \sim 4$ THz), a direct observation of the resonantlike mode which according to our calculations should lie at about 3 THz was not possible. However, an increase in scattering intensity at low frequencies was observed which we think is due to the presence of such an overdamped mode.

The band modes have important physical implications. As shown in Fig. 3 the mean-square displacement can be split into a nearly temperature-independent part due to the localized modes and the contribution of the band modes which is strongly anisotropic and temperature dependent even at low temperatures:

$$\langle u_i{}^2\rangle_{\rm band}^{\rm H} = \int d\omega \tfrac{1}{2} m^{\rm H} \omega) \coth(\hbar\omega/2kT) Z_i{}^{\rm H}(\omega)\,|_{\rm band}$$
$$\simeq kTG_{ii}{}^{\rm HH}(\omega = 0)\,. \qquad (5)$$

The calculated values $\langle \overline{u_i{}^2}\rangle^{\rm H}$ are in good agreement with Debye-Waller–factor data determined recently from quasielastic neutron-scattering experiments.[9]

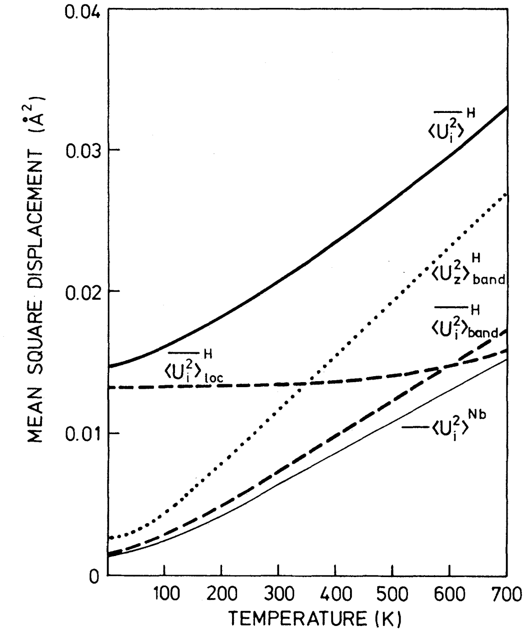

FIG. 3. Mean-square displacement of the H calculated with the general model ($\langle u_i{}^2\rangle^{\rm H}$) and of the host atoms ($\langle u_i{}^2\rangle^{\rm Nb}$). The bar denotes orientational averaging. Also shown are the contributions from the band and localized modes of the spectrum ($\langle\overline{u_i{}^2}\rangle_{\rm band}{}^{\rm H}$, $\langle\overline{u_i{}^2}\rangle_{\rm loc}{}^{\rm H}$) and the thermal displacement in z direction ($\langle u_z{}^2\rangle_{\rm band}$) due to the band modes.

The strong temperature dependence related with large values of $G_{ii}{}^{\rm HH}(0)$ suggests the possibility of a classical jump mechanism for the diffusion. In such a picture the interstitial is imagined as moving in an effective potential which includes lattice relaxations. If we assume a smooth shape (e.g., sinelike) of this potential the activation energy E_a can be estimated in terms of the static Green's function: $E_a \simeq (d^2/2\pi^2)[G_{xx}{}^{\rm HH}(0) + G_{zz}{}^{\rm HH}(0)]^{-1}$. Such an estimate holds in the case of heavy interstitials.[10] The static Green's function $G^{\rm HH}(0)$ is essentially determined by the band modes emphasizing the importance of in-phase vibrations of the H with the host-lattice atoms. The formula yields values of 65, 37, and 73 meV for Nb, V, and Ta, respectively, with the generalized model and 76, 60, and 86 meV for the simplified model. These values agree remarkably well with the low-temperature experimental values. Because of the coupling to the host modes there will be only very little isotope effect for this jump mechanism.

Future investigations will have to show how the low-frequency modes are shifted with concentration and phase and whether the low-frequency excitations observed recently by Shapiro *et al.*[11] in Nb and earlier by Chowdhury[12] in Pd-Ag alloys have, in fact, the same origin.

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Possibility of Vortex-Antivortex Pair Dissociation in Two-Dimensional Superconductors

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The possible existence of a Kosterlitz-Thouless vortex-antivortex dissociation transition in thin superconducting films is discussed. It is found that in practice the situation should be closely analogous to that predicted for superfluid-helium films. A simple relationship is found between the Kosterlitz-Thouless transition temperature and the sheet resistance. This relationship is compared with the observed broadening of the resistive transition of superconducting films with high sheet resistance.

Kosterlitz and Thouless[1] have predicted that in two-dimensional neutral superfluids a thermodynamic instability should occur in which vortex-antivortex pairs, bound at low temperatures, spontaneously dissociate into free vortices at a characteristic transition temperature T_{KT}. Similar ideas have also been discussed by Berezinskii.[2] At this transition Nelson and Kosterlitz[3] have established a universal relation between the Kosterlitz-Thouless transition temperature T_{KT} and the superfluid sheet density. Experiments on superfluid-helium films apparently confirming this prediction have been reported by several groups.[4,5] Some objections to the interpretation of these experiments have been raised, however.[6] Because of the importance of these theories to the questions of the nature of phase transitions and long-range order in two-dimensional systems generally, additional systems suitable for testing the proposed theories are of considerable interest. In this Letter we argue that if these theories are correct, a situation closely analogous to that expected in helium films should arise in very thin superconducting films, and we discuss the conditions under which such effects should be observable. A particularly simple relationship is found between T_{KT} and the sheet resistance of the film.

The existence of the predicted vortex-antivortex dissociation instability in helium films is intimately connected with the fact that in such films the interaction energy between vortex pairs depends logarithmically on the separation between them. As first shown by Pearl,[7] vortex pairs in