

Resonant scattering in germanium

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Three-beam experiments on the resonantly-excited forbidden reflection (600) in germanium are presented. It is shown that phases of resonant scattering can be reliably obtained from the asymmetry effect in azimuthal plots. For the (222) reflection, it is shown that charge and resonant scattering are out of phase.

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With the advent of synchrotron radiation, resonant scattering of x-rays has become a major tool for investigating electron densities in solids. The notion of “resonant scattering” (also called “anomalous scattering”) is often coupled to the notion of “orbital ordering.” In the absence of interactions, atoms have spherical symmetry even though most of the electronic orbitals are not spherically symmetric. Only *s* orbitals are spherically symmetric. In fact, the crystal potential will force some of the aspherical hybridized *s-p* orbitals to assume a definite configuration (orbital ordering), resulting in directed covalent bonds, which is the basis of chemical bonding.

As a consequence of orbital ordering, some x-ray reflections which are normally extinct as a result of negative interference between sublattices, may in fact turn out to be weakly present and measurable. Such reflections are called “forbidden reflections.” They correspond to existing nodes in reciprocal space, with zero intensity.

A famous example is the (222) reflection in diamond, Ge, Si, and β -tin, whose space group is Fd3m (N. 227), the same for all these elemental crystals. All these structures consist of two f.c.c. sublattices, shifted by 1/4, 1/4, 1/4. It turns out that whenever $h+k+l=4n+2$ (n =any integer) the two f.c.c. sublattices are exactly out of phase, and the corresponding x-ray reflection has zero intensity. For the purpose of this paper, we define a reflection in diamond structures to be “forbidden” whenever $h+k+l=4n+2$.

If, on the other hand, the electron density around each atom is not spherically symmetric, there may be some weak intensity due to scattering from interatomic electrons, such as bonding charges, for example. We know that in diamond, Ge, Si, and β -tin there are covalent bonds between atoms, which can be modelled using the so-called “bonding charge model.”¹⁻⁴ These bonding charges produce nonzero forbidden reflections which can be observed without resonant scattering. The (222) reflection can easily be observed and measured, both for Ge and Si, but the higher-order reflections, such as the (442) and the (622), are extremely weak, and it becomes difficult to disentangle the effects of multiple diffraction.⁵

The (600) reflection is also forbidden, but it is in a different category from the (222). While the space group Fd3m predicts a nonzero (222) for a generic, aspheric, electron density, the (600) is predicted to be zero for *any* charge density. In the language of crystallographers, they are said to be

forbidden “by the glide-plane rule.” However, when the polarization of the incident x-ray beam is taken into account, it is possible that “the screw axis and glide-plane rules for absent reflections are no longer rigorous since crystallographically equivalent atoms do not have exactly the same scattering power.”⁶ This is the case, for example, of a monoatomic crystal (like germanium) with two identical sublattices, in which the valence charge density is not spherically symmetric. The effect is probably present even without resonance, but the intensity is too weak to be detected.

We made a careful analysis of the (600) intensity scattered outside of resonance, using synchrotron radiation at the advanced photon source (APS).⁷ We were able to see an appreciable (600) intensity at energies differing from the resonant value (11,107 KeV) by 1000 eV or more. However, a careful analysis of the results showed that the (600) intensity we observed was always due to the tails of the Umweg peaks, due to multiple diffraction, which brings up an important point. What limits the ability to measure a very weak reflection is not the intensity of the source, but rather the contamination due to multiple scattering, always present at any ψ angle (ψ =azimuthal angle, for rotations around the scattering vector). When the x-ray energy coincides with the K edge (11,107 eV), the (600) reflection appears as a substantial background between Umweg peaks in ψ rotations, and can be measured without any problem (see Fig. 1). Resonant scattering, then, appears to be a method to enormously amplify the scattering from valence electrons deviating from centrosymmetry in forbidden reflections. It is a technique for studying electron densities.

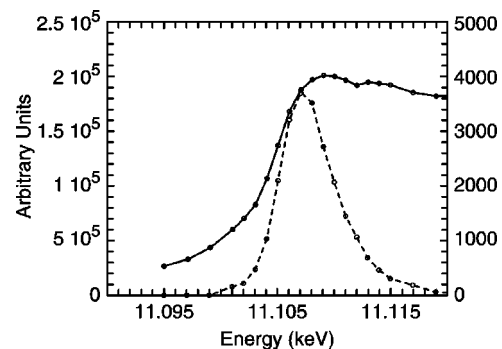


FIG. 1. Integrated intensity of the (600) reflection vs energy (dotted line). The solid line is the “background” counting rate, due to fluorescence, to which the right vertical scale applies.

