X-Ray Investigation of Bond-Charge Density in Gallium Arsenide

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The (222) and $(\bar{2}\bar{2}\bar{2})$ integrated intensities were measured in the absence of simultaneous reflections, using Co-$K\alpha$ radiation. While the integrated intensity calculated using free-atom scattering factors is the same for both (222) and $(\bar{2}\bar{2}\bar{2})$, the measured values were, respectively, 86 and 66% higher than the calculated one. The fact that both experimental intensities are higher than the calculated value indicates that a net transfer of charge occurs from Ga to As. This conclusion is in agreement with a previous result obtained by DeMarco and Weiss from the measurement of the (200) reflection, but disagrees with observations based on piezoelectric measurements and Fourier synthesis of the charge distribution. The asymmetry between (222) and $(\bar{2}\bar{2}\bar{2})$ is consistent with the existence of electron bridges between first neighbors, thus providing direct evidence of the covalent character of the bonding. It is proposed to exploit the different reflecting powers for the (222) and $(\bar{2}\bar{2}\bar{2})$ planes as an alternative method for determining the absolute polarity of a (111) face, using a characteristic x-ray radiation.

I. INTRODUCTION

A strong interest has developed in the past few years in the electron distributions of III-V compounds with Zn-Se structure. The electronic charge density of GaAs has been determined by various investigators using x-ray diffraction and some controversy has aroused in the interpretation of these experiments.

Sirota and Olekhnovich[1] first obtained the electron density distribution of GaAs by x-ray diffraction and pointed out the existence of "electron bridges" between neighboring atoms. These interstitial charge densities are consistent with a covalent bond description, common to other diamondlike crystals such as Ge and Si. A subsequent investigation by DeMarco and Weiss[2] indicated that a net transfer of charge from Ga to As was required in order to explain the (200) measured intensity from a single crystal. This result was in contrast with piezoelectric determinations of charge transfer.[3-5] Recently, Attard, Mifsud, Sant, and Sultana[6] determined the charge density distribution of some III-V compounds by Fourier synthesis of x-ray diffraction data for powder samples. Their results indicate a net transfer of charge in a direction opposite to that observed by DeMarco and Weiss. Moreover, Attard showed[7] that DeMarco and Weiss's experimental results could lead to a charge transfer in the opposite direction if Thomas-Fermi-Dirac scattering factors were used.

More recent Fourier syntheses[8] confirm the existence of the electronic bridges observed by Sirota *et al.* but are not consistent with DeMarco and Weiss's results.

The purpose of this paper is to present some experimental data on the (hhh) reflecting powers of a single crystal, including the weak (222) and $(\bar{2}\bar{2}\bar{2})$ reflections, and to use these results in order to gain further information on the electron distribution in GaAs.

II. EXPERIMENTAL

A GaAs single-crystal lamella (0.8 mm thick) was cut and ground parallel to the (111) planes within 6 min of arc. The surfaces were lapped with abrasive powders (SiC 600-800-1200) and etched using Schell's technique[9] in order to remove the disturbed layer and produce etch pits on the Ga[10,11] face. The observed dislocation density was of the order of 2×10^4 cm^2.

A Bond double-crystal spectrometer[12] was used for this experiment with a Si (220) perfect crystal as monochromator. The use of a highly collimated incident beam greatly minimized the contribution of thermal diffuse scattering. Co-$K\alpha$ radiation was used in order to avoid simultaneous diffraction effects which are expected to play a major role in intensity measurements of a weak reflection such as the (222). With a relatively long wavelength ($\lambda = 1.79$ Å) it is possible to find a suitable azimuth around the [111] normal such that undesirable effects due to the tails of "Umweganregung" peaks[13] are avoided. As a proof of this, the (222) integrated intensity was measured in some cases at different azimuths and found constant within the experimental error.

Particular attention was paid to eliminate any contribution from $\lambda/2$ and higher harmonics, which are diffracted as strong reflections when the angle of incidence is set for the (222) reflection of Co-$K\alpha$. A scintillation counter and a single-channel analyzer were used for this purpose.

The incident beam was measured with an accuracy better than 2% by an absorption technique. The (111) and (333) integrated intensities were measured

in addition to the (222) in order to gain some information on crystal perfection. Each (hkl) integrated intensity was measured in at least three different positions on the sample surface and the average values are reported in Table I. In no case were the measured values different by more than 3–4%, which was taken as a sufficient test of homogeneity.

