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Experimental determination of electric-field-induced differences in structure-factor phases of the order of 2%

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Abstract

In order to understand the induced electron-density response of covalently bonded materials to an externally applied electric field, the change of structure-factor phases of several weak reflections of GaAs has been measured by three-beam interferences. Using a modulation technique, phase variations of the order of 1° for a field strength of 1 kV mm^{-1} were determined. Although the statistics of these first experiments are rather poor, the experiment verifies qualitatively the predictions of a semi-empirical bond-charge model. The measured phase variation is the smallest value determined up to now.

1. Introduction

In recent years, considerable theoretical work has been performed to understand the mechanism of dielectric screening in crystals, especially in tetrahedrally coordinated insulators and semiconductors (Resta, 1994; Resta & Baldereschi, 1981). The change in the electron density of GaAs due to an externally applied electric field, which is the microscopical manifestation of screening, was measured indirectly by Fujimoto (1980), Pietsch *et al.* (1985) and recently by Stahn, Pucher *et al.* (1998).

GaAs crystallizes in the zinc-blende structure. The atoms of one kind are coordinated by four atoms of the other kind. They are connected by polar-covalent bonds. For data reduction and interpretation, the electron density ρ can be approximated by a superposition of spherical atomic charge densities (core and valence) and bond charges (BC) representing aspherical contributions (Pietsch, 1981) (see Fig. 1).

The measurable quantities of ρ are the Fourier coefficients (including anomalous dispersion $f' + if''$ and thermal effects T):

$$\begin{aligned} F &\approx (f_{\rm Ga} + f'_{\rm Ga} + if''_{\rm Ga})T_{\rm Ga} \\ &\quad + (f_{\rm As} + f'_{\rm As} + if''_{\rm As})T_{\rm As}\exp(i\mathbf{kr}_{\rm As}) \\ &\quad + \sum_i f_{\rm BC}\exp(i\mathbf{kr}_{{\rm BC},i}) \\ F &= |F|\exp(i\varphi). \end{aligned} \tag{1}$$

In previous works, the changes in the scattered X-ray intensity ($\sim |F|^2$) of some weak [$\exp(i\mathbf{kr}_{\rm As}) = -1$] reflections were studied (Fujimoto, 1980; Pietsch *et al.*, 1985). It has been shown that structure-factor amplitudes of low-index reflections, which are particularly affected by the covalent bond, vary nearly linearly with the applied electric field. The very small variations of the integral intensity of $\Delta|F|^2/|F|^2 \approx 1\%$ for $E = 3$ kV mm^{-1} could be determined using a modulation technique (Stahn, Pucher *et al.*, 1998). Unfortunately, these data provide information about the variation of the structure-factor amplitudes $|F|$ only.

In order to also obtain information about the structure-factor phases φ, three-beam diffraction experiments were performed. The conventional application of this method in crystal-structure analysis gives phase relations among structure factors with an accuracy of about 15–20° mean phase error using crystals of arbitrary shape. A detailed description of multiple-beam X-ray diffraction is given by Weckert & Hümmer (1997). It will be shown that the modulation technique applied to plate-shaped crystals allows the determination of phase variations one order of magnitude smaller than before.

2. Experiment

The sample is a [111]-oriented single-crystalline GaAs plate which was prepared as a capacitor by depositing silver spots on both faces. Between these spots, a DC electric field up to 1 kV mm^{-1} was applied. Since the expected variation is small, a modulation technique

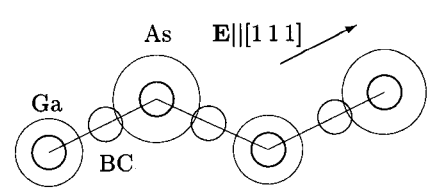

Fig. 1. Bond-charge model: the total charge density is a superposition of spherical atomic contributions (core and valence) and a bond charge between the atoms.

