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## X-ray Standing Waves at Grazing Angles

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### Abstract

X-ray diffraction from crystal surfaces at grazing angles gives rise to X-ray standing waves above and below the surface. Expressions are derived for the fluorescence observed from atoms located on or in a crystal as a result of excitation by the grazing-angle X-ray standing waves. In addition to the dependence of the fluorescence on the position of the atom with regard to the crystal plane that is responsible for the diffraction, the standing-wave amplitude also depends on the distance from the surface. We present standing-wave measurements from I on Ge(111) and the Ge atoms themselves which illustrate these effects.

### 1. Introduction

The idea of X-ray standing waves was first proposed and demonstrated by Batterman (1964, 1969), who realized that the interference between incident and diffracted beams could be used to excite atoms selectively in a crystal. The location of impurity atoms in or on the crystal is readily determined along the reciprocal-lattice vector responsible for the diffraction in the two-beam case (Golovchenko, Batterman & Brown, 1974). While X-ray standing-wave (XSW) measurements have been made in both the Bragg

(Golovchenko, Batterman & Brown, 1974) and the Laue (Materlik, Frahm & Bedzyk, 1984) geometries, their principal utility has been with systems measured in the Bragg geometry.

Concurrently, the grazing-angle-diffraction (GAD) geometry has proven to be very useful for the determination of lattices on crystal surfaces, particularly the two-dimensional lattices that occur in adsorbate studies (Marra, Eisenberger & Cho, 1979; Eisenberger & Marra, 1981). In this geometry, a collimated X-ray beam is incident on a crystal surface at a grazing angle, usually close to the angle  $\varphi_c$  for total external reflection. The X-ray beam diffracts from a reciprocal-lattice vector approximately parallel to the crystal surface and exits the crystal at a grazing angle. The dynamical theory of X-ray diffraction has been applied to this geometry (Afanas'ev & Melkonyan, 1983; Cowan, 1985) and X-ray standing-wave effects have been observed (Afanas'ev, Imamov, Maslov & Pashaev, 1984; Cowan, Brennan, Jach, Bedzyk & Materlik, 1986; Hashizume & Sakata, 1989). X-ray standing waves have recently been used for the first determination of adsorbate-atom positions in the GAD geometry (Jach & Bedzyk, 1990). The purposes of this paper are to derive the expressions for the X-ray standing-wave fields that occur in GAD in terms of the same parameters as XSW in the Bragg geometry and to demonstrate their validity over a wide range of incidence angles near the critical angle, where the penetration of the X-ray beams varies considerably.

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## 2. Theory

The geometry of GAD is shown in Fig. 1. An X-ray beam is incident on the crystal surface from a grazing angle. We consider only diffraction from crystal planes normal to the surface. The notation follows a previous description of GAD (Jach, Cowan, Shen & Bedzyk, 1989). The external field intensity is described by

$$I = |\mathbf{E}_0 \exp[-i(\mathbf{k}_0 \cdot \mathbf{r} - \omega t)] + \mathbf{E}_s \exp[-i(\mathbf{k}_s \cdot \mathbf{r} - \omega t)] + \mathbf{E}_H \exp[-i(\mathbf{k}_H \cdot \mathbf{r} - \omega t)]|^2, \quad (1)$$

where  $\mathbf{E}_0$ ,  $\mathbf{E}_s$  and  $\mathbf{E}_H$  represent the fields of the incident, specularly reflected and reflected-diffracted beams, respectively. The theory and experiment will be limited to the  $\sigma$ -polarization state, as defined previously for this geometry (Afanas'ev & Melkonyan, 1983), in which all electric fields are, to a good approximation, normal to the crystal surface. Translational invariance is not maintained across the interface. Consequently, we decompose all wave vectors into components parallel and perpendicular to the surface,  $\mathbf{k} = \mathbf{k}_\perp + \mathbf{k}_\parallel$ , where the Bragg condition is expressed by  $\mathbf{k}_{0\parallel} + \mathbf{H} = \mathbf{k}_{H\parallel}$ .

