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Thermal Vibrations and Bonding in GaAs: an Extended-Face Crystal Study

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Abstract

Accurate X-ray integrated-intensity data collected from an extended-face crystal of GaAs are analysed to provide detailed information on the thermal vibrations of atomic species, including cubic anharmonicity, at room temperature. The values obtained for the thermal parameters are $B_{\text{Ga}} = 0.622 (3) \text{ \AA}^2$, $B_{\text{As}} = 0.483 (5) \text{ \AA}^2$ and $\beta_{\text{GaAs}} = -0.6 (1) \times 10^{-18} \text{ J \AA}^{-3}$ (defined in the text). The inclusion of cubic anharmonic thermal vibrations is shown to be highly significant. In order to interpret the data collected for certain low-angle Bragg reflections for which $h+k+l = 4n+2$ (in particular, 200, 222 and 22 $\bar{2}$), it is necessary to consider bonding effects. It is shown that there is a net transfer of electron charge from gallium to arsenic [$Q = 0.12 (3) e$] and that the inclusion of bonding effects in the least-squares analysis is highly significant. The analysis includes allowance for the extremely severe extinction effects present for such a perfect sample (minimum extinction factor 0.286). The refined value of the mean radius of

perfect-crystal domains is $4.6 (2) \mu\text{m}$. The final fit, for 153 independent Bragg reflections, is excellent, as indicated by the weighted R factor of 0.683% and the goodness-of-fit parameter of 1.083. The results of the least-squares analysis are compared for the cases of relativistic Hartree–Fock, Thomas–Fermi–Dirac and relativistic Dirac–Slater atomic scattering factors, the former being favoured.

Introduction

GaAs is an extremely important semiconductor material that possesses the sphalerite (zinc blende) structure. Knowledge of the way in which the atomic species in GaAs vibrate is important in many areas of research such as studies of diffusion and for predicting band-gap temperature dependence. A survey of the literature shows that reported values of individual Debye–Waller factors for gallium and arsenic in GaAs, both experimental and theoretical, show a large variation (see also Butt, Bashir & Nasir

Khan, 1993). Table 1 lists some of these values, excluding, for the moment, the last line. Some variation is expected depending on whether or not anharmonic thermal vibrations have been considered and on whether or not a correction for thermal diffuse scattering (TDS) has been made in the experimental determinations, but such variations are relatively small in comparison with those displayed in Table 1.

In a recent study on a small spherical crystal of GaAs, Saravanan, Mohanlal & Chandrasekaran (1992) (hereinafter referred to as SMC) obtained information on bonding and cubic anharmonic thermal vibrations at room temperature from accurate X-ray integrated-intensity data. SMC found that the structure-factor magnitudes for the 'quasiforbidden' Bragg reflections of the type $h+k+l=4n+2$, which are *essentially* only nonzero because of the difference between the atomic scattering factors of Ga ($Z=31$) and As ($Z=33$) atoms, were observed to be much larger than the calculated values based on Hartree-Fock free-atom (spherical) scattering factors. While this trend is consistent with the results of De Marco & Weiss (1964) and Colella (1971), and represents the net transfer of electron charge from gallium to arsenic, the magnitude and extent of the effect observed by SMC is rather puzzling. The percentage increase found by them in the observed structure factors over the calculated structure factors for the $h+k+l=4n+2$ reflections is of the order of 100% or more and is not just confined to low-angle reflections but extends over the entire range out to $\sin\theta/\lambda \sim 1 \text{ \AA}^{-1}$, e.g. the value is 206 (11)% for the Mo $K\alpha$ $\bar{8}\bar{6}\bar{4}$ reflection. Bonding effects in such X-ray integrated-intensity data are normally confined to a few low-angle Bragg reflections, the percentage increases observed by De Marco & Weiss (1964) for the Mo $K\alpha$ 200 reflection and by Colella (1971) for the Co $K\alpha$ 222 and $\bar{2}\bar{2}\bar{2}$ reflections being considerably less than those of SMC.