(Cousins, 1988; Stahn, Pucher *et al.*, 1998) has been applied to detect the scattered radiation from the sample with and without an applied field quasi-simultaneously. The voltage was switched on and off with a frequency of 20 Hz and for different voltages the intensity was collected in separate counter channels. The experiment was performed at the six-circle diffractometer at beamline ID22 at the ESRF using a wavelength of 0.9042 Å.

The interesting quantity for a phase determination from a three-beam case is the ψ-scan profile. This is the integral intensity of the primary reflection H with structure factor $F(\mathbf{h})$ plotted as a function of ψ. ψ is the rotation angle about $\mathbf{h}$ relative to an arbitrary reference direction. Close to a three-beam point, a third reflection G (besides H and 0) approaches the Ewald sphere. The triplet phase $\phi = \varphi_{\mathbf{g}} + \varphi_{\mathbf{h}-\mathbf{g}} - \varphi_{\mathbf{h}}$ determines the shape of the ψ-scan profile (Hümmer & Weckert, 1990). If $\phi = \pm 90^\circ$, the interference pattern is almost symmetric with respect to the three-beam Lorenz point. The profiles in Fig. 2(*a*) are of this type. Since $|F(\mathbf{g})|$ and $|F(\mathbf{h}-\mathbf{g})|$ are considerably larger than $|F(\mathbf{h})|$, the interference profiles show additional *Umweganregung* effects. For $\phi = 0, 180^\circ$, the interference pattern is almost antisymmetric. Thus, an induced phase shift would cause a tiny asymmetry in the ψ-scan profile – and

