Local Defect Structure of Highly Mobile Deuterium in Niobium

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We report measurements of the coherent elastic diffuse scattering of thermal neutrons from the local lattice distortions around deuterium in niobium. We show unambiguously that the heretofore accepted Kanzaki force model does not describe the experimental findings. Model calculations which include relaxation-time effects of the distortion field due to rapid motion of the defect give a satisfactory agreement with the measured intensity distribution. This model provides an explanation of the absence of a Snoek relaxation and relates the defect location, the defect-induced lattice distortion, and the defect diffusion in a self-consistent way.

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Metal-hydrogen systems (like H,D in Nb,Ta) exhibit a series of fundamental condensed-matter phenomena.[1] Extensive studies have been devoted to key questions like the defect location,[1,2] the lattice distortions around the defect,[3,4] and the defect diffusion mechanism.[5] Because these three defect properties are intimately related, many efforts have been made to achieve a conclusive, self-consistent picture. The present answers, however, are still quite puzzling: On one hand it is experimentally well established[2] that H,D occupy the tetrahedral sites in Nb,Ta; the absence of a Snoek relaxation,[6] on the other hand, revealed that the long-range displacement field has cubic symmetry, later confirmed by diffuse scattering.[4,7] Thus the tetrahedral symmetry of the defect site is not imposed on the lattice distortions. This fundamental puzzle in the understanding of metal-hydrogen systems has never been solved, albeit many speculations about its possible physical origin have been made. One of them is the idea that lattice distortions are influenced by the rapid motion of the defect (10^{11} jumps/sec at room temperature).[6] Another, and finally accepted, possible explanation is that the interaction between the proton (deuteron) and the host lattice atoms creates the cubic displacements. In the framework of the Kanzaki forces this concept leads to adjusted forces $f_1 = 1.0$ eV Å^{-1} and $f_2 = 0.23$ eV Å^{-1} on the first- and second-nearest-neighbor atoms.[4,7] Conclusive answers to the physical origin of the absence of a Snoek effect can be expected if the structure and strength of the local distortions in the close vicinity of the defect can be determined experimentally. We present in what follows a diffuse neutron-scattering study which is most sensitive to these very local lattice distortions. It can be shown unambiguously that the two-force model does not describe the local defect environment correctly and that relaxation-time effects due to rapid motion of the defect have to be included in order to explain the observed diffuse intensities.

Static displacements $\mathbf{u}_m^p$ ($\mathbf{u}_m^p$ is the displacement of atom at $\mathbf{R}_m$ due to defect at $\mathbf{R}_p$) give rise to an elastic diffuse scattering intensity. As a result of the properties of the Fourier transformation, the *local* distortions around the defect produce *delocalized* scattering intensities in reciprocal space. Thus, this very weak, smoothly varying diffuse scattering can be detected far away from reciprocal lattice points. The absolute value and the variation of this intensity with scattering vector $\mathbf{Q}$ give detailed information on the strength and symmetry of the local lattice distortion structure. The neutron-scattering cross section of this scattering process can be written as

$$S(\mathbf{Q}) = c_D b^2 \langle | b_D/b \exp(i\mathbf{Q}\cdot\mathbf{R}_p) + \textstyle\sum_m [\exp(i\mathbf{Q}\cdot\mathbf{u}_m^p) - 1] \exp(i\mathbf{Q}\cdot\mathbf{R}_m) | \rangle_p , \quad (1)$$

where c_D is the defect concentration, and b and b_D are the coherent scattering lengths of the host lattice atoms and the defect, respectively. The angular brackets $\langle\ \rangle_p$ indicate the average over all defect sites $\mathbf{R}_p$. $S(\mathbf{Q})$ can be calculated numerically[8] for various defect sites and Kanzaki forces.

The experiments have been performed in a purely (quasi)elastic mode on the triple-axis spectrometer IN2 (Institut Laue-Langevin, Grenoble) with a wave vector of 5.4 Å^{-1} and a 120-60-60-60-min collimation. The scans (at room temperature) have been chosen in order to provide maximum information on the local defect structure (Table I). The defect-induced diffuse scattering has been determined through comparison of a $NbD_{0.017}$ single crystal with a pure Nb reference crystal and calibrated to an absolute scale by the use of transverse-acoustic phonons of the host lattice. (The details are described elsewhere[9].) The final results for $S(\mathbf{Q})$ along scans 1 and 2 are shown in Fig. 1 together with calculated intensity distributions for various defect models.

