Unusual diffuse scattering intensities from nitrogen in niobium

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Coherent elastic diffuse scattering of neutrons is observed far from reciprocal-lattice points in $NbN_{0.014}$ crystals. We give evidence that the unusual intensity distribution originates from randomly distributed N impurities which induce strong and extended local distortions into the host lattice. A three-force Kanzaki model is able to describe the measured structure function quantitatively.

The diffuse scattering of neutrons and x-rays due to interstitially dissolved nitrogen in niobium has been reported by several authors.[1–3] Most surprising are the results obtained in a neutron scattering study[1] on a Nb single crystal loaded with 0.15 at.% nitrogen. Diffuse peaks were observed at positions corresponding to a reduced scattering vector (units of $2\pi/a$) of $(\frac{2}{3},\frac{2}{3},\frac{2}{3})$, the points at which the [111] LA phonon dispersion curve has a local minimum.[4] These diffuse peaks, however, do not have the periodicity of the reciprocal lattice. Similar results were obtained for small concentrations of substitutional Zr in Nb (Ref. 5), and for the ω phase transition in Nb-Zr alloys.[6] (In the case of substitutional Zr in Nb, however, the diffuse scattering pattern is periodic in reciprocal space.) The essential question raised by Rowe *et al.*,[1] "why do 0.15 at.% N atoms per Nb atom give rise to a diffuse pattern similar to that of the ω phase?", is still open. In the following we present additional experimental evidence for existence of this unusual diffuse scattering and propose a simple model which is able to explain all the reported findings.

We have measured the coherent elastic diffuse scattering of neutrons far away from reciprocal-lattice points with high accuracy and on an absolute scale. The samples were two identical Nb single crystals (cylinders oriented along the [110] axis) which were degassed at about 2200 °C in a vacuum of 10^{-9} Torr. One sample was loaded with nitrogen by the following standard procedure. The Nb crystal was heated up to 1700 °C and then exposed to a nitrogen atmosphere with a pressure of 1.2×10^{-6} Pa for 36 h. In order to avoid nitrogen precipitation the sample was quenched afterwards in He gas to room temperature.[3,7] The actual N concentration was determined from the weight increase of the sample amounting to 1.4 at.%. This value was confirmed by lattice-parameter and residual-electrical-resistivity measurements.

TABLE I. Measuring program: linear scans in the reciprocal space $\mathbf{Q}=\mathbf{Q}_i+\Delta\mathbf{Q}$ ($\mathbf{Q}_i$ is the initial point, $\mathbf{Q}_f$ is the final point; units of $2\pi/a$).

Scan	$\mathbf{Q}_i$			$\mathbf{Q}_f$			$\Delta\mathbf{Q}$
1	1.60	2.25	2.25	1.60	3.50	3.50	$\xi(011)$
2	3.62	0.43	0.43	3.62	1.68	1.68	$\xi(011)$
3	2.65	1.86	1.86	3.40	3.00	3.00	$\xi(233)$

The neutron scattering experiments were performed at the high-flux reactor (HFR) of the Institut Laue-Langevin (ILL), Grenoble. The triple-axis IN2 spectrometer was used in a purely elastic mode. A 120-60-60-60-min col-

