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1993 J. Phys.: Condens. Matter 5 8643

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Theory of the polarization and orientational dependences of the x-ray reflectivity fine structure

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Received 21 August 1992, in final form 4 May 1993

Abstract. The permittivity tensor of low-symmetry crystals could be essentially anisotropic in the soft-x-ray region if the wavelength is close to some atomic core level absorption edge. Simple Fresnel's formulae are generally invalid in this case for calculations of the x-ray reflectivity, and a number of effects well known in crystal optics occur. The method of permittivity tensor calculations near the K absorption edge is proposed in the present paper. The method is used in order to study the dependence of the x-ray reflectivity fine structure on the polarization and orientation of the incident wave in the case of a uniaxial crystal and small glancing angles. It is shown that, using such dependences, one could obtain complete information about the atomic scattering factor tensor in the crystal in the anomalous dispersion region. The x-ray reflectivity fine structure for different faces of a hexagonal BN crystal has been calculated and compared with experiment. The results obtained have shown evidence of strong crystal optic effects in the case treated.

1. Introduction

The progress achieved since 1971 in studies of the atomic structure of solids and molecules by the x-ray absorption fine structure (XAFS) stimulated a number of related techniques. The spectra involved in the majority of these (x-ray fluorescence, electron yield, photostimulated desorption of ions, etc) are proportional directly to the corresponding x-ray absorption cross sections, i.e. the imaginary parts of the permittivity. On the contrary, the x-ray reflectivity fine structure (XRFS) which is employed sometimes in order to study solid surfaces [1–4] is determined by both the imaginary and the real parts of the permittivity; therefore the usual method of data processing cannot be used directly in this case. To obtain structural information from the near-edge XRFS, it is transformed firstly into XAFS taking into account the Kramers–Kronig relations [3, 4] and then traditional methods of XAFS analysis are used. Such a transformation could be easily carried out in the case of cubic crystals when the permittivity tensors (PTs) are isotropic and simple Fresnel's formulae for reflectivity are valid. The isotropy of the PT in the normal dispersion region of the x-ray spectrum where the x-ray wavelength is far from any absorption edge is usually assumed. Meanwhile experimental studies of the XAFS polarization and orientational dependences have shown that imaginary parts of the PT could be essentially anisotropic tensors in the vicinity of the K and L atomic edges in the case of low-symmetry crystals. (See [5] for example.) It is reasonable to suppose that the anisotropy of the PT in this case may cause phenomena similar to crystal optic phenomena in the visible part of spectrum. These phenomena could be observed if one studies the x-ray reflection or penetration processes in the anomalous dispersion region where the x-ray wavelength is close to some core atomic edge. Indeed, it

was shown in [4] that the XRFS above the boron K edge for two different faces of a hexagonal BN crystal differ from each other. Unfortunately the use in [4] of the unpolarized radiation of the x-ray tube and the difficulties of preparing ideal reflection faces weakened the effect.

In the present paper, two problems are discussed. The first is how noticeable could be the crystal optic effects in the x-ray reflectivity spectra. The second is how the information about the PT components in low-symmetry crystals can be obtained through reflectivity data. In order to clarify the questions above, the method of XRFS calculations in near-edge regions of the x-ray spectrum for crystals with arbitrary symmetry and ideally sharp and flat surfaces has been developed, and calculations of XRFS for a hexagonal BN (h-BN) crystal near the boron K edge have been carried out. The results obtained have shown that, at a fixed glancing angle, XRFS noticeably depends on the choice of crystal face and on the orientation and polarization of the incident radiation. Employing these dependences, one could obtain, in principle, complete information about the PT of a crystal.

