

Comparison of x-ray and neutron diffuse scattering intensities in niobium*

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It is not clear whether or not the x-ray diffuse intensity scattered by crystals outside the Bragg spots can be entirely explained by considering thermal vibrations. Striking discrepancies are found in some cases, when x-ray data are compared with phonon dispersion relations determined via inelastic neutron scattering. A careful analysis is carried out for niobium, which exhibits anomalies (humps) in the elastic neutron diffuse scattering intensity. These anomalies are not found in the x-ray diffuse scattering, which can be very accurately accounted for by considering incoherent (Compton) scattering plus first- and higher-order phonon scattering. The latter was calculated using dispersion relations obtained by neutron inelastic scattering. It seems unlikely that hydrogen may be responsible for the extra scattering observed with neutrons. No explanation is found for this discrepancy between x-ray and neutron results.

I. INTRODUCTION

The oldest experimental method capable of providing information about dispersion curves of phonons in crystals is based on the study of x-ray thermal-diffuse scattering¹ (TDS). This method was first proposed by Laval in 1938,² and subsequently applied by Olmer to aluminum³ and by Curien to α -iron.⁴ It soon became apparent, however, that large corrections (up to 50% or more) had to be applied to the measured intensities before dispersion curves could be extracted from the data. These corrections consist principally of incoherent (Compton) scattering and multiphonon processes, and large errors may result from the uncertainty with which these effects can be evaluated. With the advent of inelastic neutron scattering, x-ray techniques have been practically abandoned for lattice-dynamics studies, except for those elements for which neutron scattering is not feasible, such as vanadium,⁵ and cadmium.⁶ It is known, in fact, that neutron-scattering techniques are much more reliable because the energies of the phonons are measured *directly*, whereas in the x-ray case phonon frequencies are extracted from intensity data through a tortuous process involving the kind of corrections mentioned above.

As soon as the first neutron-scattering dispersion curves became available the question was asked whether the two techniques, neutron and x-ray scattering, give the same results. If we consider the dispersion curves of aluminum, for example, and compare the data obtained with x rays⁷ and neutrons,⁸ we find that the agreement is fairly good, within, say, 10%. However, when we turn to zinc and copper, for which the x-ray data are presented in Refs. 9 and 10, and the neutron data in Refs. 11 and 12, respectively, we find large discrepancies. In the case of vanadium no com-

parison can be made because neutron data are not available. However, the frequency spectrum calculated from the x-ray data is in excellent agreement with that measured experimentally by incoherent neutron scattering, which gives reliable results in the case of vanadium, an almost totally incoherent scatterer.

A striking discrepancy between x-ray and neutron data was found for lead,¹³ up to 60%. One is forced to recognize, at this point, that x rays and neutrons are scattered through different mechanisms, and that perhaps it is this difference which is responsible for the discrepancies reported above.

It was pointed out by Buyers *et al.*¹⁴ in 1968, using theoretical as well as experimental arguments, that ionic distortion cannot be neglected in x-ray scattering. The importance of anharmonic effects in x-ray experiments, interference between harmonic one phonon and many-phonon scattering, was pointed out by Maradudin and Ambegaokar¹⁵ and by Cowley and Buyers.¹⁶ These anharmonic effects have been evaluated by Pirie *et al.*¹⁷ for KCl and Al and experimentally confirmed by Hervet and Ober.¹⁸ It is unfortunate that the same calculations are not available for other metals such as copper, zinc, and lead, for which large anomalies have been observed.

The program of this work is to measure x-ray diffuse scattering in a metal such as niobium, along principal symmetry directions, and to compare with intensities calculated from neutron-diffraction data.¹⁹ Niobium is an interesting metal, in which electron-phonon interaction is particularly strong, as evidenced by the conspicuous Kohn anomalies present in its dispersion curves. The first question is, then, whether or not the same anomalies are visible in the x-ray experiments.

