X-Ray Measurement of the Coupling between Static and Thermal Displacements around Hydrogen in Niobium

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The authors report x-ray measurements of the attenuation of integrated Bragg intensities which is attributed to the static Debye-Waller factor, exp($-2L$), due to hydrogen in Nb single crystals in the homogeneous α phase. For small hydrogen concentrations, the dependence of $2L$ versus the scattering vector, $\vec{K}$, can be explained by the nonlinear coupling between static and thermal displacements around point defects. Detailed information about both types of displacements of the Nb atoms nearest to the interstitial hydrogen atom has been obtained.

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Hydrogen dissolves in the bcc lattice of Nb in tetrahedral interstitial sites, which are occupied randomly at low concentrations or high temperatures (α phase). Besides a homogeneous lattice expansion,[1] the four Nb atoms closest to the H impurity will be strongly displaced and thus the equilibrium position of their thermal vibrations is removed from the average lattice position, as determined by lattice parameter measurements. As the static displacements around point defects are known to decrease like $1/r^2$ with the distance r from the defect, this coupling effect between static and thermal displacements can also be expected to decrease rapidly for the Nb atoms beyond the first coordination shell of the interstitial hydrogen. The influence of this nonlinear coupling, between static and dynamical displacements around point defects, on the reduction of Bragg diffraction intensities as described by a Debye-Waller factor (DWF), has been treated by Krivoglaz.[2,3] It has been predicted that static DWF measurement will give information on the local structure around point defects: The static displacements of the host lattice atoms closest to a point defect can be determined[4] and the mean square thermal displacement of these atoms, vibrating in a different potential from the rest of the atoms, can be obtained. Although static DWF measurements of various defect systems have been reported in the literature,[5-7] the authors were not aware of this coupling effect which eventually could change the evaluation of their data in cases where local atomic displacments rather than the mean square static displacement has been deduced.[5]

In this Letter we report x-ray measurement of the static DWF, exp($-2L$), from NbH$_x$ single crystals in the homogeneous α phase at 200 °C. $2L$ as a function of the scattering vector $\vec{K}$ has been measured up to the (10 0 0) reflection. The information about the coupling of static and thermally activated atomic displacements close to point defects can only be received from the measurement of $2L$ at high K values. Using the theory of the nonlinear coupling between static and thermal displacements[2,3] we were able to fit the dependence of $2L$ on K with two parameters: the displacement of the first four Nb atoms around the H atom on a tetrahedral site and the *change* of the thermal vibrations of these Nb atoms.

Nb single crystals oriented along ⟨110⟩, ⟨100⟩, and ⟨111⟩ directions have been used after a purification at 2100 °C under UHV conditions. The hydrogen doping has been performed at 650 °C on the x-ray spectrometer,[8] with the actual concentration determined from simultaneous lattice parameter measurements using the calibrating value[9] ($\Delta a/a$) per at.% H of 5.4×10^{-4}. The integrated Bragg intensities for different concentrations and scattering vectors have been measured by both an angle-dispersive and an energy-dispersive method.[8,10] The hydrogen-induced attenuation of the integrated Bragg intensities is attributed to the static DWF which is given by $I^c = I^0 \exp(-2L)$, where I^0 and I^c are the intensities from the pure and the H-loaded crystals, respectively. $2L$ has been reported to increase linearly with the H concentration in NbH$_c$ for $c \leq 0.2$.[2,8] The slope of the corresponding straight line $2L/c$ for each reflection is plotted versus K^2 in Fig. 1 [the scattering vector $\vec{K}$ is the reciprocal lattice vector $\vec{G}(hkl)$]. Open symbols stem from the angle-dispersive method, filled symbols from the energy-dispersive method. It is clearly demonstrated that $2L/c$ is isotropic and deviates from the linear increase with K^2 for $K \geq 8$ Å^{-1}. For completeness it should be pointed out that $2L$ is not simply given by the logarithm of the measured intensity ratio

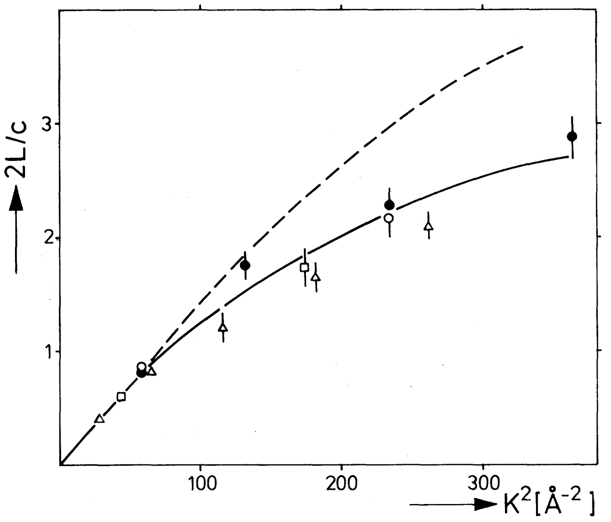

FIG. 1. The static DWF $2L$ per unit concentration vs the scattering vector K^2. Open symbols from angle-dispersive method, filled symbols from energy-dispersive method. Circles, $(h00)$; triangles, $(hh0)$; squares, (hhh). For further details see text.