III. COMPARISON WITH THEORY

Given the moderate value of the dislocation density observed by etch pit counting ($N \simeq 2 \times 10^4$), one would expect a behavior intermediate between the perfect- and the mosaic-crystal model. When comparing experimental intensities with theory one has therefore to compute the theoretical values in the two extreme cases of a perfect crystal (dynamical theory) and a mosaic crystal (kinematical theory). For a crystal which does not possess a center of symmetry such as GaAs, it is not possible to use the usual formulas of the dynamical theory.[14] Cole and Stemple[15] gave a treatment of the noncentrosymmetric-crystal leading to a set of formulas very similar to those given by Hirsch and Ramachandran.[14] We found it more convenient, however, to evaluate the integrated intensities directly by numerical integration of Eq. 3–189 from Zachariasen[16] in which no assumption is made on centrosymmetry.

The real parts of the scattering factors, without dispersion corrections, were calculated using tables published by various authors[17–20] as indicated in Table I. The corresponding values for the calculated intensities are presented in the same table in order to show the degree of uncertainty associated with a particular choice of scattering factors.

The anomalous dispersion corrections were evaluated for Co-$K\alpha$ by interpolation of published values[21] for Cu-$K\alpha$, Fe-$K\alpha$, and Cr-$K\alpha$.

Since the Ga and As atomic masses are almost equal, an average Debye parameter $B = 0.906$ Å^2 was adopted.[8]

The monochromator was a perfect crystal. The polarization ratio was therefore evaluated by computing the (220) integrated intensities for the two polarizations separately, using the formulas of dynamical theory.[14] This ratio turned out to be 0.524, which can be compared with 0.783 calculated for a mosaic crystal.

Table I shows that the (111) and ($\overline{111}$) experimental intensities are in good agreement with the perfect-crystal values, whereas for (333) and ($\overline{333}$) the experimental values are intermediate between the two extreme cases. These results indicate that the degree of crystalline perfection is such that the low-order reflections are almost exclusively dynamical whereas for higher orders kinematical effects are more important.

The difference between (111) and ($\overline{111}$) is probably associated with kinematical effects considering the large interval between the dynamical and kinematical theoretical values. This difference is considerably reduced for (333) and ($\overline{333}$). The (222) values will be discussed in Sec. IV.

IV. DISCUSSION

When the origin is set at the point $(\frac{1}{8}, \frac{1}{8}, \frac{1}{8})$ of the cubic crystal cell with As atoms on the corners, the (222) structure factor is given by

$$F_{222} = 4i \ (f_{As} - f_{Ga}) = - F_{\overline{222}},$$

where f_{As} and f_{Ga} are the complex atomic scattering factors.

The above expression shows that, even taking into account the imaginary parts of the structure factors and the consequent failure of Friedel's law, the sym-

TABLE I. Experimental and theoretical values for (hhh) integrated intensities. The calculations were based upon both dynamical and kinematical theories. Different sets of atomic scattering factors were used, corresponding to different choices of atomic wave functions.

(hkl)	(111) (10^5)	($\overline{111}$) (10^5)	(222) (10^7)	($\overline{222}$) (10^7)	(333) (10^5)	($\overline{333}$) (10^5)
Calculated[a]						
perfect	9.48	9.59	2.25	2.25	1.97	1.94
mosaic	42.5	43.0	2.53	2.53	5.12	5.06
Calculated[b]						
perfect	9.49	9.60	2.30	2.30	1.97	1.95
mosaic	42.7	43.2	2.58	2.58	5.13	5.07
Calculated[c]						
perfect	9.27	9.37	3.11	3.11	1.85	1.82
mosaic	40.9	41.4	3.43	3.43	4.64	4.57
Calculated[d]						
perfect	9.32	9.43	2.70	2.70	1.90	1.88
mosaic	41.3	41.8	3.02	3.02	4.85	4.79
Expt	10.0	9.05	4.20	4.71	2.41	2.31

[a]Reference 17.
[b]Reference 18.
[c]Reference 19.
[d]Reference 20.

metry of this lattice is such that the (222) integrated intensity is the same as the $(\bar{2}\bar{2}\bar{2})$. An examination of Table I shows, however, that the (222) and $(\bar{2}\bar{2}\bar{2})$ experimental intensities differ by 11.5%, which is outside the experimental error. Moreover, both values are appreciably higher, 86 and 66%, respectively, than the kinematical value, which is an upper limit. Neglecting for a moment the difference between the two experimental intensities, it is apparent from Table I that the observed differences between experimental and calculated values are well outside the uncertainties associated with the different procedures for calculating the scattering factors.

As to the temperature factor, the only direct experimental determination published in the literature indicates a diffraction Debye temperature $\Theta_M = 247$ °K[22] corresponding to $B = 0.792$ Å^2, which would further decrease the calculated values.

This considerable discrepancy can only be explained by assuming a net charge transfer from Ga to As in the bound state,[23-25] so that the difference between the two scattering factors is increased over the free-atom value.