It is known that when niobium is alloyed with

zirconium, a metastable structure is formed, known as omega phase,²⁰ which gives rise to diffuse reflections. As the Nb concentration is increased the extra reflections become weaker and more diffuse. It has been reported by Sass²⁰ that some diffuse scattering can be observed even in pure Nb, along [111], in proximity of the zone boundary, suggesting some kind of a linear fault parallel to [111], endemically present in Nb. Sass's report, however, is based on electron-diffraction patterns, and therefore, it is not possible to discriminate against thermal diffuse scattering, which has a peak around $\frac{1}{3}\frac{1}{3}\frac{1}{3}$, in correspondence of the LA softening typical of bcc crystals. Another puzzling phenomenon concerning Nb is the presence of a well-pronounced broad elastic peak at $\frac{1}{3}\frac{1}{3}\frac{1}{3}$ observed in neutron scattering experiments.²¹ This peak cannot be due to phonon scattering, has been observed in several crystals, and is temperature independent. Could this peak be attributed to the static linear fault propounded by Sass?

II. EXPERIMENTAL TECHNIQUE AND RESULTS

Niobium single crystals with less than 100 ppm impurity content were obtained from two different sources. Two (111) and (100) crystals were spark cut from an ingot,²² and the surfaces parallel to the desired crystallographic planes were electro-polished. Some splitting was observed in the Laue spots obtained in back reflection photographs, but the mosaic spread did not exceed 30–40 min of arc. Another set of crystals were prepared at Oak Ridge National Laboratory by the strain anneal method,²³ in form of thin lamellas (typical dimensions: $12 \times 24 \times 0.5$ mm), from which several extended grains could be chosen with appropriate orientations.

In most cases the direction normal to the planes of these lamellas was close to [100] or [110]. These grains exhibited unusually high quality of crystal perfection, with virtually zero mosaic spread, as tested by double crystal diffractometry. The surfaces of these crystals were neither polished nor etched. These samples were annealed for 50 h at 2250 °C in ultra-high-vacuum (10^{-10} Torr), in order to remove H₂ and other contaminants. It was proved that the same TDS intensity was measured for the same \vec{q} in reciprocal space when crystals of different origin were compared. Mo K α radiation was used in this experiment. A long-fine-focus diffraction tube (focus apparent dimensions: 0.4×1.2 mm), connected to a constant potential generator, was coupled to a singly curved asymmetric quartz monochromator, from which a beam with an angular spread $\approx 1^\circ$ in the

diffraction plane was focused in proximity of the sample. The beam cross section, at the sample, was about 0.5×3 mm. The detector, a scintillation counter, was located at 27 cm from the crystal and its aperture was circular, with a diameter of $\frac{1}{8}$ in. The overall divergence of the slits and source system was about 1° , both on the scattering plane and on a plane normal to it. For a scan between 222 and 333 this divergence corresponded to an uncertainty $\Delta q/q_{\max} \approx 0.08$. For the low-temperature measurements (80 °K), the crystals were kept in a vacuum chamber.

Care was taken to make sure that no spurious scattering from the Mylar windows or from the aluminized Mylar foil wrapped around the crystal for thermal shielding ("superinsulation") could reach the counter aperture.

Room-temperature measurements were performed in air with a lead baffle at 2 mm from the crystal surface. With a lead beam catcher replacing the sample, it was proved that no measurable scattering was contributed by the open air path (2 mm) at the smallest angles at which the measurements were taken. Typical background with the x-ray beam shut off was 2–3 counts/min. Working conditions for the generator were: 55 kV and 30 mA.

A single-channel analyzer was used to discriminate against $\frac{1}{2}\lambda$. However, some $\frac{1}{2}\lambda$ contribution was observed at points located on zone boundaries, such as 111, where $\frac{1}{2}\lambda$ is diffracted as 222. These points were excluded from the final data. Mo K α radiation does not excite fluorescence from Nb, but $\frac{1}{2}\lambda$ does. A substantial contribution from Nb fluorescence, whose wavelength is very close to Mo K α , was observed and evaluated by comparing with measurements taken at 30 kV in a few

