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Reciprocity in Electron Energy-Loss Spectra from Non-centrosymmetric Crystals

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Abstract

The energy losses of fast electrons propagating through a thin crystal show a strong effect associated with the interference term between Bloch-wave eigenstates. Reversing the direction of the electrons gives the same spectrum, and reciprocity is observed in the interference term between eigenstates in inelastic electron scattering. The reciprocity principle may be used to advantage to observe for GaAs a very large difference in the characteristic energy-loss spectra for pairs of experimental arrangements related by a mirror operation around the polar (111) planes. This provides a sensitive way of determining the polarity of a crystal based on simple two-beam arguments, and may also be used to obtain direct structure-factor phase information.

Introduction

When a plane wave enters a crystal under Bragg reflecting conditions, a modulated wave field with current-density minima and maxima is built up in the crystal. The pattern of this standing wave in the crystal has been studied by monitoring secondary emission caused by localized inelastic scattering processes, in particular element-characteristic X-ray emission using incident neutrons (Knowles, 1956), electrons (Duncumb, 1962) and X-rays (Batterman, 1964). In electron diffraction the corresponding energy losses of the transmitted electrons have also been studied (Taftø & Lehmpfuhl, 1982; Taftø & Krivanek 1982*a*). These standing-wave or channeling experiments were interpreted using the Bloch-wave picture (see *e.g.* Howie, 1970).

In the sixties was discussed whether the individual Bloch waves induce X-ray emission independently, or whether a correct treatment required the interference term between the Bloch waves to be included. Cherns, Howie & Jacobs (1973) showed experimentally that the interference terms between the Bloch-wave eigenstates contribute to the electron-induced X-ray emission, and thus it is possible to use localized secondary emission to obtain structure-factor phase information associated with lack of centrosymmetry, and to determine the sense of a polar direction. This has been demonstrated by observing a large difference in the electron-induced X-ray spectra for incident electron beams forming an angle θ and $-\theta$ relative to a polar plane (Taftø, 1983). This has similarities to the use of the Bragg-reflection intensities in many-beam dynamical diffraction to obtain structure-factor phase information (Kambe, 1954; Goodman & Lehmpfuhl, 1968; Post 1977), where it is also the interference terms between the Bloch-wave eigenstates that give rise to the phase sensitivity. A fundamental difference, however, is that when localized secondary emission is monitored it is sufficient to excite one Bragg beam (two-beam case).

In a standing-wave experiment, where the characteristic energy losses are monitored, the crystallographic direction of the inelastically scattered electrons to be energy analyzed has also to be considered, because according to the reciprocity principle (see *e.g.* Pogany & Turner, 1968), the directions of the incoming and outgoing beam are equally important. Reciprocity in electron energy-loss spectroscopy has been studied previously (Taftø & Lehmpfuhl, 1982; Taftø & Krivanek, 1982*a*) but not under experimental conditions where it was possible to study the effect of the interference term between the eigenstates. By performing electron energy-loss experiments when electrons are scattered from the (111) polar planes of GaAs, we shall show that the reciprocity principle also applies to the interference terms between the Bloch-wave eigenstates. This makes it possible to enhance the sensitivity to lack of inversion symmetry in electron energy-loss spectra as compared to electron-induced X-ray spectra, and this will also be demonstrated experimentally.

The interference term between Bloch waves

Many Bragg beams are simultaneously excited in an electron diffraction experiment, but for the present purpose a two-beam treatment is sufficient. Inside a perfect crystal, where the Coulomb potential is periodic, the solution of the Schrödinger equation for the incident electrons can be expressed as a superposition of Bloch-wave eigenstates (see *e.g.* Howie, 1970). In a two-beam case (incident beam and one Bragg beam), assuming the Bragg beam G to be at the exact

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Bragg position, we have

$$\psi(x, z) = 2^{-1/2}[b^{(1)} + b^{(2)}] \quad (1)$$

where the two Bloch waves are

$$b^{(1)}_{(2)} = 2^{-1/2}(1 \pm \exp 2\pi i G x) \exp 2\pi i(k \pm \tfrac{1}{2}\Delta k)z. \quad (2)$$