Consider first the theoretical curves obtained as best fits for the tetrahedral (solid curve), the octahedral (dashed curve), and the triangular (dotted curve) sites [Table II; see also inset in Fig. 1(a)]. Within these

TABLE I. Linear scans in reciprocal space $\mathbf{Q}_n = \mathbf{Q}_0 + n\Delta\mathbf{Q}$ (in units of $2\pi/a = 1.9$ Å^{-1}).

Scan	Starting point $\mathbf{Q}_0$	Step width $\Delta\mathbf{Q}$	Number of points
1	(3.62, 0.43, 0.43)	(0.000, 0.025, 0.025)	50
2	(1.60, 2.25, 2.25)	(0.000, 0.025, 0.025)	50
3	(2.30, 1.25, 1.25)	(0.050, 0.025, 0.025)	29
4	(2.65, 1.86, 1.86)	(0.025, 0.038, 0.038)	27

models we conclude that the tetrahedral-site occupancy gives the best agreement with the data points, whereas the octahedral sites are clearly ruled out (see R factors in Table II). Note the comparably good fit for the triangular sites. These sites have been discussed by Flynn and Stoneham[10] as being important in the understanding of the microscopic diffusion of the defect. The best fit for the tetrahedral sites requires Kanzaki forces on first- *and* second-neighbor atoms which shows that the local distortions exhibit components with cubic symmetry. In addition, however, we observe strong intensity mismatches between the tetrahedral-site model and the experimental points, which demonstrates for the first time that the two-force model is not yet correct. This has two important consequences: (a) The interaction between the interstitial deuterium and the lattice atoms *cannot* be described by the proposed Kanzaki force model. (b) The origin of the cubic symmetry of the long-range displacements in this system requires a different explanation.

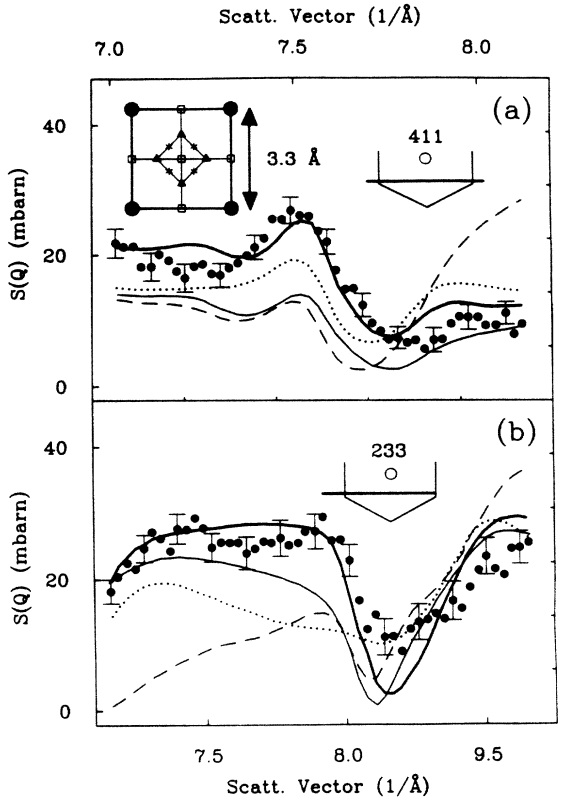

FIG. 1. Experimental results (circles) obtained (a) on scan 1 and (b) on scan 2 compared with numerical calculations for various defect models: solid curve, tetrahedral site (triangles); dotted curve, triangular site (asterisks); dashed curve, octahedral site (squares); boldface curve, new model (see text). The symbols refer to the inset in (a) which shows the locations of the discussed interstitial sites in the (100)-(010)-plane of the bcc unit cell. The insets in both figures illustrate the corresponding scans in reciprocal space.

For the rest of this Letter we develop a new model which is based on the intriguing idea that the understanding of the observed diffuse intensities has to include decaying lattice relaxations around previously occupied defect sites. Such effects become important when the inverse jumping frequency of the defect is comparable to the relaxation time t_R of the lattice distortions. So far no theoretical value for t_R is known; however, an estimate is possible following Emin, who has calculated t_R in the framework of the small polaron[11]:

$$t_R = (12/\pi\Delta\omega)(2E/kT)^{2/3}. \quad (2)$$

t_R is essentially determined by the bandwidth $\Delta\omega$ of those phonons which contribute to the dissipation of the elastic energy E stored in the lattice distortions. Taking[12] $E = 169$ meV and the full Nb phonon dispersion width $\Delta\omega = 6.0\times10^{12}$ s^{-1}, we get $t_R = 4\times10^{-12}$ s, which is indeed comparable to ν^{-1} (ν being 5×10^{11} s^{-1} at room temperature[5]).