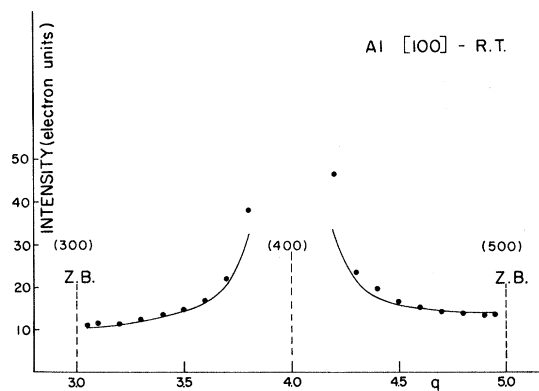


FIG. 1. Total TDS intensity along [100] at room temperature from aluminum. Units on abscissa: $1/a = 0.247 \text{ \AA}^{-1}$. Solid circles: experimental points. Solid line: calculated from phonon frequencies taken from Ref. 8.

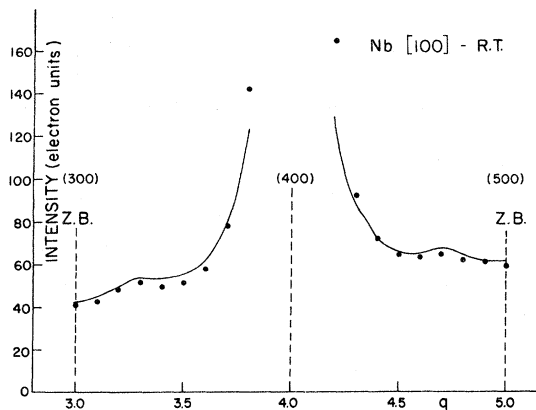


FIG. 2. Total TDS intensity along [100] at room temperature. Units on abscissa: $1/a = 0.303 \text{ \AA}^{-1}$. Solid circles: experimental points. Solid line: calculated from phonon frequencies.

selected points.

The fluorescence contribution was found constant in \vec{q} space after reduction to electron units. This quantitative evaluation of fluorescence was later checked by means of an intrinsic Ge solid-state detector, whose resolution (205 eV at 5.9 keV) was adequate for resolving Nb fluorescence from Mo $K\alpha$. Using high voltage (55 kV) enabled us to obtain high intensity on the $K\alpha$ line. Typical count rate was of the order of 5 counts/sec. Each data point was taken for 4000 sec and many points were repeated to ensure accuracy and reproducibility. The count-rate data were converted into absolute units (electron units) by comparing with scattering data from amorphous samples such as lucite, polystyrene, and silica. More details on this conver-

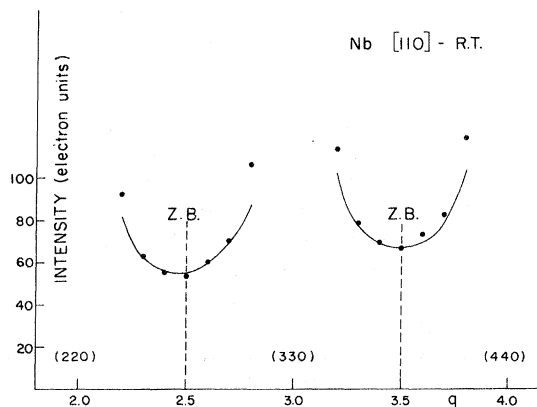


FIG. 3. Total TDS intensity along [110] at room temperature. Units on abscissa: $\sqrt{2}/a = 0.429 \text{ \AA}^{-1}$. Solid circles: experimental points. Solid line: calculated from phonon frequencies.

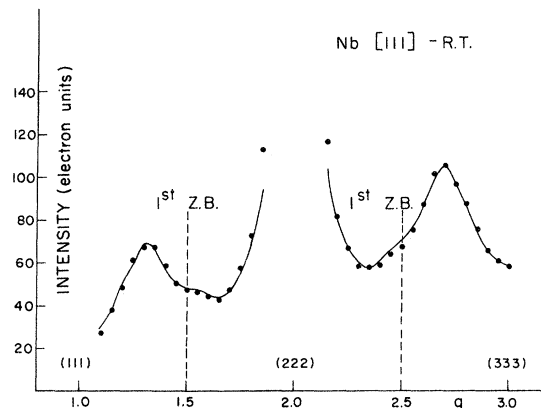


FIG. 4. Total TDS intensity along [111] at room temperature. Units on abscissa: $\sqrt{3}/a = 0.525 \text{ \AA}^{-1}$. Solid circles: experimental points. Solid line: calculated from phonon frequencies.

sion will be given in Sec. III. The experimental results are shown in Figs. 1-6.