2. Calculations of the permittivity tensor of the anisotropic crystal in the anomalous dispersion region

All optical properties of an anisotropic crystal in the soft-x-ray region are determined by its PT which could be calculated through the tensor of the atomic scattering factor (TASF) by the following relation [6]:

$$\epsilon_{\alpha\beta} = \delta_{\alpha\beta} - \sum_i \frac{4\pi n_i c^2 r_0}{\omega^2} f_{\alpha\beta}^{(i)} \quad (1)$$

where the Greek subscripts denote the tensor components ($\alpha = x, y, z$), i denotes the kind of atom in the crystal, n_i is the concentration of atoms, c is the velocity of light, r_0 is the classical electron radius, ω is the radiation frequency, $\delta_{\alpha\beta}$ is the Kronecker symbol and $f_{\alpha\beta}^{(i)}$ is the TASF of the atom in a solid.

The TASF of a single free atom is obviously a diagonal tensor, and detailed tables [6, 7] are available which contain information about both the imaginary and the real parts of the ASF for all elements. Of course the TASF of an atom in a solid is not completely identical with that of the free atom even in the normal dispersion region because the TASF in a crystal contains a small anisotropic fraction caused by anisotropic components of the electron density around the atoms. Nevertheless the effect of the electron charge redistribution in solids on the TASF is very small and it is neglected in the present paper. On the contrary, in the anomalous dispersion region the TASF of the atom in a solid can differ significantly from that of the solitary free atom. This difference is caused by the strong interaction between slow virtual electrons which appear at the intermediate stage of the photon elastic scattering process and neighbouring atoms [8, 9]. In the case of a low-symmetry position of the scattering atom this interaction can give rise to the appearance of an appreciable anisotropic contribution to the TASF. Also, the isotropic part of the TASF could be affected significantly by this interaction. Therefore the tables [6, 7] enable one only to estimate roughly the values of the TASF near atomic thresholds, and direct calculations are needed in this case, especially for the anisotropic part of the TASF.

The method of the TASF calculations in solids near K absorption edges was developed by the present authors previously [9]. We have applied the method proposed in order to calculate the PT for an h-BN crystal near the boron K edge. The h-BN is a uniaxial crystal with a crystalline structure similar to that of graphite. If one directs the z axis of

the coordinate system along the optic axis of the crystal, then the PT is a diagonal tensor and $\epsilon_{xx} = \epsilon_{yy}$ for arbitrary orientation of the x and y axes. It is convenient to use the notation $\epsilon_{\parallel} = \epsilon_{zz}$ and $\epsilon_{\perp} = \epsilon_{xx} = \epsilon_{yy}$ for components of the PT in uniaxial crystals. The anomalous part of the boron TASF has been calculated by the multiple-scattering method for the central atom of the 39-atom three-layer cluster. The details of the TASF calculation have been presented in the previous paper [9]. The TASF of the nitrogen atom is taken from the tables [7] as also is the contribution to the TASF of boron valence electrons. The calculated real and imaginary parts of ϵ_{\perp} and ϵ_{\parallel} for the h-BN crystal are shown in figure 1. For comparison the permittivity calculated with the help of the ASF values taken from the tables [7] is also presented. It is easy to see that the anisotropic part of the PT in the h-BN crystal is comparable with its isotropic part near the boron K edge and hence one could expect noticeable crystal optic phenomena in this case. One could note that the h-BN crystal is not quite a favourable system for calculations of its Green function by the multiple-scattering method because the muffin-tin approximation for the crystalline potentials which is employed in this method is not quite adequate for a layered crystal with a strong in-plane covalent bonding and large interplane separation. Nevertheless there are several reasons which impel us to treat the h-BN crystal in order to illustrate the method developed. Firstly, as we have already mentioned, the boron ASF in this crystal is essentially an anisotropic tensor near the boron K edge [9]; therefore one could expect the appearance of sharp polarization and orientational dependences of the XRFS. Secondly, the h-BN crystal is uniaxial, and a theoretical description of the reflectivity for this crystal is simpler than in the general case of a biaxial crystal. Finally, experimental reflection spectra of an h-BN crystal taken near the boron K edge are available [4].

The fine structure of the imaginary part of the TASF for a boron atom in h-BN was compared with the K absorption spectrum in the previous paper [9], and it was shown that in spite of the above-mentioned shortcomings of the muffin-tin approximation the main features of the experimental spectrum, i.e. π exciton and σ resonance, are reproduced well by the calculations.