For a quantitative consideration of relaxation-time effects in the defect-induced lattice distortions the

TABLE II. Defect models for D in Nb: defect location $\mathbf{R}_p$, Kanzaki forces $f_{1/2}$, and obtained R factors $R := \sum(I_{\text{obs}} - I_{\text{calc}})/I_{\text{obs}}$.

	$\mathbf{R}_p(a/2)$	Kanzaki forces (eV Å^{-1})	R factor
Tetrahedral	(1.5, 1.0, 0.0)	$f_1 = 1.00$ $f_2 = 0.23$	2.08
Octahedral	(1.0, 1.0, 0.0)	$f_1 = 1.02$ $f_2 = 0.72$	3.24
Triangular	(0.75, 0.75, 0.0)	$f_1 = 1.00$ $f_2 = 0.50$	2.75
New model	See text	$f_1 = 1.00$	0.76

knowledge of the microscopic jumping path of the defect is necessary: It has been shown[13] that the rapid motion of protons in transition metals has to be described by a two-state model at temperatures $T \geq 300$ K. In the so called *mobile state* the defect is allowed to perform fast, repeated jumps between tetrahedral sites; the number of tetrahedral sites involved is 3.2 at 293 K and increases with temperature. In the second, the *immobile state*, the defect stays at one tetrahedral site.

Lattice relaxations can be introduced into this diffusion model in the following way: We propose that the defect-lattice interaction preserves the symmetry of the defect site and should be describable by Kanzaki forces applied at the nearest-neighbor atoms only. A reasonable force is $f_1 = 1.0$ eV Å^{-1}, according to the observed lattice parameter change.[14] These forces parametrize the immobile state. We conclude that in the mobile state the inverse jumping frequency ν^{-1} of the deuteron is comparable to the lattice relaxation time t_R: The defect then performs repeated jumps within a distorted region established around (according to Ref. 13) three adjacent tetrahedral sites. For sake of simplicity we assume that the lattice relaxations are (in a first approximation) the same around the three defect sites involved and calculate the resulting distorted region by linear superposition of the three individual force fields. This determines the structure factor $S_{\mathrm{mb,t}}(\mathbf{Q})$ of one mobile state, where the defect is located at *one* tetrahedral site within a distorted region extended over three sites. Consider one tetrahedral site in the bcc lattice [see also inset in Fig. 1(a)]: Since it has four tetrahedral sites as nearest neighbors, there are six possible configurations of three adjacent tetrahedral sites. In the actual calculation $S_{\mathrm{mb,t}}$ has to be averaged over all these configurations (altogether eighteen because of the tetrahedral symmetry), denoted by $\langle\ \rangle_c$. With these assumptions the structure factors of the immobile state $\langle S_{\mathrm{im}}(\mathbf{Q})\rangle_p$ and mobile state $\langle S_{\mathrm{mb,t}}(\mathbf{Q})\rangle_c$ can be calculated without any free parameter (Fig. 2). In a further step a finite flight phase of the defect in the mobile state is taken into account by an occupation probability $p_{\mathrm{mb,tg}}$ of triangular sites