Here x and z are the components of the position vector in the crystal parallel and normal to G and Δk is the difference in *Anpassung* between the Bloch waves. See Fig. 1 for detailed definitions of the symbols. The density distribution of the fast electrons in the crystal is now

$$\rho(x, z) = \psi\psi^* = \tfrac{1}{2}[|b^{(1)}|^2 + |b^{(2)}|^2 + b^{(1)}b^{(2)*} + b^{(1)*}b^{(2)}]$$
$$= 1 - \sin(2\pi G x) \sin(2\pi \Delta k z), \quad (3)$$

whereas if the interference term is omitted we have

$$\hat{\rho}(x, z) = \tfrac{1}{2}[|b^{(1)}|^2 + b^{(2)}|^2] = 1. \quad (4)$$

Fig. 1 also shows the arrangement of atomic planes along the [111] direction of Ge. Fig. 2 shows that ρ is different on the left, Ge_L, and right, Ge_R, of two adjacent atomic planes when the 111 reflection is at the exact Bragg position. From the inversion symmetry of the crystal it immediately follows that $\rho(Ge_R, 111) = \rho(Ge_L, \bar{1}\bar{1}\bar{1})$ and $\rho(Ge_L, 111) = \rho(Ge_R, \bar{1}\bar{1}\bar{1})$ where 111 and $\bar{1}\bar{1}\bar{1}$ refer to the reflection at the Bragg position. Using a GaAs crystal instead we substitute As atoms for Ge_L and Ga atoms for Ge_R (Fig. 1). This gives, to a good approximation, the same $\rho(x, z)$ because of the proximity of these three elements in the Periodic Table. What has now changed is that we have introduced two different types of 'detectors' on adjacent planes in the crystal, namely the Ga and the As atoms. These can be used to probe the thickness-integrated electron density on the two types of planes by monitoring element-specific signals produced by localized inelastic scattering events, *e.g.* core-energy losses of the fast electrons, or the accompanying X-ray emission. Thus, by comparing pairs of experiments $(\theta, -\theta)$ where the experimental arrangement is related by a mirror operation around the (111) planes $(\theta \rightarrow -\theta)$, the effect of the interference term between the eigenstates can be studied. Any experimentally significant difference when $\theta \rightarrow -\theta$ has its origin in the interference terms because the relationship between the Hamiltonians is $H_{-\theta} = H_\theta^*$ so that $\hat{\rho}_{-\theta} = \hat{\rho}_\theta$. This is a general statement which also applies when all excited Bragg beams and inelastic scattering are included.

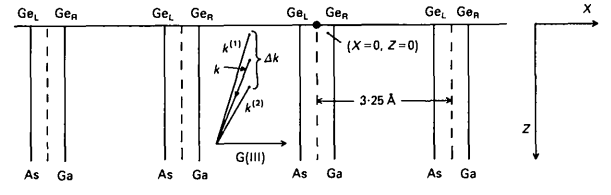

Fig. 1. A crystal with lattice planes indicated by vertical dashed lines. The origin used in equation (2) is the intersection between the entrance surface and any of these dashed lines. The position of the (111) atomic planes in Ge and GaAs (to a good approximation) consistent with this choice of origin is indicated by full lines. Also indicated is the splitting of the incident plane wave **k** into two wave vectors $\mathbf{k}^{(1)}$ and $\mathbf{k}^{(2)}$ associated with the two Bloch waves when the 111 reflection is at the Bragg position. Notice that **k** and **G** are not to scale. For 100 keV electrons **k** is 27 $Å^{-1}$ whereas **G** is only 0·3 $Å^{-1}$, so that **k** is nearly parallel to the (111) planes.