The intensity of the wave field near the surface takes the form

$$I = |E_0 \exp\{-i[k_0(\sin \varphi)z + \mathbf{k}_{0\parallel} \cdot \mathbf{r}_\parallel]\} + E_s \exp\{i[k_0(\sin \varphi)z - \mathbf{k}_{0\parallel} \cdot \mathbf{r}_\parallel]\} + E_H \{\exp i[k_0(\sin \varphi_H)z - \mathbf{k}_{0\parallel} \cdot \mathbf{r}_\parallel - \mathbf{H} \cdot \mathbf{r}_\parallel]\}^2, \quad (2)$$

where  $\varphi$  is the angle of incidence and  $+\hat{z}$  is the surface normal into the crystal. The takeoff angle of the diffracted beam  $\varphi_H = \varphi'_H + i\varphi''_H$  is complex since the diffracted beam may vanish in the external direction. When the common factors are removed and with the assumption that  $\varphi$  and  $\varphi_H$  are small, the intensity takes the form

$$I = |E_0 \exp(-ik_0\varphi z) \exp(-i\mathbf{k}_{0\parallel} \cdot \mathbf{r}_\parallel) \times [1 + (E_s/E_0) \exp(i2k_0\varphi z) + (E_H/E_0) \times \exp\{i[k_0(\varphi_H + \varphi)z - \mathbf{H} \cdot \mathbf{r}_\parallel]\}]^2. \quad (3)$$

Since  $I = E^*E$ , we may evaluate the expression using

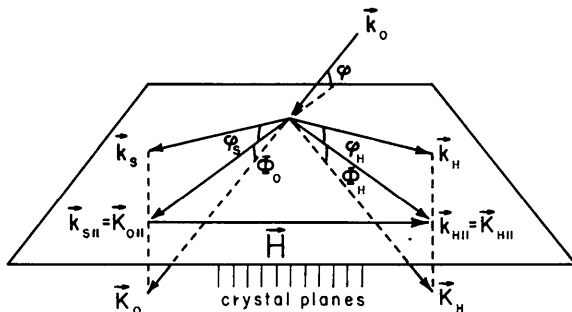


Fig. 1. Diagram of the grazing-angle geometry.

the substitutions

$$E_s/E_0 = R_1 \exp(iv_1) \quad (4)$$

and

$$E_H/E_0 = R_2 \exp(iv_2), \quad (5)$$

where the  $E_s = E_s(k_0, \varphi, \theta)$  and  $E_H = E_H(k_0, \varphi, \theta)$  are readily determined by boundary conditions and dispersion relations (Afanas'ev & Melkonyan, 1983; Cowan, 1985).

Expansion of (3) leads to the result

$$I = E_0^2 \{1 + R_1^2 + R_2^2 \exp(-2k_0\varphi''_H z) + 2R_1 \cos(v_1 + 2k_0\varphi z) + 2R_2 \exp(-k_0\varphi''_H z) \times \cos[v_2 + k_0(\varphi'_H + \varphi)z - \mathbf{H} \cdot \mathbf{r}_\parallel] + 2R_1 R_2 \exp(-k_0\varphi''_H z) \times \cos[v_2 - v_1 + k_0(\varphi'_H - \varphi)z - \mathbf{H} \cdot \mathbf{r}_\parallel]\}. \quad (6)$$

The probability of electronic excitation of atoms in the dipole approximation is directly proportional to the intensity of the radiation at the atomic site. We assume a two-dimensional distribution of atoms above the surface at a constant distance  $z < 0$  with a general density in the plane of  $\rho(\mathbf{r})$ . In such a case, Hertel, Materlik & Zegenhagen (1985) defined a yield proportional to the density projected along the reciprocal-lattice vector  $\mathbf{H}$ , which will be observed as fluorescent radiation, Auger electrons *etc.* With this definition,

$$Y = 1 + R_1^2 + R_2^2 \exp(-2k_0\varphi''_H z) + 2R_1 \cos(v_1 + 2k_0\varphi z) + 2R_2 f_H \exp(-k_0\varphi''_H z) \times \{\cos[v_2 + k_0(\varphi'_H + \varphi)z + 2\pi p_H] + R_1 \cos[v_2 - v_1 + k_0(\varphi'_H - \varphi)z + 2\pi p_H]\}, \quad (7)$$