III. TREATMENT OF EXPERIMENTAL DATA AND DISCUSSION

The total measured diffuse intensity is contributed by first-order TDS, Compton incoherent scattering, second- and higher-order TDS, and electronic and cosmic background. While the latter contribution is a very small percentage of the total and can be easily measured, Compton and multiphonon scattering contribute large fractions and cannot be easily measured experimentally.

The Compton-scattering factors are obtained from linear extrapolation of those calculated for

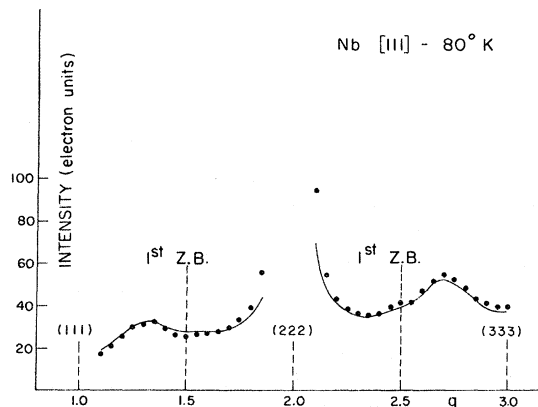


FIG. 5. Total TDS intensity along [111] at $T = 80^\circ\text{K}$. Units on abscissa: $\sqrt{3}/a = 0.525 \text{ \AA}^{-1}$. Solid circles: experimental points. Solid line: calculated from phonon frequencies.

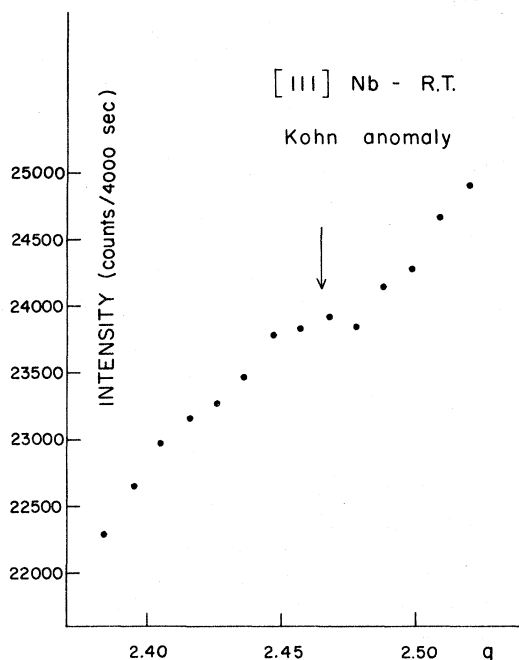


FIG. 6. Total TDS intensity along [111] at room temperature. Detailed scan in the neighborhood of $q=2.46$, where a Kohn anomaly is expected (see Ref. 19). Units on abscissa: $\sqrt{3}/a=0.525 \text{ \AA}^{-1}$.

Mo and Tc.²⁴ The phonon frequencies along symmetry directions are recent neutron data taken by Powell, Martel, and Woods.¹⁹ Second-order TDS was evaluated using the procedure followed by Walker in his investigation of TDS in aluminum,⁷ with the numerical tables prepared by Colella and Batterman for cubic elemental crystals.⁵

Higher-order TDS was evaluated using the Debye-Jauncey expression,¹³ which neglects the small peaking of multiphonon scattering near reciprocal-lattice points. Higher-order TDS never exceeded 10% of the total, in our experiments.