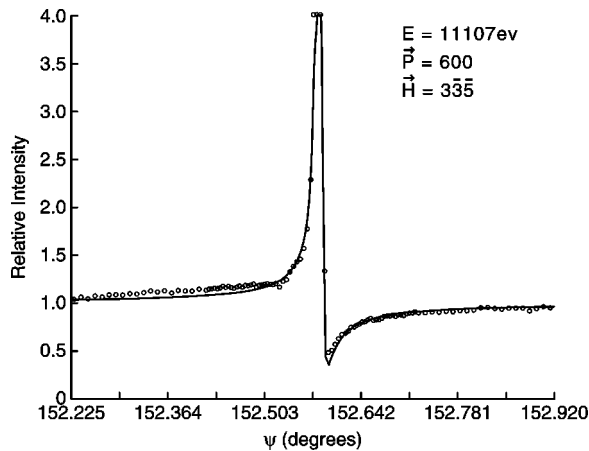


FIG. 2. Azimuthal dependence of the (600) near a peak due to three-beam diffraction [the (335)]. Circles represent experimental data. Every point represents an integrated intensity (over θ , the angle of incidence) at a given azimuthal angle ψ . Solid line is theory.¹¹ All intensities have been normalized to the two-beam integrated intensity (corresponding to 1 on the vertical axis). The best fit is obtained for $F_{600}=0.475$ electrons, and ϕ_{600} (phase) = -90.00 or -150.64° .

Resonant scattering has been recently used to study the details of the electron density in manganates [LaMnO₃ (Ref. 8) and similar compounds] and in magnetite Fe₃O₄.⁹

Our aim is to explore the possibility of extracting phase information from the scattering data, and for this reason we chose germanium, a very well-known crystal structure, easily available as a perfect crystal.

The first question we asked was whether or not resonant scattering would give rise to the asymmetry effect in ψ scans, which is the source of phase information in our technique for solving the phase problem.¹⁰ Several three-beam experiments were performed on beamline ID-32 of the European synchrotron radiation facility (ESRF) and they all showed very clear asymmetry effects. The incident beam, being generated by an undulator, had a very small angular divergence (of the order of four μ rad in the plane perpendicular to the scattering plane). Therefore the widths on the ψ scale of the umweg peaks are not affected by the beam divergence, and can be directly compared with the calculated profiles. Figure 2 is an example of our results. The solid line is theory,¹¹ with phase and magnitude of F_{600} being the only adjustable parameters. The perturbation theory developed by Shen¹² shows that, if plane-polarized x-rays are used, the quantity determined in a multibeam experiment is $\cos \delta$, with $\delta = \phi_H + \phi_{P-H} - \phi_P$, called triplet invariant, because it does not depend on the origin chosen in the unit cell. ϕ_P is the phase of the main reflection [the (600) in our case], ϕ_H and ϕ_{P-H} are the phases of the simultaneous and coupling reflections, respectively. Since δ can be positive or negative, there is an ambiguity in determining ϕ_P . The ambiguity can be removed if circularly polarized x-rays are used, because in this case we determine $\sin(\delta)$,¹³ but we were not able to perform this experiment. We believe that -90° is the good value, because we expect F_{600} to be imaginary at full resonance.¹⁴ The magnitude of F_{600} is 0.475 electrons, which

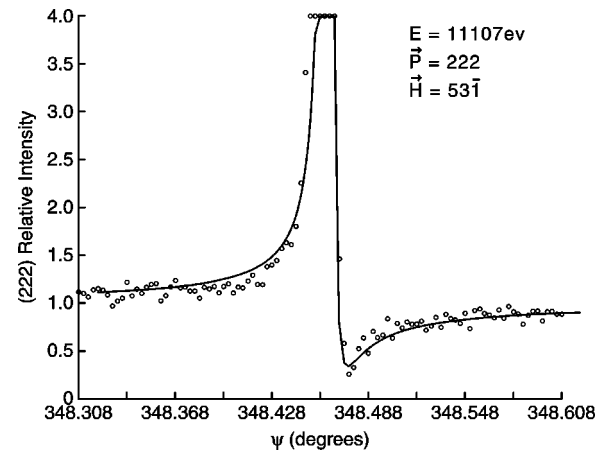


FIG. 3. Azimuthal plot of the (222), at resonance, vs ψ , azimuthal angle. The central peak is due to simultaneous excitation of the (531). The intensity values have been normalized to the two-beam value. The best fit yields: $F_{222}=0.8$ electrons; ϕ_{222} (phase) = 40.0° or 45.5° .

is about half of F_{222} outside of resonance (=1.08 electrons¹⁵). It means that the (600) resonant intensity is about four times weaker than the nonresonant (222).

At this point we asked ourselves the question: what is the effect of resonance on the (222)? One would expect an increase of intensity, as it always happens when some kind of resonance is involved. We then performed another experiment on the same beamline ID32 of ESRF. Since we were interested in possible changes of intensity and phases, we performed a three-beam experiment at two different energies: 11,107 eV and 11,440 eV. The profiles are shown in Figs. 3 and 4. In both figures, the central peak is due to simultaneous excitation of the (531) reflection. In this experiment our main interest is the two-beam value of the (222), in and out of resonance. It turns out that the most accurate procedure to get a two-beam value in this case is to perform an azimuthal scan around an “umweg” and then take the average of the counting rates to the left and to the right of the “umweg.”