Using the traditional methods of the electrodynamics of continuous media [10] we have developed the computational codes for reflectivity calculations. With the help of these codes the XRFS in the case of an h-BN crystal face perpendicular to the optic axis have been calculated for a glancing angle equal to 4° . The results obtained shown in figure 2 have been compared with the experimental XRFS presented in [4]. As the radiation from the x-ray tube utilized in [4] was not polarized in order to compare experimental and theoretical spectra, the latter have been averaged appropriately. As one can see, the most prominent features of the theoretical and experimental spectra are in reasonable agreement. Nevertheless the weaker features of these structures disagree with each other. We consider this disagreement to be caused by many-electron effects which have not been taken into account in our calculations but which are more important in the case of x-ray² reflection processes than in the case of x-ray absorption processes. The discrepancy between the absolute values of theoretical and experimental reflectivities could be explained naturally by a decrease in the experimental reflectivity values due to surface defects of the sample studied.

3. Polarization and orientation dependences of the XRFS in uniaxial crystals

As follows from traditional Fresnel's formulae the x-ray reflectivity in the near-critical-angle region almost does not depend on the polarization direction of the incident radiation. In the present paper we should like to emphasize that in the case of low-symmetry crystals the

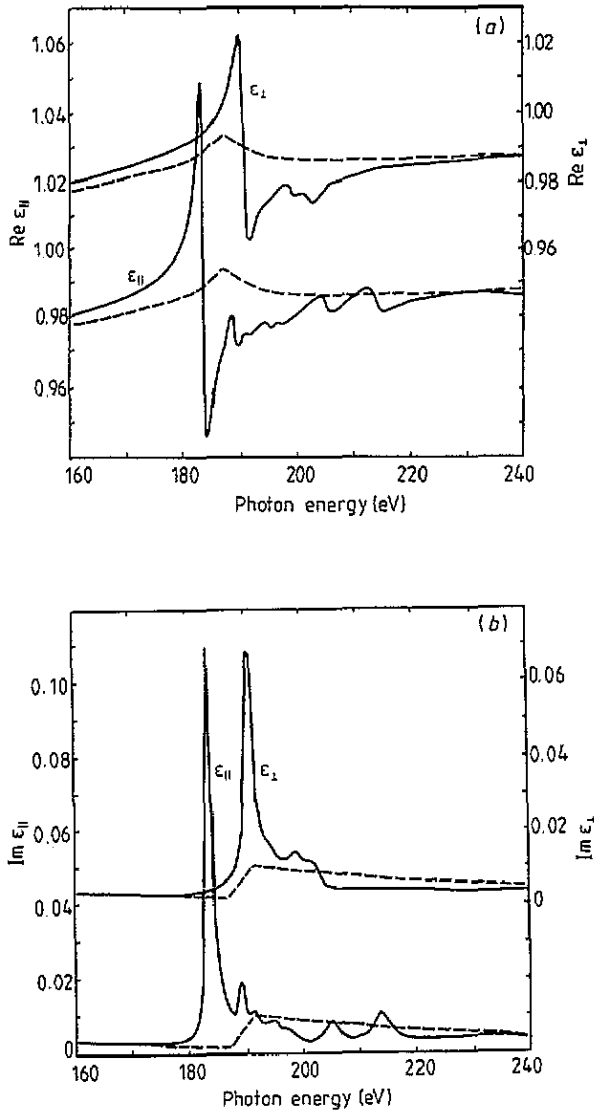


Figure 1. (a) Real and (b) imaginary parts of the PT components in an h-BN crystal. For comparison the permittivity calculated with the ASF taken from the tables [7] is also shown (---).

reflectivity near the absorption edges does depend on the polarization and orientation of the incoming radiation even if the glancing angle is close to the critical value. For simplicity, only the case of the uniaxial crystal is considered below.