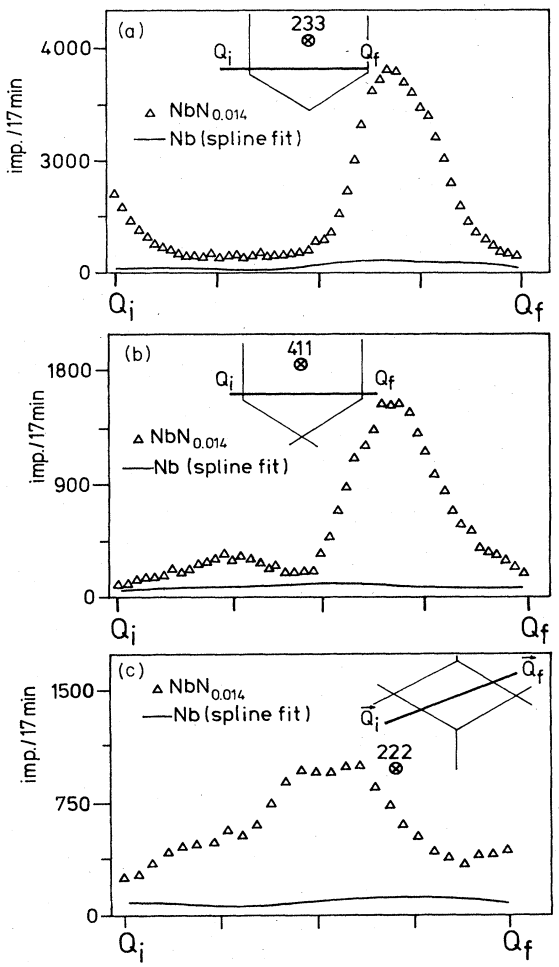

FIG. 1. Raw data obtained along three scans in reciprocal space (Table I). The weak incoherent scattering from Nb is smoothed by a spline-fit program (solid line). Intensities are normalized to equal sample volumes.

limation together with an incident wave vector of 5.4 Å^{-1} was used. The background scattering was reduced by this setup to the weak incoherent scattering and very little inelastic scattering of Nb, which was determined experimentally from the Nb reference crystal. A very accurate calibration of the diffuse intensities on an absolute scale was obtained by relating them to the intensities of some TA phonons of Nb. This novel procedure and the details of the data treatment will be described in detail elsewhere.[8] The scattering intensities have been measured along the three scans summarized in Table I. Large scattering vectors and low-symmetry areas of reciprocal space in various Brillouin zones were used in order to gain the optimum amount of information about the defect structure.

The raw data for $NbN_{0.014}$ and Nb are shown in Fig. 1. The salient features of the observed intensity profiles for $NbN_{0.014}$ are their similarity to the scattering structures found by Rowe *et al.*[1] along the [111] direction. In order to demonstrate that these intensities originate from single-N impurities and the local lattice distortions produced by them we discuss the following scattering function[2,9]

$$S(\mathbf{Q})=c\left\langle\left|b_D e^{i\mathbf{Q}\cdot\mathbf{r}^D}+b\sum_m e^{i\mathbf{Q}\cdot(\mathbf{r}^m+\mathbf{u}^m)}\right|^2\right\rangle . \tag{1}$$

c is the impurity concentration, b_D and b are the coherent scattering lengths of the impurity (N) and the host-lattice atom (Nb), respectively, $\mathbf{Q}$ is the scattering vector, $\mathbf{r}^D$ denotes the location of the impurities, and $\mathbf{u}_m$ the displacement of the lattice atoms from their average positions $\mathbf{r}^m$. Evidently, $S(\mathbf{Q})$ is determined by two scattering amplitudes, one from the impurity itself (first term), the other from the distorted host-lattice atoms (second term). The angled brackets indicate the average over all nonequivalent defect sites $\mathbf{r}^D$. The displacements $\mathbf{u}^m$ can be calculated using the Green's functions[10] G_{ij}^{m-n},

$$u_i^m=\sum_{n,j} G_{ij}^{m-n} f_j^n . \tag{2}$$

f_j^n are Kanzaki forces[11] applied to the lattice atoms n in order to produce the same displacements as the actual defect. They are related to the experimentally determined force-dipole tensor by

$$P_{ij}=\sum_n r_i^n f_j^n . \tag{3}$$

The force-dipole tensor on N in Nb has been determined experimentally by means of Huang diffuse x-ray scattering[3]

TABLE II. Defect models for N in Nb (octahedral-site occupancy assumed): Kanzaki forces $f_{1,2,3}$ on first, second, third Nb-shell local distortions $u_{1,2,3}$ of first, second, third Nb neighbors.