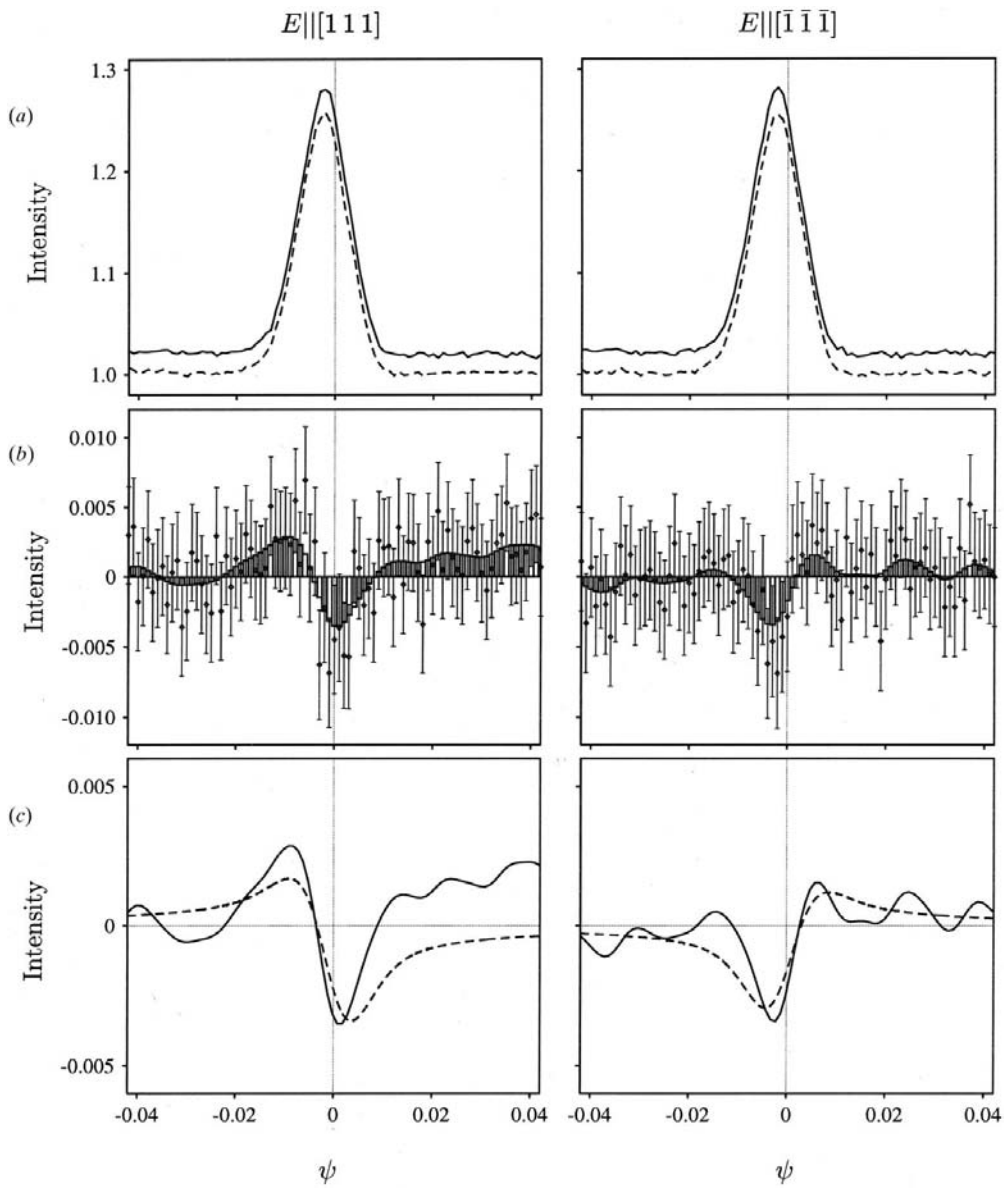

Fig. 2. Interference patterns of the three-beam case 222/$\bar{7}$57 with (dashed line) and without (solid line, shifted for clarity) an electric field on the sample (*a*), the differences between them with error bars (*b*) and a smoothed experimental difference (solid) with a fitted curve (dashed) (*c*).

Table 1. *Fitted phase and amplitude differences of the primary reflections of all measured three-beam cases*

The field strength was approximately ± 1 kV mm^{-1}.

	E||[111]		E||[$\bar{1}\bar{1}\bar{1}$]	
	$\Delta\varphi$ (°)	$\Delta\|F\|$	$\Delta\varphi$ (°)	$\Delta\|F\|$
222	−2.0 (10)	+0.01 (2)	+1.5 (10)	+0.02 (2)
$\bar{2}\bar{2}\bar{2}$	+1.5 (10)	+0.02 (2)	−1.0 (10)	+0.02 (2)
442	0.0 (20)	−0.05 (6)	+3.0 (10)	+0.03 (2)
$\bar{4}\bar{4}\bar{2}$	+2.0 (10)	−0.01 (2)	−2.5 (10)	+0.04 (2)

this should be visible in the difference between the profiles with and without an electric field.

In Fig. 2(*a*), ψ-scan profiles are shown for the case $222/\bar{7}57$ with and without an external field. The profiles are normalized to 1 outside the three-beam case.

In Fig. 2(*b*), the differences of the ψ-scan profiles from Fig. 2(*a*) are given with error bars. The boxes show a smoothed difference curve (convolution with a Gaussian curve). The difference is small compared with the statistical error – but the pattern of the (smoothed) difference curves are qualitatively reproducible. Indeed, the difference profiles exhibit the expected asymmetry. For each three-beam case ($222/\bar{7}57$, $\bar{2}\bar{2}\bar{2}/75\bar{7}$, $442/73\bar{9}$ and $\bar{4}\bar{4}\bar{2}/7\bar{3}9$), at least five ψ-scan profiles were determined (except for $442/73\bar{9}$, E||[111]). All showed reproducible patterns in the difference profile.