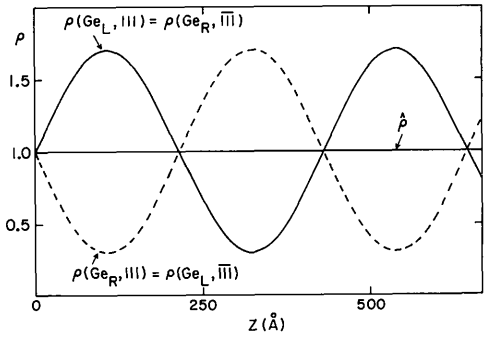

Fig. 2. Idealized two-beam calculation (equation 3) of the electron density as a function of crystal thickness in Ge at the Ge_L and Ge_R planes when the 111 and $\bar{1}\bar{1}\bar{1}$ reflections are at the Bragg position. Attenuation owing to diffuse scattering out of the initial state is not included (see Knowles, 1956). For the GaAs crystal As corresponds to Ge_L and Ga to Ge_R.

Experiment

An ion-thinned crystal of GaAs was studied with 100 keV incident electrons using a JEM 100C electron microscope equipped with an LaB_6 cathode. The transmitted electrons were energy analyzed with a Gatan 607 electron energy-loss spectrometer. The electron-illuminated area was about 2000 Å in diameter with a thickness of about 300 Å.

Before presenting the electron energy-loss spectra we show two electron-induced X-ray spectra with the 111 and $\bar{1}\bar{1}\bar{1}$ reflection at the Bragg position (Fig. 3). These show a considerable difference in the intensities of the electron-induced X-ray emission from Ga and As. A more detailed discussion of this can be found in Taftø (1983).

For the energy-loss experiments, the angle between the incident and the outgoing beam to be energy analyzed was six times the Bragg angle for the 111 reflection. This relatively large scattering angle of 2° is used to ensure that localized energy losses were detected (Taftø & Krivanek, 1982*a*). In Fig. 4 the experimental conditions are shown by indicating the positions and diameter of the incident and outgoing beam relative to the Brillouin-zone boundaries which is easily determined from the Kikuchi pattern. In the two energy-loss spectra shown in Figs. 4(*a*) and (*b*), the only experimental difference is that we have used post-specimen beam-deflection coils to allow different parts of the diffuse background in the diffraction

pattern, *i.e.* different outgoing beams, to enter the energy-loss spectrometer. The reversed-beam-direction experiments, in which for practical reasons we take advantage of the horizontal mirror symmetry in the middle of the crystal (see insets in Figs. 4*a*, *b*), gave within the experimental accuracy the same two spectra as shown in Figs. 4(*a*) and (*b*). From the geometry in the two reversed-direction experiments, which have common outgoing beam direction, the connection with the X-ray spectra of Fig. 3 is apparent. With the 111 reflection at the Bragg position the signals from As are strong, Figs. 3(*a*) and 4(*a*), and with the $\bar{1}\bar{1}\bar{1}$ reflection at the Bragg position the signals from the Ga atoms are strong, Figs. 3(*b*) and 4(*b*). By proper choice of direction of the incident and outgoing beam we can enhance the difference between $(\theta, -\theta)$ related spectra, Figs. 4(*c*) and (*d*), or the outgoing beam can undo the effect of the incident beam, Figs. 4(*e*) and (*f*).

Discussion

We have presented several electron energy-loss spectra from a thin crystal of GaAs with pronounced differences in the ratio between the intensity of the *L* edge of Ga and the *L* edge of As in pairs of spectra where the experimental geometry is related by a mirror operation around the polar (111) planes. The degree of asymmetry around the (111) planes in the energy-loss spectra for different pairs of experimental arrangements can be accounted for by considering the interference term between the Bloch waves for the incident beam and the inelastically scattered outgoing beam. In particular we observe by comparing the spectra in Figs. 4(*a*) and (*b*) that the interference term has to be included for the inelastically scattered outgoing beam, because the direction of the incident beam is the same in these two spectra. The spectra of Figs. 4(*e*) and (*f*) are identical within the experimental accuracy, showing that the directions of the incident and outgoing beams are equally important. By taking advantage of the reciprocity in the interfer-