Kanzaki forces (eV Å^{-1})	$2f$ model	$3f$ model	Literature (Ref. 10)
f_1	3.88	3.00	3.88
f_2	0.94	-0.92	0.67
f_3	0	0.50	0
Distortions (Å)			
u_1	0.517	0.502	0.519
u_2	0.0048	-0.220	0.0031
u_3	0.0292	0.052	

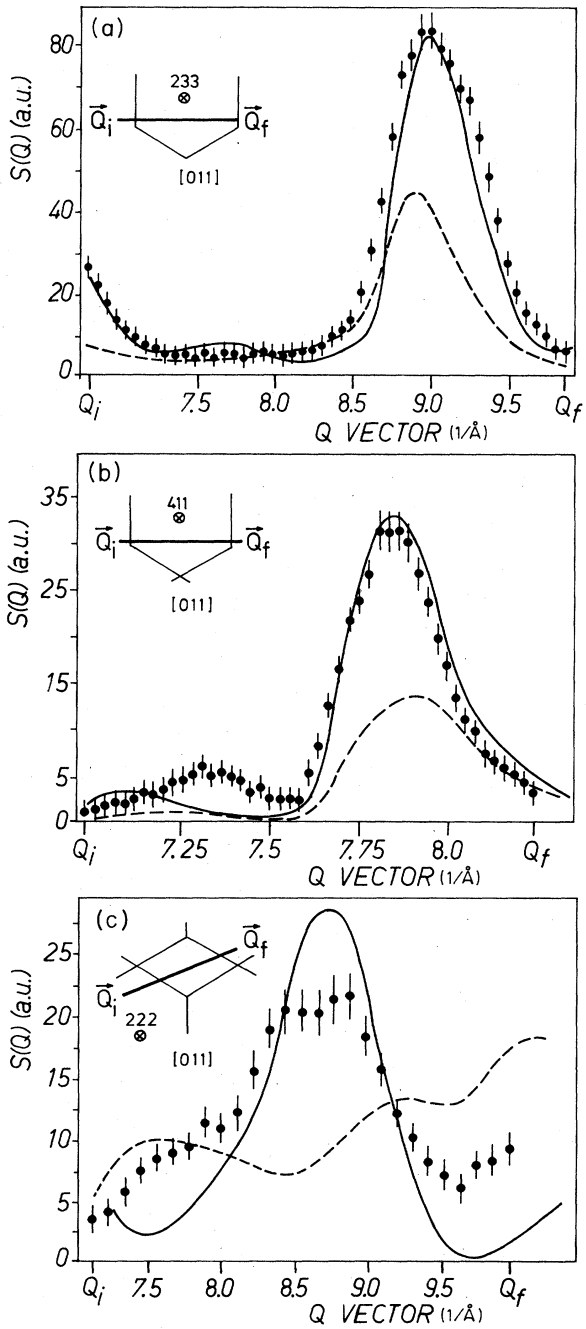

FIG. 2. Final experimental results (absolute scale) compared with numerical calculations for the $2f$ model (dashed line) and the $3f$ model (solid line).

$$P_{ij}=\begin{bmatrix}12.6 & 0 & 0\\ 0 & 5.0 & 0\\ 0 & 0 & 5.0\end{bmatrix} \quad (4)$$

measured in eV. Assuming that N occupies the octahedral sites in the *bcc* lattice[12] we have calculated from Eqs. (2)—(4) two sets of Kanzaki forces and the corresponding distortions which are summarized in Table II and compared with those calculated by Tewary.[10] The simplest model that can produce P_{ij} according to Eq. (3) is radial forces f_1 and f_2 on the nearest and next-nearest Nb atoms around the octahedral site ("2f model"). Calculations were also done for a more extended force model with radial forces up to the third shell ("3f model"). We want to draw the reader's attention to the values of u_1 which are about 0.5 Å in all three cases. This value is in good agreement with a recent Stokes-Wilson scattering study[2] on $NbN_{0.011}$.