where  $f_H$  and  $p_H$  are called the coherent fraction and coherent position, respectively. They are the amplitude and phase of the  $H$ th Fourier component of the atomic density function of excited atoms projected along  $\mathbf{H}$ ,

$$p_H = -\mathbf{H} \cdot \mathbf{r}_\parallel / 2\pi. \quad (8)$$

For atoms below the surface of the crystal, excitation occurs as a result of the coherent action of the penetrating or Laue solutions. The intensity of the field inside the crystal is

$$I = |\mathbf{D}_{0\alpha} \exp[-i(\mathbf{K}_{0\alpha} \cdot \mathbf{r} - \omega t)] + \mathbf{D}_{0\beta} \exp[-i(\mathbf{K}_{0\beta} \cdot \mathbf{r} - \omega t)] + \mathbf{D}_{H\alpha} \exp[-i(\mathbf{K}_{H\alpha} \cdot \mathbf{r} - \omega t)] + \mathbf{D}_{H\beta} \exp[-i(\mathbf{K}_{H\beta} \cdot \mathbf{r} - \omega t)]|^2, \quad (9)$$

where  $\mathbf{D}_{0i}$  and  $\mathbf{D}_{Hi}$  are the fields of the undiffracted and diffracted beams, respectively, for  $i = \alpha, \beta$ , the two branches of the diffraction solution in the crystal. The wave vectors  $\mathbf{K}_{0i}$  and  $\mathbf{K}_{Hi}$  are the internal wave vectors for the undiffracted and diffracted beams.

We decompose the wave vectors as before into components parallel and perpendicular to the surface and assume again that the polarization is approximately normal to the surface. Since  $\mathbf{H}$  is parallel to the surface,  $\mathbf{K}_{H\alpha\perp} = K_{0\alpha\perp}$ , and we obtain

$$I = |D_{0\alpha} \exp(-iK_{0\alpha}\Phi_{0\alpha}z) + D_{0\beta} \exp(-iK_{0\beta}\Phi_{0\beta}z) + [D_{H\alpha} \exp(-iK_{0\alpha}\Phi_{0\alpha}z) + D_{H\beta} \exp(-iK_{0\beta}\Phi_{0\beta}z)] \exp(-i\mathbf{H} \cdot \mathbf{r}_{\parallel})|^2. \quad (10)$$

The fields  $D_{0i}$  and  $D_{Hi}$  are complex and we define  $D_{0i} = D'_{0i} + iD''_{0i}$  and  $D_{Hi} = D'_{Hi} + iD''_{Hi}$ . To first order, we can say that  $K_{0i}\Phi_{0iz} = k_0\Phi_{0iz}$ , where  $\Phi_{0i} = \Phi'_{0i} + i\Phi''_{0i}$ . Expressions for the fields  $D_{0i} \approx E_{0i}$  and  $D_{Hi} \approx E_{Hi}$  (Afanas'ev & Melkonyan, 1983; Cowan, 1985) and the angles  $\Phi_{0i}$  (Jach, Cowan, Shen & Bedzyk, 1989) are readily determined from boundary conditions at the surface and dispersion relations.

Evaluating  $I = D^*D$ , we obtain

$$I = |E_{0\alpha}|^2 d_1 + E_{0\alpha} E_{0\beta}^* d_3 + E_{0\alpha}^* E_{0\beta} d_3^* + |E_{0\beta}|^2 d_2 + |E_{H\alpha}|^2 d_1 + E_{H\alpha} E_{H\beta}^* d_3 + E_{H\alpha}^* E_{H\beta} d_3^* + |E_{H\beta}|^2 d_2 + \exp(i\mathbf{H} \cdot \mathbf{r}_{\parallel}) [E_{0\alpha} E_{H\alpha}^* d_1 + E_{0\alpha} E_{H\beta}^* d_3 + E_{0\beta} E_{H\alpha}^* d_3^* + E_{0\beta} E_{H\beta}^* d_2] + \exp(i\mathbf{H} \cdot \mathbf{r}_{\parallel}) [E_{0\alpha}^* E_{H\alpha} d_1 + E_{0\alpha}^* E_{H\beta} d_3^* + E_{0\beta}^* E_{H\alpha} d_3 + E_{0\beta}^* E_{H\beta} d_2], \quad (11)$$