$\ln I^0/I^c$, but a correction has to be applied because of the hydrogen-induced change of the thermal DWF $\exp(-2M)$. The total reduction of the measured Bragg intensity is caused by static displacements around the H atoms and by the change of the thermal vibrations. The separation of these two effects can easily be performed by the measurement of integrated Bragg intensities either keeping the temperature constant and varying the hydrogen concentration (static DWF) or by keeping the H concentration constant and varying the temperature (thermal DWF). In the latter case the mean square thermal displacement $\langle u_{\mathrm{th}}^2\rangle$ is obtained by use of the harmonic approximation in the high-temperature limit (kT per normal mode) where $2M = K^2\langle u_{\mathrm{th}}^2\rangle$ and $\langle u_{\mathrm{th}}^2\rangle \sim T$ holds.[11] $2M$ or $\langle u_{\mathrm{th}}^2\rangle$ can then be normalized to 200 °C, the temperature at which the static DWF has been measured. The two contributions can thus be compared and turn out to be of the same order of magnitude and therefore have to be measured with the same accuracy. Figure 2 shows the thermal DWF exponent $2M$ at 200 °C as a function of K^2. For pure Nb (open symbols) and $\mathrm{NbH}_{0.2}$ (filled circles) the obtained straight lines prove the validity of the harmonic approximation and show that the corresponding mean square thermal displacement $\langle u_{\mathrm{th}}^2\rangle$ decreases with the hydrogen content in the sample. For pure Nb $\langle u_{\mathrm{th}}^2\rangle = 7.8 \pm 0.3$ Å^2 at 200 °C has been found and from other measurements we obtained a linear decrease of $\langle u_{\mathrm{th}}^2\rangle$ with the hydrogen concentration (details of the method and further results are published elsewhere[8,12]). Other corrections to the integrated intensities are negligible. For instance, the contributions of thermal diffuse scattering to the temperature-dependent integrated intensity (thermal DWF) and of Huang diffuse scattering in the case of the concentration-dependent measurement (static DWF) are less than 1%.[8,12] Before we further discuss the K dependence of $2L/c$, we want to emphasize that the above mentioned correction of $2M$ is proportional to K^2 and thus does not influence the nonlinearity of the increase of $2L/c$ with K^2.

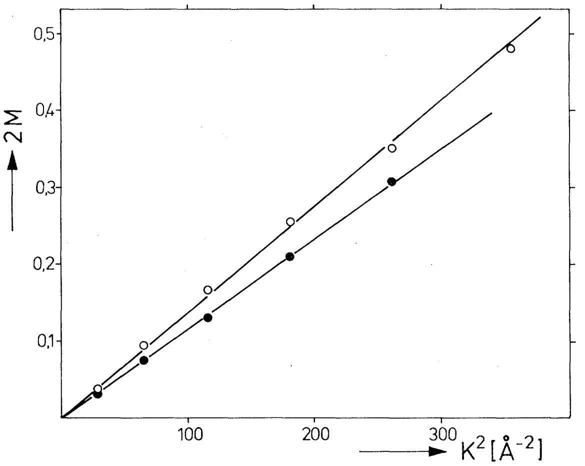

FIG. 2. Thermal DWF $2M$ at 200 °C as a function of K^2 for (open circles) pure Nb and (solid circles) $\mathrm{NbH}_{0.2}$.