Based on these two models we have calculated the diffuse scattering cross section[13] and compared it to our experimental results (Fig. 2). The experimental data points have been plotted on an absolute scale. Clearly, the 2f model can by no means reproduce the observed scattering intensities whereas the 3f model gives good agreement everywhere. Thus the 3f model confirms the octahedral-site occupancy of N in Nb and explains the origin of our observed peaks as well as the results reported by Rowe *et al.*[1] This is demonstrated in Fig. 3 where we expect a diffuse peak at $\mathbf{Q}_1=(\frac{4}{3},\frac{4}{3},\frac{4}{3})$ and at $\mathbf{Q}_2=(\frac{7}{3},\frac{7}{3},\frac{4}{3})$ and no peak at $\mathbf{Q}_3=(\frac{5}{3},\frac{5}{3},\frac{4}{3})$. This is exactly what is observed. The reason why these intensities do not occur at all equivalent points in the reciprocal lattice can be understood by inspection of Eq. (1) which shows that the variation to the structure function $\mathbf{Q}$ is influenced by the phase factor $e^{i\mathbf{Q}\cdot\mathbf{r}^D}$. It does not have the periodicity of the lattice in the case of an interstitial defect, such as N in Nb. For a substitutional defect (Zr in Nb), however, $e^{i\mathbf{Q}\cdot\mathbf{r}^D}=1$, independent of $\mathbf{Q}$, and we would expect a periodical diffuse intensity. Analogous calculations show that the same peaks should be observable with x-rays. This, indeed, has been observed.[14] Another consequence of the strong local distortions around interstitial N is a remarkably high static Debye-Waller factor which can be observed as an attenuation of the Bragg reflections and the phonon scattering.[15]

Finally, we want to emphasize that all the observed scattering phenomena, the Huang diffuse scattering, the Stokes-Wilson scattering, and the diffuse peaks between Bragg reflections can be explained by one and the same model: They stem from randomly distributed N impurities which induce strong and extended local distortions into the host lattice. The relation between the ω phase transition in NbZr which creates similar diffuse scattering (short-range-order scattering) and the model proposed here is not evident and can only be achieved beyond the Kanzaki-force formalism. We suggest that impurities such as N, O, or Zr favor the instability of the *bcc* lattice and induce a local condensation of a new structure in the close neighborhood of the defect which is called "local distortion" in the Kanzaki formalism. The volume mismatch of this local structure leads to long-ranged static displacements which can be detected by Huang diffuse scattering. In this picture the observed peaks appear as the "freezing" of some special lattice modes in the presence of impurities ("central peak").[16] For a confirmation of these new ideas, further experiments are under way.

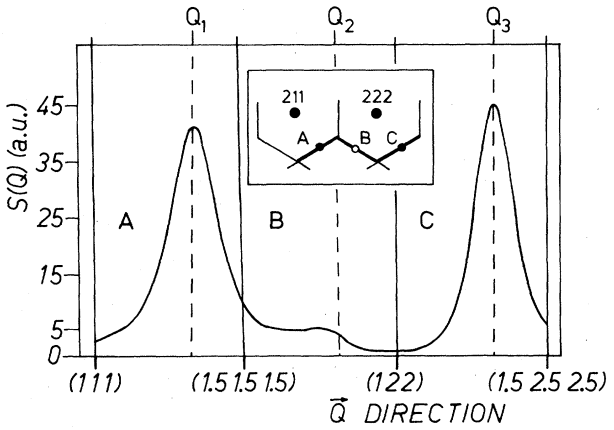

FIG. 3. Prediction of the intensity distributions along the scans A,B,C as measured by Rowe *et al.* (Ref. 1) according to the 3f model. Solid circles represent points where intensity was found experimentally, open circles where no intensity was found. (For $\mathbf{Q}_1,\mathbf{Q}_2,\mathbf{Q}_3$ see text.)

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