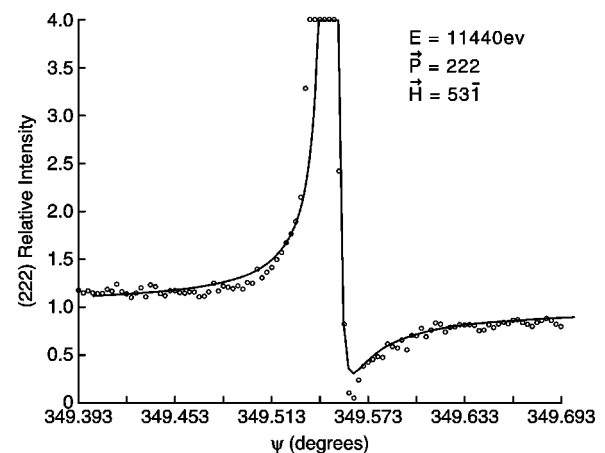


FIG. 4. Same as Fig. 3 except that the x-ray energy is out of resonance. The best fit yields: $F_{222}=1.4$ electrons; $\phi_{222}=28.0^\circ$ or 28.5° .

The reason for this apparently complicated procedure is that the umweg peaks have long tails, and there are many umwegs at an x-ray energy close to 11,000 eV. In other words, it is practically impossible to find a ψ angle such that the (222) diffracted intensity is really umweg-free.

The two profiles of Figs. 3 and 4 yield different values of magnitudes and phases for F_{222} . The actual values are given in the captions. The ratio, squared, of the magnitudes yields an attenuation of the (222) intensity, at resonance, equal to 67.3% which is to be compared with the value we actually measured: 37.9%. The reason for this discrepancy has most likely to do with the fact that a static structure factor incorporated in the n -beam theory of Ref. 11 is probably inappropriate in dealing with resonant scattering. We also see a change in phase: from 40° at resonance to 28° out of resonance. In this case the ambiguity resulting from the sign of δ is not important. The change in phase has a strong effect on the minimum value of the (222) intensity, which is close to zero out of resonance (Fig. 4).

The profiles of Figs. 2, 3 and 4 have been normalized in such a way that the average counting rate, on the left and the right side, is set equal to 1. In keeping with the prescriptions of “virtual bragg scattering,”¹⁶ we use the asymmetry effect near the umweg peaks as a source of phase information. Consequently, only weak scattering photons are utilized, and all umweg peaks, in our azimuthal plots, have been arbitrarily truncated to 4. In other words, only scattering data less than four times the two-beam intensity have been considered. In Figs. 3 and 4, the *effective* values of the averaged counting rates are 2.93 at resonance and 5.03 out of resonance ($E=11,440$ eV). In comparing the two intensities we must take into account that, according to mosaic theory, the integrated intensity of any (hkl) reflection depends on angle θ , wavelength λ and absorption. Specifically:

$$R_{hkl} \propto \frac{\cos^2 2\theta \lambda}{\cos \theta} \frac{1}{f''}, \quad (1)$$

where f'' is the imaginary part of the scattering factor.^{17,18} Our crystal is germanium, which is highly perfect. So it

would seem that mosaic crystal theory would not be appropriate for germanium. On the other hand, the (222) is very weak, and in the limit of weak scattering, crystal perfection does not affect the diffracted intensity. Perfect crystal theory and mosaic crystal theory converge to the same values for the integrated intensities of weak reflections.¹⁹

The correction due to Eq. (1) predicts a weakening of the intensity for the (222) at resonance by 93.9%. When this correction is taken into account, we can conclude that the (222) at resonance is weaker, compared to its value out of resonance, by 37.9%, which is definitely outside of the experimental error ($\pm 2-3\%$).

This conclusion is somewhat surprising, because we would have thought that resonance always increases the intensity of a weak reflection.

The inescapable conclusion is that, in this case, the (222) resonant scattering is out of phase with respect to charge scattering. If we naively describe resonant scattering of forbidden reflections as being due to virtual charge buildup between atoms, we may conclude that the attenuation of the (222) at resonance is due to virtual “lobes” of charge along the [111] directions, on the opposite sides to the locations of the bonding charges and the first nearest neighbors, similar to the effect of temperature on the anharmonic thermal vibrations.^{20,21} On the other hand, a quantitative theory of resonant scattering in germanium is not available at the present time,²² therefore, we are not in a position to compare our results with theoretical predictions.

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¹The first explanation of nonzero (222) interstitial charges was given by Ewald and Hönl.² The idea, the bond-charge model, was taken up and amply developed by Phillips,^{3,4} who extended it to polar semiconductors.

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