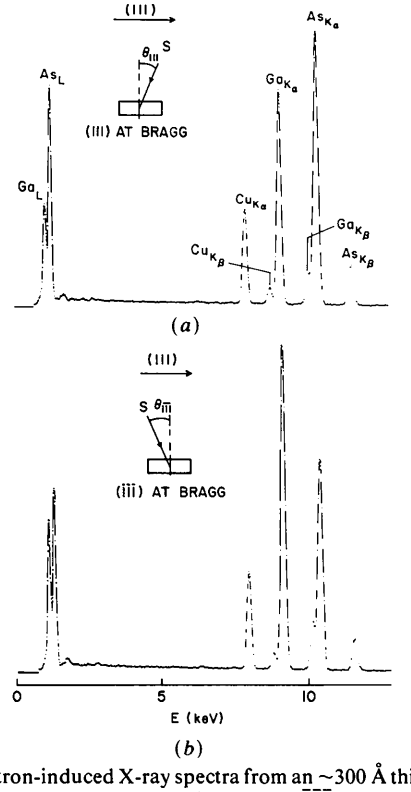

Fig. 3. Electron-induced X-ray spectra from an ~300 Å thick GaAs crystal when the 111 reflection (*a*) and the $\bar{1}\bar{1}\bar{1}$ reflection (*b*) are at the Bragg position. The Cu lines come from the surroundings in the specimen chamber. The suppression of the *L* line of Ga relative to the *L* line of As is an instrumental effect.

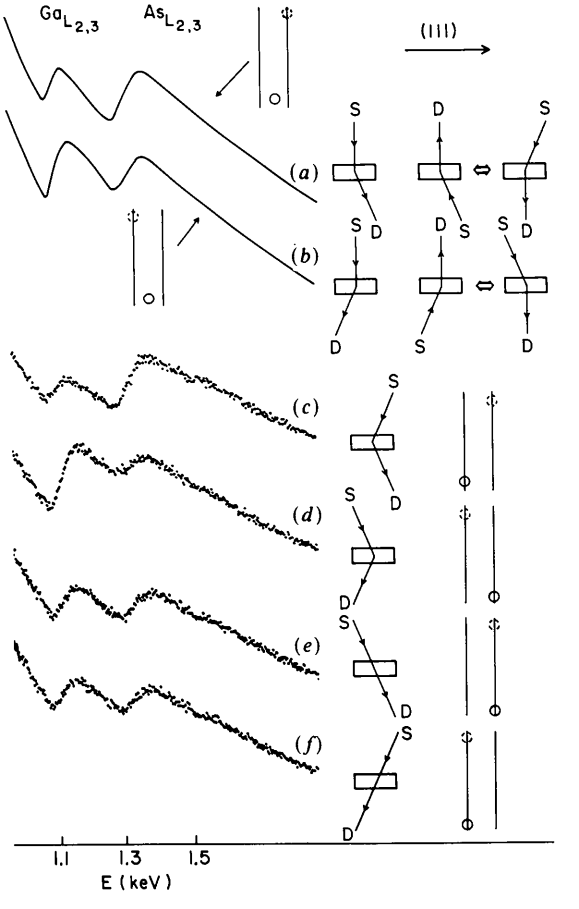

Fig. 4. Energy-loss spectra, including the background which falls off with energy, from a 300 Å thick GaAs crystal which show the $L_{2,3}$ edges of Ga and As. The experimental conditions are indicated by rays between the source (*S*) and the detector (*D*), which either are parallel to the (111) planes, or fulfil the Bragg condition for the 111 or $\bar{1}\bar{1}\bar{1}$ reflections. In addition, the experimental conditions are indicated by the position of the incoming beam (full circle) and the outgoing beam (dashed circle) relative to the (111) Brillouin-zone boundaries (Kikuchi lines). (*a*) and (*b*) are smoothed spectra with common incident and different outgoing beam directions. To the right in the inset is also indicated the geometry in the reciprocal experiment. (*c*), (*d*), (*e*) and (*f*) are raw spectra from the same crystal area with different directions of the incident and outgoing beams.