where we define

$$d_1 = \exp(2k_0\Phi''_{0\alpha}z), \quad (12)$$

$$d_2 = \exp(2k_0\Phi''_{0\beta}z) \quad (13)$$

and

$$d_3 = \exp[ik_0(\Phi''_{0\beta} - \Phi''_{0\alpha})z] = R_3 \exp(iv_3). \quad (14)$$

Expressions (12), (13) and (14) contain the entire depth dependence of the intensity.

We also define the first term in brackets in (11) as a complex number  $V_0 = R_0 \exp(iv_0)$ . By expanding the fields into their complex parts we obtain

$$I = |E_{0\alpha}|^2 d_1 + |E_{0\beta}|^2 d_2 + |E_{H\alpha}|^2 d_1 + |E_{H\beta}|^2 d_2 + 2T_1 R_3 \cos v_3 + 2T_2 R_3 \sin v_3 + 2R_0 \cos(v_0 + \mathbf{H} \cdot \mathbf{r}_{\parallel}), \quad (15)$$

where

$$T_1 = E'_{0\alpha} E'_{0\beta} + E''_{0\alpha} E''_{0\beta} + E'_{H\alpha} E'_{H\beta} + E''_{H\alpha} E''_{H\beta} \quad (16)$$

and

$$T_2 = E'_{0\alpha} E''_{0\beta} - E''_{0\alpha} E'_{0\beta} + E'_{H\alpha} E''_{H\beta} - E''_{H\alpha} E'_{H\beta}. \quad (17)$$

To calculate a yield, we start by assuming again a distribution of atoms in two dimensions at a constant distance  $z > 0$  beneath the surface. With the coherent fraction and coherent position defined as before, the fluorescence yield takes the form

$$Y = \exp(-\mu z) \{ |E_{0\alpha}|^2 d_1 + |E_{0\beta}|^2 d_2 + |E_{H\alpha}|^2 d_1 + |E_{H\beta}|^2 d_2 + 2T_1 R_3 \cos v_3 + 2T_2 R_3 \sin v_3 + 2R_0 f_H \cos(v_0 - 2\pi p_H) \}, \quad (18)$$

where

$$v_3 = [k_0(\Phi'_{0\beta} - \Phi'_{0\alpha})z] \quad (19)$$

and  $\mu$  is the escape length of the fluorescent radiation or Auger electron being observed.

Expression (18) for a layer at depth  $z$  is seen to have the usual standing-wave appearance, with some added features. The expressions in  $v_3$  incorporate the vertical *Pendellösung* due to the interference between the internal fields generated by the  $\alpha$  and  $\beta$  branches.

For the case where impurities are distributed homogeneously throughout the crystal or where we are looking at fluorescence from the lattice itself, (12)–(14) may be integrated over all  $z$  with the exponential factor that contains the escape length of the fluorescence radiation. If we assume that the detector sees fluorescent radiation, Auger electrons *etc.* leaving the surface primarily in the normal direction, the expressions in (18) may be replaced by

$$d_1 = (\mu - 2k_0\Phi''_{0\alpha})^{-1}, \quad (20)$$

$$d_2 = (\mu - 2k_0\Phi''_{0\beta})^{-1} \quad (21)$$

and

$$R_3 \cos v_3 = [\mu - k_0(\Phi''_{0\alpha} + \Phi''_{0\beta})] \times \{ [\mu - k_0(\Phi''_{0\alpha} + \Phi''_{0\beta})]^2 + [k_0(\Phi'_{0\beta} - \Phi'_{0\alpha})]^2 \}^{-1}, \quad (22)$$

$$R_3 \sin v_3 = k_0(\Phi'_{0\beta} - \Phi'_{0\alpha}) \times \{ [\mu - k_0(\Phi''_{0\alpha} + \Phi''_{0\beta})]^2 + [k_0(\Phi'_{0\beta} - \Phi'_{0\alpha})]^2 \}^{-1}. \quad (23)$$