The PT of the uniaxial crystal is the diagonal tensor in the rectangular coordinate system x', y', z' if one axis of this system coincides with the optic axis of the crystal. This is correct even in the case of the complex PT with absorption being taken into account. We shall call the plane parallel to the wavevectors of incident and reflected radiation the scattering plane hereafter. In the case when the x' and z' axes belong to the crystal face and the y' and z' axes belong to the scattering plane it is easy to write boundary conditions for incident, reflected and refracted waves and to obtain Fresnel-like formulae for the reflectivities of s-

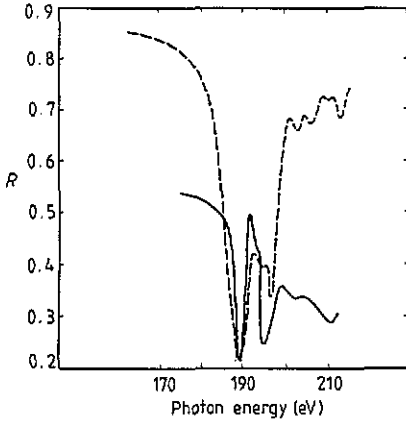


Figure 2. Experimental (—) [4] and calculated (---) XRFs for the h-BN crystal face perpendicular to the optic axis. The glancing angle of the unpolarized incident beam is equal to 4°.

and p-polarized incident radiation:

$$R_s = \left| \frac{[\sin \theta - (\epsilon_{x'x'} - \cos^2 \theta)^{1/2}]}{[\sin \theta + (\epsilon_{x'x'} - \cos^2 \theta)^{1/2}]} \right|^2 \tag{2}$$

$$R_p = \left| \frac{[(\epsilon_{y'y'}\epsilon_{z'z'})^{1/2} \sin \theta - (\epsilon_{z'z'} - \cos^2 \theta)^{1/2}]}{(\epsilon_{y'y'}\epsilon_{z'z'})^{1/2} \sin \theta + (\epsilon_{z'z'} - \cos^2 \theta)^{1/2}} \right|^2.$$

Let us consider first the case when the crystal face is perpendicular to the optic axis. In this case the optic axis coincides with the z' axis: so $\epsilon_{z'z'} = \epsilon_{\parallel}$ and $\epsilon_{x'x'} = \epsilon_{y'y'} = \epsilon_{\perp}$. As follows from equations (2) the coefficient R_s is determined by ϵ_{\perp} entirely. On the contrary the coefficient R_p depends in general on both ϵ_{\perp} and ϵ_{\parallel} . However, near the critical angle where $\theta \ll 1$ the dependence of R_p on ϵ_{\perp} becomes negligible and one could consider that the coefficient R_p depends on ϵ_{\parallel} only. So, using the experimental coefficients R_s and R_p one could easily determine all components of the PT of the uniaxial crystal from equations (2) by the usual method developed for isotropic crystals [3, 4]. XANES studies [11, 12] and the calculations carried out in the previous section show that ϵ_{\perp} could differ from ϵ_{\parallel} significantly in the near-edge regions of the spectra. Therefore, the XRFs for the s and p polarization directions could be quite different. As far as the present authors know, such a polarization dependence of XRFs has not been studied experimentally yet.

If the crystal face is parallel to the optic axis, then the coefficient R_s depends on the angle between the scattering plane and the optic axis at a fixed glancing angle. For instance as follows from (2) the coefficient R_s is determined by ϵ_{\parallel} when the scattering plane is perpendicular to the optic axis and by ϵ_{\perp} when it is parallel to the optic axis. On the contrary the coefficient R_p does not depend on the scattering plane orientation if the glancing angle is sufficiently small and this coefficient is determined by ϵ_{\perp} only. Using the orientational dependence of the coefficient R_s in the case of the crystal face parallel to the optic axis, one could also determine all components of the uniaxial crystal PT.

To illustrate the XRFs polarization and orientational dependences we have calculated them near the boron K edge in the h-BN crystal. The theoretical XRFs in the case of the crystal face perpendicular to the optic axis is shown in figure 3. The spectra have been calculated for linearly s- and p-polarized incident waves. The polarization dependence of the XRFs has been studied for three values of the glancing angle: 3°, 5.5° and 7°. Comparison of the XRFs for different polarization directions with the PT components (figure 1) proves that the sharp polarization dependence of the XRFs is caused by anisotropy of the PT. It is interesting to note that different reflectivities for s and p incoming waves result in polarization of the reflected wave even in the case of unpolarized incident radiation and the degree of polarization dramatically depends on the photon energy near the B K edge.