ence term between the Bloch-wave eigenstates, we can enhance the sensitivity to lack of centrosymmetry in electron energy-loss spectra compared with electron-induced X-ray spectra: the ratio between the X-ray emissions from As and Ga changes from 0·65 to 1·5 depending on whether the $\bar{1}\bar{1}\bar{1}$ or 111 reflection is at the Bragg position, Fig. 3, whereas the corresponding ratios for the electron energy-loss signals are 0·45 and 2·2 when the energy losses are monitored with optimum crystallographic direction of the outgoing inelastically scattered beam, Figs. 4(*c*) and (*d*). In terms of particle channeling we here combine the channeling and blocking effect (Picraux, Brown & Gibson 1972) to maximize the structure-factor phase sensitivity.

By using the reciprocity principle we can now find some simple symmetry rules with respect to the position of the incident and outgoing beams in the diffraction pattern, *i.e.* the directions of the beams relative to the Brillouin-zone boundaries or the Kikuchi lines. Neglecting higher-order Laue zone effects we have: an incident beam at position **s** from the center of the Brillouin zone is equivalent to an outgoing beam at position $-\mathbf{s}$. Or, by considering both the incident and the outgoing energy-analyzed beams, Fig. 5: interchange of the position of the incident and outgoing beams followed by an inversion through the center of the Brillouin zone leaves the energy-loss spectrum invariant. This rule is general in the sense that it applies to projections with and without inversion symmetry. For a projection with inversion symmetry it thus follows that the interchange of the position of the incident and outgoing beams gives the same electron energy-loss spectrum, as is also indicated in Fig. 5.

In the energy-loss spectra presented here we observe transitions between superposition of eigenstates, equation (3), rather than between the individual eigenstates (4). These states are referred to as pure states and mixed states respectively (see *e.g.* Scully, Shea & McCullen, 1978). From this observation it appears that the concepts of interband and intraband transitions are inadequate for inelastic scattering of fast electrons. In a recent paper, dealing with the measurement problem in quantum mechanics, it was proposed that the interference term between eigenstates only shows up in elastic Bragg scattering (Bussey, 1984). We observe a strong effect associated with the interference between eigenstates and transition between pure states rather than between mixed states in inelastic-scattering experiments.

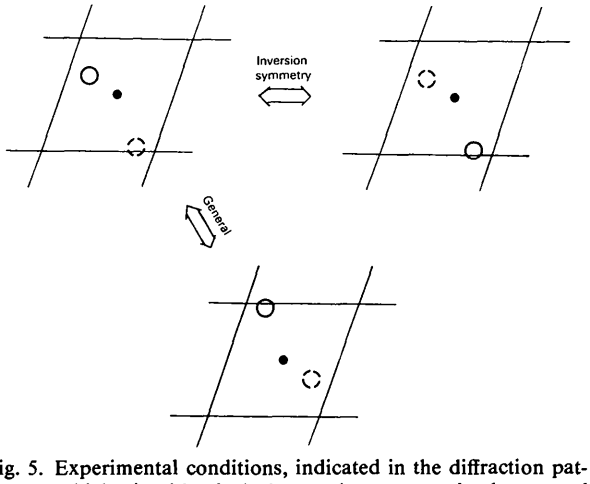

Fig. 5. Experimental conditions, indicated in the diffraction pattern, which give identical electron-loss spectra in the general case, and for a projection with inversion symmetry. Small filled circle: center of the Brillouin zone. Open circle: incident beam. Dashed circle: energy-analyzed beam.

To summarize, it is experimentally verified that the reciprocity principle, which is closely related to time reversibility, applies to the interference term between eigenstates in inelastic scattering. This enables us greatly to enhance the structure-factor phase sensitivity by monitoring the electron energy losses rather than the electron-induced X-ray emission under standing-wave conditions. Thus, in addition to the capability of locating small concentrations of atoms, 0·01 at.%, (Taftø & Spence, 1982) and valency states in a crystal (Taftø & Krivanek, 1982*b*), an electron standing wave can also be used to determine the absolute configuration, *i.e.* polarity and handedness, in very small crystals, $\sim(500\ \text{Å})^3$.

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