### 3. Experimental

To test the calculations, we carried out a series of XSW measurements at the Cornell High Energy Synchrotron Source (CHESS). The sample consisted of iodine chemisorbed on the (111) surface of Ge. We observed the diffraction from a (220) plane normal to the surface with a monochromatic X-ray beam at an energy of 5.98 keV. The experimental configuration, including the manner of monochromating and collimating the X-ray beam, has been described previously (Jach, Cowan, Shen & Bedzyk, 1989; Jach & Bedzyk, 1990). The experiment consisted in monitoring the specularly reflected beam flux, the diffracted-

reflected beam flux, the Ge *L* fluorescence at 1.18–1.22 keV and the I *L* fluorescence at 3.93–4.80 keV.

#### 4. Results and analysis

Figs. 2(a)–(i) summarize the results for angles of incidence  $\varphi$  that are considerably below the critical angle (a–c), near the critical angle (d–f) and considerably above the critical angle (g–i). A considerable difference is observed in the fluorescence yield between the I fluorescence and the Ge fluorescence.

The fitting procedure followed was similar to Bragg diffraction XSW. In this case, the specular beam was fitted in Figs. 2(a), (d), (g) to obtain first-order corrections to the diffraction-angle scale and the angle of incidence. Using the corrected values, we fitted the I fluorescence yield according to (7) and the Ge fluorescence yield according to (18)–(23) to obtain the coherent fraction  $f$  ( $\pm 0.05$ ) and the coherent position  $p$  ( $\pm 0.04$ ). A value of  $z = -2.86$  Å (above the surface), obtained from Bragg XSW measurements (Bedzyk, Shen, O’Keeffe, Navrotsky & Berman, 1989), was used for the height above the (111) diffraction plane of the I chemisorbed atoms.

The structure factor of Ge was calculated using a centrosymmetric origin. Consequently,  $p = 0.0$  corresponds to an atom that is located in a (220) diffraction plane. Of the three possible sites in this diffraction plane (above,  $T_4$  or  $H_3$ ), the ‘above’ site is the only

one consistent with the  $z$  position obtained independently.

The fitted parameters obtained in Figs. 2(b), (e), (h) and 2(c), (f), (i) demonstrate the validity of the standing-wave expressions under a wide variety of diffraction conditions and fluorescence dependence. Unlike the Bragg XSW case, the standing wave here never goes completely from a pure  $\alpha$ -branch (antinode on diffraction plane) solution to the pure  $\beta$ -branch (node on diffraction plane) solution and the linear combination depends on the angle of incidence  $\varphi$ . The integrated bulk Ge fluorescence that is observed is markedly different from the I fluorescence for atoms in the same diffraction plane. This illustrates our theoretical observation that the rapid variation of the standing-wave amplitude parallel to the surface is accompanied by a depth variation that changes with angle. This could, in principle, be used to obtain the depth of a layer of impurity atoms beneath the surface. Our expressions for the integrated bulk fluorescence of Ge are also consistent with the observations of Hashizume & Sakata (1989).

Slight differences in the fitted coherent positions between different angles  $\varphi$  as well as between the overlayer and substrate are attributed to the contamination of the incident beam with harmonic radiation, which was above the Ge *K* edge. The strong attenuation of the observed Ge *L* fluorescence radiation under the experimental conditions made it difficult