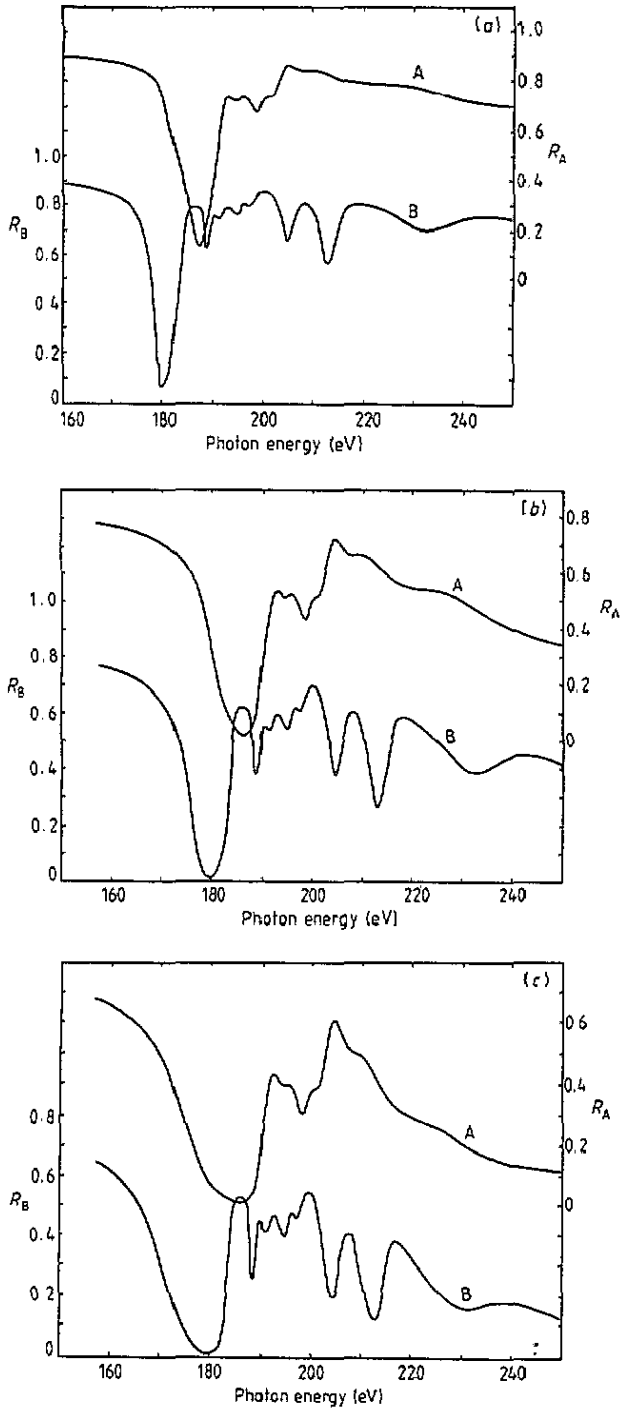


Figure 3. Polarization and orientational dependences of the XRFs for an h-BN crystal near the boron K edge at glancing angles equal to (a) 3° , (b) 5.5° and (c) 7° for linearly s- and p-polarized incident wave. The reflection geometries considered are as follows: (i) the crystal face perpendicular to the optic axis; (ii) the crystal face and the scattering plane parallel to the optic axis; (iii) the crystal face parallel to the optic axis, and the scattering plane perpendicular to the optic axis. Curves A represent R_s in case (i), $R_s \approx R_p$ in case (ii), and R_p in case (iii). Curves B represent R_p in case (i), and R_s in case (iii).