This is in qualitative agreement with previous results obtained by DeMarco and Weiss.[2] A reinterpretation of these results was proposed by Attard[7] who showed that an opposite conclusion on the direction of the charge transfer could be obtained by using Thomas-Fermi-Dirac[19] scattering factors. Our results based on the (222) and $(\bar{2}\bar{2}\bar{2})$ reflecting powers show, however, that even in this case the observed intensities are strikingly higher than the calculated ones and are in favor of a charge transfer from Ga to As.

This assumption cannot explain, however, the observed difference between (222) and $(\bar{2}\bar{2}\bar{2})$.

According to a model developed by Warekois, Lavine, and Gatos,[26] GaAs single crystals are likely to exhibit different crystal perfection on the (111) and $(\bar{1}\bar{1}\bar{1})$ surfaces of even highly etched samples. There is little hope, however, to invoke such an argument in our case since the two measured integrated intensities are well above the kinematical limit valid for an ideal mosaic crystal.

One is tempted at this point to assume for GaAs a model in which an interstitial charge is placed midway between neighboring atoms in order to take into account the charge pileup due to covalent bonding. Such a model was originally introduced for diamond[27,28] in order to explain the "forbidden" reflection (222), which was subsequently observed also in Ge and Si.[29,30]

If each interstitial charge has a real[31] scattering factor ϵ at the appropriate $(\sin\theta/\lambda)$ value for the (222) reflection, the structure factor of the GaAs crystal cell becomes

$$F'_{222} = F_{222} - 16\epsilon \quad \text{and} \quad F'_{\bar{2}\bar{2}\bar{2}} = -F_{222} - 16\epsilon \ .$$

Clearly, F'_{222} is no longer equal to $F'_{\bar{2}\bar{2}\bar{2}}$. The interstitial charges scatter all in phase as far as (222) is concerned, but a phase difference $\pi/2$ is introduced with respect to the GaAs lattice. The new real term 16ϵ is therefore to be combined with the difference between the imaginary parts of the scattering factors.

Two unknowns ϵ and γ are introduced in the new expression for the structure factor, the latter term being related with a charge transfer from Ga to As:

$$\gamma = \Delta \text{ (bound state)} - \Delta \text{ (free atom)} \ ,$$

where Δ is the difference between the real parts of the scattering factors.

The (222) is a weak reflection for which the difference between the dynamical and kinematical integrated intensities is very small. Since the crystal is not perfect (see previous section) it can be safely assumed that (222) is diffracted kinematically. If the integrated intensities are supposed to be proportional to the squares of the structure factors, a linear system of two simultaneous equations is obtained for ϵ and γ, involving the (222) and $(\bar{2}\bar{2}\bar{2})$ experimental intensities. The result is

$$\epsilon = 0.109, \quad \gamma = 0.425.$$

These values have been corrected for the temperature effect, with the assumption that the valence electrons involved in covalent bonds have the same Debye-Waller factor as the core electrons.[32] The portion of the structure factor due to the interstitial charges amounts to 1.74 (temperature corrected) which is very close to the corresponding value for silicon. The difference between the real parts of the bound-state scattering factors amounts to 1.84 instead of 1.42 for free atoms. Since the $(\sin\theta/\lambda)$ dependence of both ϵ and γ is not known, it is not possible to use these results for a quantitative evaluation of bonding and transfer charges, respectively.

The observed direction for the charge transfer is in agreement with linear-combination-of-atomic-orbitals (LCAO) calculations[33] and with experimental results based on K absorption-edge measurements.[34]

The difference between the (222) and $(\bar{2}\bar{2}\bar{2})$ integrated intensities offers an alternative method for determining the absolute polarity of a (111) face using a characteristic radiation. This feature makes perhaps this method more feasible than those based on the use of much weaker radiations picked up from the continuous spectrum in the vicinity of the absorption edges.

V. CONCLUSIONS

The (hhh) and $(\bar{h}\bar{h}\bar{h})$ integrated reflecting powers of a GaAs single crystal were measured up to the third order using a Co-$K\alpha$ radiation. Particular

care was taken in order to avoid contributions from weakly excited simultaneous reflections. The two (222) and (2̄2̄2̄) integrated intensities are appreciably higher than the calculated value for a mosaic crystal, which is an upper limit. Moreover, the two experimental intensities differ by 11.5%, whereas the theoretical value is the same for both (222) and (2̄2̄2̄).

The fact that both experimental intensities are higher than the theoretical value, based upon free-atom scattering factors, suggests that a net charge transfer occurs from Ga to As, in the opposite direction to that observed with piezoelectric measurements and Fourier synthesis of the charge distribution.

The difference between the (222) and (2̄2̄2̄) experimental intensities is consistent with a model of covalent bonds in which interstitial isolated charges are placed midway between neighboring atoms. This circumstance offers an alternative method for determining the absolute polarity of a (111) face using a characteristic x-ray radiation.

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