The atomic-scattering factors were taken from Cromer and Mann,²⁵ and the dispersion corrections from Cromer and Liberman.²⁶ A value of $\Theta_M = 284 \text{ }^\circ\text{K}$ was used for the Debye temperature, measured by x-ray diffraction,²⁷ and the sound velocities used in the two-phonon scattering calculation were deduced from a set of elastic constants ($C_{11} = 23.5$, $C_{12} = 12.1$, $C_{44} = 2.82$ in 10^{11} dyn/cm^2 units) given in Ref. 28.

Count-rate data were converted into electron units by comparing with scattering from amorphous materials. In this way geometrical factors related to slit size, divergence, beam size, etc., do not need to be determined. Lucite and polystyrene are relatively transparent to Mo $K\alpha$ radiation. It was therefore found preferable to use

thin scatterers and introduce a finite thickness correction in the calculations. In this way multiple scattering could also be reduced. Several determinations were done at various thicknesses and angles.

A thick SiO_2 sample (fused quartz) was also employed, for which the infinite thickness approximation could be used. In interpreting the data from fused quartz, the ionic state $\text{Si}^{4+}\text{O}^{2-}$ was considered.²⁹ All these determinations agreed within (3–4)%. A contribution due to multiple scattering (8%) was subtracted from the average. Such a value was evaluated for Rh $K\alpha$ ($\lambda=0.615 \text{ \AA}$) scattered by fused quartz,³⁰ and should be a reasonable value also for Mo $K\alpha$. Since this conversion of raw data into absolute units is one of the most crucial steps in comparing experiments with calculations, a test was performed by measuring TDS along [100] from an aluminum single crystal, for which we know that there is agreement between x-ray TDS and lattice-dynamics calculations (see Sec. I). As can be seen from Fig. 1, the overall agreement is pretty good, except in the neighborhood of the Bragg peak, where some extra elastic intensity may have been easily picked up on account of the mosaic spread of the crystal.

The raw-intensity data from Nb, after background correction, have thus been converted into electron units and the solid curves represent calculated intensities, the sum of one-phonon, two-phonon, higher-order TDS, and Compton scattering (Figs. 2–5). We observe that the percentage difference between experiments and calculations is usually within (2–3)%, reaching maximum values of (8–9)% only in a few cases. Points close to Bragg peaks, as in the case of Al, exhibit greater discrepancies, for the same reason mentioned above. It is surprising to see how nicely experimental data and calculated profiles agree between 222 and 333 at room temperature (Fig. 4). In this region the second-order TDS is 20% of the total, and first-order TDS is 50% of the total. At 80 °K (Fig. 5), the approximation of equipartition, implicit in Eq. (A1) of Ref. 5, is no longer valid, but second-order TDS becomes less important (4% of the total). Figure 6 shows a detailed scan along [111], in the neighborhood of the Kohn anomaly observed by neutron diffraction,¹⁹ at $q=2.46$. The arrow indicates a clearly discernible discontinuity in our x-ray data.

We are now convinced that Nb is a well-behaved metal, as far as x-ray TDS is concerned, and that the effects mentioned in Sec. I, such as ionic distortion and anharmonicity, are not important.

When we turn to the triple-axis neutron-scattering results²¹ (Fig. 7), however, we see a huge temperature-independent broad *elastic* peak, at