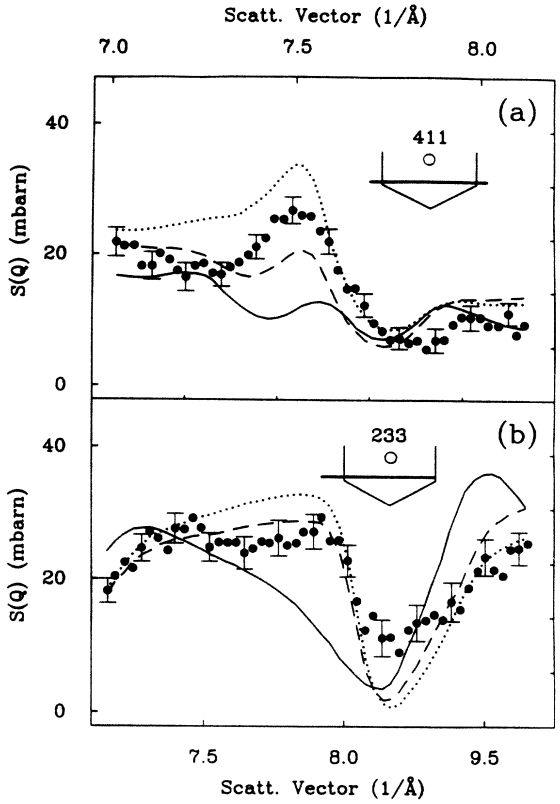

FIG. 2. Experimental results (circles) obtained (a) on scan 1 and (b) on scan 2 compared with numerical calculations for the intensity contributions of the immobile and mobile states (see text): solid curve, $\langle S_{\mathrm{im}}(\mathbf{Q})\rangle_p$; dashed curve, $\langle S_{\mathrm{mb,t}}(\mathbf{Q})\rangle_c$; dotted curve, $\langle S_{\mathrm{mb,tg}}(\mathbf{Q})\rangle_c$. The insets show the corresponding scans in reciprocal space.

within the distortions associated with the mobile state. (Eventual additional lattice relaxations due to the triangular occupation have been neglected.) The corresponding structure factor $\langle S_{\mathrm{mb,tg}}(\mathbf{Q})\rangle_c$ is shown as the dotted lines in Fig. 2. Note that the only difference between $\langle S_{\mathrm{mb,t}}(\mathbf{Q})\rangle_c$ and $\langle S_{\mathrm{mb,tg}}(\mathbf{Q})\rangle_c$ is the position of the deuteron within the same lattice distortions of the mobile state.

Within this model the total scattering cross section $S(\mathbf{Q})$ is composed as follows:

$$S(\mathbf{Q}) = p_{\mathrm{im}}\langle S_{\mathrm{im}}(\mathbf{Q})\rangle_p + p_{\mathrm{mb,t}}\langle S_{\mathrm{mb,t}}(\mathbf{Q})\rangle_c + p_{\mathrm{mb,tg}}\langle S_{\mathrm{mb,tg}}(\mathbf{Q})\rangle_c. \quad (3)$$

We use the unknown occupation probabilities p_{im} (immobile state), $p_{\mathrm{mb,t}}$ (mobile state, defect on tetrahedral sites) and $p_{\mathrm{mb,tg}}$ (mobile state, defect on triangular sites) as fitting parameters. Because $p_{\mathrm{im}} + p_{\mathrm{mb,t}} + p_{\mathrm{mb,tg}} = 1$ must be fulfilled, there remain only two independent parameters for a least-squares fit of Eq. (3) to our data points. The final result is shown as the bold lines in Fig. 1 and gives $p_{\mathrm{im}} = 0.2$, $p_{\mathrm{mb,t}} = p_{\mathrm{mb,tg}} = 0.4$, which is remarkably close to the values obtained from the incoherent quasielastic linewidths[13] ($p_{\mathrm{im}} = 0.35$). The R factor of our fit is $R = 0.76$ which has to be compared with $R = 2.08$ for the two-force tetrahedral-site model (Table II), both models using two free parameters. This is a strong evidence that the concept of the proposed relaxation model is correct.

The final results enable us to determine the properties of the long-range displacement field by calculation of the force dipole $\langle P_{ij}\rangle$ averaged over the immobile

and mobile states ($\langle\ \rangle$). We get $\mathrm{Tr}\langle P_{ij}\rangle = 10$ eV in agreement with values from literature[4,14] and an anisotropy of $t := (\langle P_{11} - P_{22}\rangle / \mathrm{Tr}\langle P_{ij}\rangle = 0.05$ which is very close to $t = 0$ for perfect cubic symmetry (the observed value[4] is $t = 0.02$). Thus the absence of a Snoek relaxation should not be referred to specially adjusted Kanzaki forces, but to the action of decaying lattice distortions accompanying the rapid motion of the defect. Furthermore, our data analysis reveals a finite occupation of triangular sites during the rapid motion in the mobile state. We suggest that this should be attributed to the flight phase.[10,15]

In summary we emphasize that our lattice-relaxation model provides for the first time a consistent relation between the defect location, the defect-induced lattice distortions, and the microscopic defect diffusion mechanism. The decaying lattice distortions should be detectable as an additional line broadening of the *coherent* quasielastic diffuse neutron scattering. Measurements of the temperature dependence of the coherent line width are under way.

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