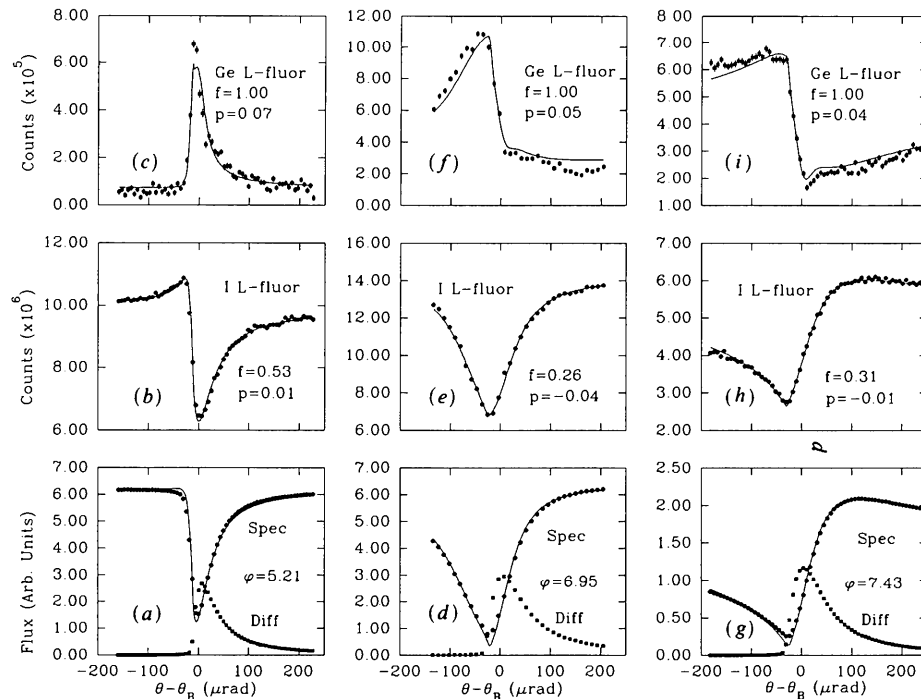


Fig. 2. (a), (d), (g) Specular and diffracted beam flux; (b), (e), (h) I fluorescence; (c), (f), (i) Ge fluorescence; for (a), (b), (c)  $\varphi = 5.21$ ; (d), (e), (f)  $\varphi = 6.95$ ; (g), (h), (i)  $\varphi = 7.43$  mrad. The error bars take account of counting statistics only; error limits on the fits are given in the text.

to compensate accurately for this spurious component, which was small in any case. A second source of error could be due to the assumption of an abrupt discontinuous step in the dielectric susceptibilities  $\chi_0$ ,  $\chi_{220}$  at  $z=0$  (Batterman & Cole, 1964). A more accurate approximation for the fields near the surface would take into account the electron density for an actual crystal surface and perhaps even the presence of the chemisorbed species and surface roughness as well.

Although the sample was prepared chemically and thereafter kept in an inert He atmosphere, the coherent fraction was observed to degrade as a function of time.

In summary, we have obtained expressions that parametrize glancing-angle X-ray standing-wave fluorescence yields in the same manner as X-ray standing waves created in the Bragg geometry. The expressions permit fitting the fluorescent intensity from atoms above or below the surface of a crystal to obtain the coherent position of the atoms parallel to the surface and their coherent fraction. The fluorescence yield includes a dependence on the distance of the atoms from the surface because of a changing extinction of the wave fields above and below the surface.

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## On the Relation Between the Diffraction Ratio, the Doublet Values and the Reliability of the Triplet Estimates

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### Abstract

A diffraction ratio is proposed that predicts the differences to be expected between the intensities of two-isomorphous data sets. This ratio is important for the *ab initio* structure determination of isomorphously related structures by means of direct methods. The diffraction ratio is shown to be linearly related to the average doublet phase sum of the isomorphous data. It is argued that the doublets are essential for correct triplet-phase-sum estimates. The

diffraction ratio and the idealized average triplet-phase-sum error, as calculated from a recent probabilistic theory, turn out to be related. A minimum diffraction ratio is required to obtain a triplet-phase-sum-error level comparable with that of small structures that are solved routinely by conventional direct methods. The diffraction ratio can be used to maximize the triplet-phase-sum reliability before collecting the data by choosing the optimal wavelength in a single anomalous-scattering experiment, selecting the most suitable heavy-atom derivative in a single-