The case of the h-BN crystal face parallel to the optic axis has also been studied. The results of XRFs calculations for linearly s- and p-polarized incident waves for the scattering plane parallel and perpendicular to the optic axis and glancing angles equal to 3° , 5.5° and

7° are presented in figure 3. The case of intermediate orientation of the scattering plane has been considered for the glancing angle equal to 3° . The orientation of the scattering plane is shown in the inset of figure 4. The results obtained for linearly s- and p-polarized and for right-hand and left-hand circularly polarized incident waves are presented in figure 4. One can see that the XRFS for the p-polarized wave indeed almost does not depend on the scattering plane orientation in the case of the crystal face parallel to the optic axis. On the contrary the XRFS for s-polarized and circularly polarized incident waves contain features of both the ϵ_{\parallel} and the ϵ_{\perp} components of the PT and depend on the scattering plane orientation significantly. It is interesting to note that the fine structures for right-hand and left-hand polarized incident waves in the case of the scattering plane shown in figure 4 are not completely identical.

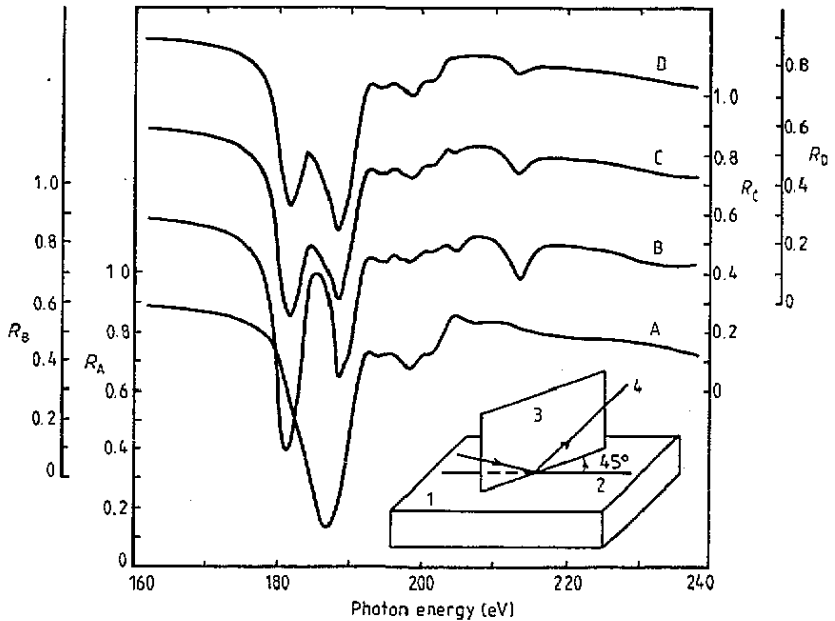


Figure 4. Polarization dependence of the XRFS for an h-BN crystal face parallel to the optic axis and the scattering plane orientation shown in the inset. The polarizations of incident wave considered are as follows: curve A, linearly p-polarized wave; curve B, linearly s-polarized wave; curve C, left-hand circularly polarized wave; curve D, right-hand circularly polarized wave. The curves are shifted for display. The angle between the scattering plane and the optic axis is equal to 45° . In the inset the orientation of the scattering plane (3) relative to the optic axis (2) and the crystal face (1) and the incident and reflected beams (4) is shown.

It is worth paying attention to the fact that the x-ray reflectivity is a non-linear function of permittivity. So the averaged XRFS of polycrystal or amorphous systems is not connected directly with the averaged PT through Fresnel-type equations and a simple method of XAFS determination from averaged XRFSS for low-symmetry crystals is not valid.

4. Conclusions

In this paper a method of calculation of the permittivity tensor and XRFS near K absorption edges is proposed. It is shown that near the absorption edges of atomic core levels the PT

could be essentially anisotropic in the case of low-symmetry crystals. The polarization and orientational dependences of the XRFS are studied for the uniaxial crystal case. The method proposed is illustrated by calculations of the XRFS for the h-BN crystal. Calculations of the PT tensor in the x-ray anomalous dispersion region enable one to study a variety of phenomena of crystal optics in the soft-x-ray region.

Acknowledgment

This work has been supported by the Ministry of Science of the Russian Federation by grant 15-51-14.

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