3. Interpretation of the difference profiles

From a set of structure factors involved in a three-beam interference, $F(\mathbf{h})$, $F(\bar{\mathbf{h}})$, $F(\mathbf{g})$, $F(\bar{\mathbf{g}})$, $F(\mathbf{h}-\mathbf{g})$ and $F(\mathbf{g}-\mathbf{h})$, a theoretical ψ-scan profile is calculated according to the plane-wave dynamical theory of X-ray diffraction (Pinsker, 1978; Weckert & Hümmer, 1990). The structure factors are obtained with a bond-charge model (Stahn, Möhle & Pietsch, 1998) including thermal effects and anomalous dispersion [see equation (1)].

'Theoretical difference profiles' can be obtained by altering the amplitudes or phases of the model structure factors. In the studied cases with weak low-index H ($\mathbf{h} = 222, 442, \ldots$) and medium–high-index G ($\mathbf{g} = \bar{7}57, 73\bar{9}, \ldots$), the measurable variation of ϕ can be interpreted as a variation in the phase of $F(\mathbf{h})$ because H is very sensitive to a small rearrangement of the valence-charge density.

$F(\mathbf{h})$ is modified in a way that the theoretical difference profile looks like the experimentally determined one. This is demonstrated in Fig. 2(*c*). Table 1 gives the results of such fits for all measured reflections. While the phase shift hardly depends on the data reduction, the amplitude variation is very sensitive to the normalization of the profiles. Therefore, the evaluated amplitude variations are rather uncertain but the phase variations are significant. The choice of the initial structure factors (depending on different model assumptions) hardly affects the results.

4. Discussion

The phase shifts (Table 1) can be compared with the findings of former experiments probing the amplitude variations (Stahn, Pucher *et al.*, 1998). There are qualitative conformities: The signs of both $\Delta\varphi$ and $\Delta|F|^2/|F|^2$ depend on the direction of the applied field **E**. For one field direction, $\Delta\varphi(222)$ and $\Delta\varphi(442)$ have the same sign and negative indexed reflections show opposite behaviour. For positive indexed reflections, the shift of φ and the change in amplitude seem to be larger than for negative indexed ones (to verify this, measurements with better statistics have to be performed). These findings suggest that the measured ψ-scan profile differences have the same physical origin as $\Delta|F|^2/|F|^2$, which are statistically more reliable.

For a quantitative comparison of the two experiments, a bond-charge model was used as mentioned above. The model parameters were fitted to the measured intensity variations. According to this model, the essential effects are internal strain accompanied by a change of the anharmonicity of the thermal motion and a redistribution of the charge density away from the bonding region for E||[111]. The distortion of the unit cell hardly affects the integral intensity since the piezoelectric coefficient is rather small: $d_{14} = 2.7 \times 10^{-9}$ V mm^{-1} (Arlt & Quadflieg, 1968). The model predicts phase variations of the same sign but of only 30% of the experimentally determined quantities.

A reason for this discrepancy may be that the distortion of the unit cell (the converse piezoelectric effect) was not considered explicitly at the data reduction of the ψ-scan profiles. To estimate its influence, theoretical ψ-scan profiles were calculated with a unit cell distorted in the [111] direction. This also leads to a shift of the ψ-scan profile but the resulting antisymmetrical difference profile is much broader in ψ than the measured one. The contribution of the converse piezoelectric effect can be determined directly by measuring the angular positions of reflection G. In the present case, this was not possible for geometrical reasons.

A better insight into the quality of the effect may be obtained by measuring the dependence of the phase shift on the field strength (Stahn, Pucher *et al.*, 1998). Those measurements were impossible because GaAs will become conducting if higher field strengths or more intense synchrotron radiation are applied to the sample.

On the present level, the experiment does not allow one to deduce the phase differences with the precision of the amplitude variations of the structure factors. To use the reliable amplitude variations from the former experiments during the data reduction (instead of fitting them), one first has to find the reason for the quantita-

tive discrepancy in the predictions of the bond-charge model.

Considering all the mentioned uncertainties, one can conclude that the determination of phase variations of the order of 1° is possible using the modulation technique. This opens new possibilities for improving the accuracy of structural analysis.

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