In order to explain the observed K dependence of $2L/c$ in Fig. 1, we compared it with Krivoglaz's theory of the coupling between static and thermal displacements. This theory is based on the fact that in a crystal with point defects the averaging in the general expression for the DWF, $\exp(-\vec{K}\cdot\delta\vec{R}_s)$, has to be performed both by a time average and a configurational average. Here $\delta\vec{R}_s$ is the total displacement of the atoms due to static and thermal contributions. The main difference with respect to a defect-free crystal is that the mean square thermal displacements are no longer the same for all atoms in the crystal, but depend on the distance from the defect. Therefore the configurational average over a binomial defect distribution of point defects induces a coupling between static and thermal displacements. Quantitatively the exponent $2M^*$ of the total DWF is given by (small concentration c)[2,3]

$$2M^* = 2M + 2c\sum_s [1-\cos(\vec{K}\cdot\vec{u}_s^{\,st})] \times (1-\tfrac{1}{2}K^2\Delta v_s^2). \qquad (1)$$

Here $2M=\langle u_{\mathrm{th}}^2\rangle K^2$ is the average thermal effect of all Nb atoms, where $\langle u_{\mathrm{th}}^2\rangle$ decreases with the H concentration (Fig. 2).[12] The second expression in Eq. (1) represents the static DWF and the coupling term. $\vec{u}_s{}^{\mathrm{st}}$ is the static displacement of the atom s and $\Delta v_s{}^2$ is the difference between $\langle u_{\mathrm{th}}^2\rangle$ for all atoms and the actual mean square displacement of the atom s. The summation in Eq. (1) has to be carried out in principle over all lattice atoms around the H atom. It has been pointed out, however, that 95% of this summation is taken care of if only the nearest neighbors around the defect (displacements $u_1{}^{\mathrm{st}}$) are considered.[4] Within this approximation we therefore obtain for the static DWF of H in Nb from Eq. (1)

$$2L/c=\tfrac{8}{3}[1-\cos(\vec{K}\cdot\vec{u}_1{}^{\mathrm{st}})](1-\tfrac{1}{2}K^2\Delta V_1{}^2). \qquad (2)$$

For $K^2\Delta V_1{}^2 \ll 1$ we can fit the K dependence of $2L/c$ for small K only (dashed line in Fig. 1), using for the displacement of the first atomic shell $u_1{}^{\mathrm{st}}=0.1$ Å (see also Refs. 4 and 8). For higher K we have to take the coupling term into account, which is approximately a function of K^4. The full line in Fig. 1 shows the complete fit with $u_1{}^{\mathrm{st}}=0.1$ Å and $\Delta V_1{}^2=1.6\times10^{-3}$ Å^2 at $T=200\,^\circ\mathrm{C}$. In order to get a feeling for the meaning of $\Delta V_1{}^2$, we want to compare it with the mean square thermal displacement $\langle u_{\mathrm{th}}^2\rangle$ of all Nb atoms at 200 °C as determined from Fig. 2. We obtain $\Delta V_1{}^2/\langle u_{\mathrm{th}}^2\rangle \approx 0.2$ which means that the mean square vibrational amplitude of the Nb atoms nearest to H differs by about 20% with respect to $\langle u_{\mathrm{th}}^2\rangle$. As can be seen from Eq. (1), the coupling effect should in principle appear in the measurement of $2M$ also. Here it can be neglected, however, because the number of nearest-neighbor atoms is much smaller than the rest of the host-lattice atoms, which mainly determine the average thermal DWF $2M$. Therefore the thermal DWF is rather insensitive to the coupling effect.

We have shown here, for the first time, that the measurement of the static DWF in a crystal with point defects is a sensitive method to determine static and vibrational displacements of host-lattice atoms nearest to the defects. It should be pointed out that the coupling of static and thermal displacements can only be obtained from the measurement of the static DWF at high orders of reflection. The large anharmonic change of the vibrational amplitudes for the Nb atoms directly adjacent to the H impurity must eventually be taken into account in considering, for example, the diffusion behavior of these systems.

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[1] J. D. Eshelby, J. Appl. Phys. 25, 255 (1953).

[2] M. A. Krivoglaz, Kristallografiya 4, 813 (1959).

[3] M. A. Krivoglaz, *Theory of X-Ray and Thermal Neutron Scattering by Real Crystals* (Plenum, New York, 1969).

[4] H. Metzger, H. Behr, and J. Peisl, Z. Phys. B 46, 295 (1982).

[5] S. C. Moss, Acta Metall. 15, 1815 (1967).

[6] F. H. Herbstein, B. S. Borie, Jr., and B. L. Averbach, Acta Crystallogr. 9, 466 (1956).

[7] W. R. McEntire and J. B. Cohen, Acta Metall. 23, 953 (1975).

[8] H. Behr, H. Metzger, and J. Peisl, to be published.

[9] H. Pfeiffer and J. Peisl, Phys. Lett. 60A, 363 (1977).

[10] G. Steyrer, diplom thesis, Universität München, 1982 (to be published).

[11] B. T. Willis and A. W. Pryor, *Thermal Vibrations in Crystallography* (Cambridge Univ. Press, Cambridge, England, 1975).

[12] H. Behr, G. Steyrer, H. M. Keppler, H. Metzger, and J. Peisl, to be published.