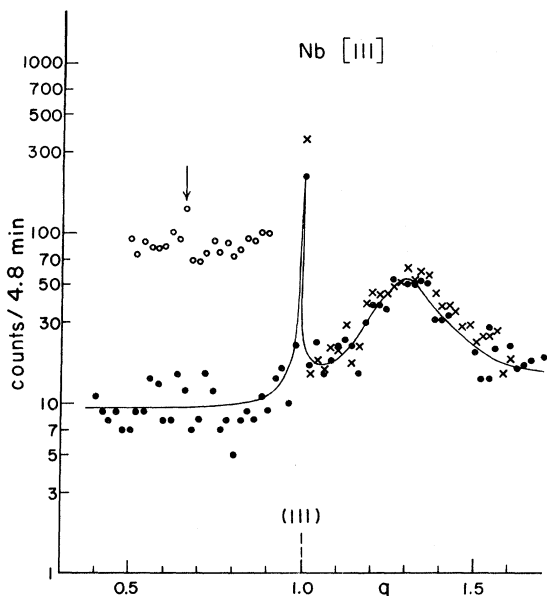


FIG. 7. Neutron-elastic TDS measured along [111] at room temperature (solid circles) and 77 °K (crosses). Line is guide to eye. Units on abscissa: $\sqrt{3}/a = 0.525 \text{ \AA}^{-1}$. The sharp peak at $q=1.0$ is due to $\frac{1}{2}\lambda$ diffracted as 222. Open circles: measurements repeated with higher statistical accuracy. Monitor count was increased by a factor of 9. The open circle marked with an arrow is third order 222, which shows that $\frac{1}{3}\lambda$ contribution is very small.

(1.3, 1.3, 1.3), which has no counterpart in the x-ray data. When the third crystal (analyzer) was tuned on the L phonon energy (14 meV), the count rate increased to the same peak value as the elastic peak (≈ 50 counts/4.8 min).³¹ It appears, therefore, that the elastic extra scattering observed with neutrons at (1.3, 1.3, 1.3), has the same intensity as first-order TDS at 77 °K. Since, in the x-ray measurements at 80 °K, first-order TDS constitutes 60% of the total scattering at the same \vec{q} point (1.3, 1.3, 1.3), we deduce that if the same extra scattering was present in the x-ray measurements, we would have observed a 60% discrepancy at $q=1.3$ in Fig. 5. This is not clearly the case, since the agreement between experiment and calculations, in this q region, is within 5%.

There have been other conflicting reports (all unpublished) concerning this elastic extra diffuse scattering of neutrons in pure niobium. There seems to be no doubt as to the existence of the effect, but the intensity and reproducibility from sample to sample of this phenomenon is a matter of controversy.³²

It has been pointed out that hydrogen may be present in small quantity in "pure" niobium, even when not deliberately introduced into the materi-

al.³³ It is difficult to think of any effect, structural distortion or hydride formation, detectable with neutrons but not with x rays. If hydrogen is responsible for this extra scattering, it must be due to some sort of long-range order of the H_2 atoms in the Nb lattice, but it is doubtful that the amount of H_2 accidentally present in a "pure" Nb crystal may be enough to produce the observed effect.

IV. CONCLUSIONS

X-ray thermal-diffuse scattering has been measured accurately in several Nb single crystals of different sources and quality, along symmetry directions, at 300 and 80 °K. The intensity data have been compared with calculations based on phonon frequencies determined by inelastic neutron scattering.

The overall agreement is excellent, even in cases in which Compton and two-phonon scattering are a large fraction of the total. We conclude that in the case of niobium x-ray diffuse scattering can satisfactorily be explained by considering Compton and harmonic-phonon scattering. Anharmonic effects due to interference between harmonic one phonon and many-phonon scattering, and ionic deformation, do not play a major role in Nb. The elastic extra scattering observed with neutrons at $\vec{q}=(1.3, 1.3, 1.3)$ cannot be observed with x rays.

It is speculated that this extra scattering might arise either from a hydrogen sublattice, or from magnetic ordering. It has been suggested³⁴ that electronically driven lattice instabilities might be responsible for this elastic scattering in niobium, with a corresponding decrease of inelastic scattering, which would be consistent with the x-ray results. This effect could be impurity dependent, which would explain the observed lack of reproducibility from sample to sample.

It is also possible that a domain structured region of the crystal might be responsible for this elastic diffuse scattering. In this case too one would expect different intensities from sample to sample, although the average over all the equivalent directions in the same crystal should be the same for all samples. This is the case, for example, of magnetic scattering in chromium due to a spin density wave. Unfortunately, these measurements along equivalent directions in the same crystal are not available, so that no firm conclusion can be drawn at this stage. Neutron-polarization experiments could help to solve this puzzle.

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³²N. Wakabayashi reports a much weaker effect than that found by Werner and Rowe (Ref. 21). R. Pynn and S. Shapiro found the effect in two samples with different intensities, one of which, however, agreed with Werner and Rowe's results (private communication).

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