It was therefore decided that an X-ray integrated-intensity data collection for an extended-face crystal of GaAs would be most timely. The use of extended-face crystals, when available, has many advantages, such as elimination of the need for absorption correction of relative intensities and, by virtue of the crystal face intercepting the entire incident beam, higher diffracted intensities (facilitating the measurement of weak reflections). Details of the extended-face crystal technique are given by, for example, Mair, Prager & Barnea (1971*a,b*) and Barnea (1973, 1975). Such a study on GaAs was performed by Barnea, McIntyre & Moss (1974) using 50 independent Mo $K\alpha$ Bragg reflections. In the present study, considerably more data are collected in the hope of obtaining better estimates of refined parameters and for comparison with the data presented by SMC.

Table 1. *Experimental and theoretical values of Debye-Waller factors for GaAs at room temperature*

$B_{\text{Ga}} (\text{\AA}^2)$	$B_{\text{As}} (\text{\AA}^2)$	Comments	Reference
0.20	0.56	X-ray, powder	(1)
0.92	0.92	X-ray, powder	(2)
0.418	0.418	Theoretical	(3)
0.66 (2)	0.48 (2)	X-ray, extended-face single-crystal	(4)
0.411	0.411	Theoretical	(5)
0.73	0.61	X-ray	(6)
0.61	0.50	X-ray, single-crystal	(7)
0.75	0.67	X-ray, extended-face single-crystal	(8)
0.65	0.82	Neutron, single-crystal	(9)
0.637	0.685	Theoretical, shell model	(10)
0.670 (3)	0.470 (2)	X-ray, small spherical single-crystal	(11)
0.622 (3)	0.483 (5)	X-ray, extended-face single-crystal	(12)

References: (1) Sirota (1969); (2) Uno, Okano & Yukino (1970); (3) Vetelino, Gaur & Mitra (1972); (4) Barnea, McIntyre & Moss (1974); (5) Talwar & Agarwal (1974); (6) Bilderback (1975); (7) Bublik & Gorelik (1977); (8) Kyutt (1978); (9) Nielsen, Larsen, Damgaard, Petersen & Weyer (1983); (10) Reid (1983); (11) Saravanan, Mohanlal & Chandrasekaran (1992); (12) this work.

Structure-factor formalism

The cubic zinc blende structure has the space group $F\bar{4}3m$ and the four atoms of one species (here gallium) present in the unit cell are assigned to the special positions 4(*a*), the four atoms of the other species (here arsenic) being assigned to the special positions 4(*c*). With Dawson's (1967) generalized structure-factor formalism (see also McIntyre, Moss & Barnea, 1980), the square of the structure-factor magnitude can be written, with the functional dependence suppressed, as

$$|F|^2 = 16(f'_{c,\text{Ga}}{}^2 + f''_{\text{Ga}}{}^2)T_{c,\text{Ga}}{}^2 + 16(f'_{c,\text{As}}{}^2 + f''_{\text{As}}{}^2)T_{c,\text{As}}{}^2 \\ \pm 32[(f'_{c,\text{Ga}}f'_{c,\text{As}} + f''_{\text{Ga}}f''_{\text{As}})T_{c,\text{Ga}}T_{c,\text{As}} \\ + (f'_{c,\text{Ga}}f''_{\text{As}} - f'_{c,\text{As}}f''_{\text{Ga}})T_{c,\text{Ga}}T_{c,\text{As}}\tau_{a,\text{GaAs}}] \quad (1)$$

for $h+k+l=4n$ (upper sign) and $h+k+l=4n+2$ (lower sign) (n being an integer), and

$$|F|^2 = 16(f'_{c,\text{Ga}}{}^2 + f''_{\text{Ga}}{}^2)T_{c,\text{Ga}}{}^2 + 16(f'_{c,\text{As}}{}^2 + f''_{\text{As}}{}^2)T_{c,\text{As}}{}^2 \\ \pm 32[(f'_{c,\text{Ga}}f'_{c,\text{As}} + f''_{\text{Ga}}f''_{\text{As}})T_{c,\text{Ga}}T_{c,\text{As}}\tau_{a,\text{GaAs}} \\ - (f'_{c,\text{Ga}}f''_{\text{As}} - f'_{c,\text{As}}f''_{\text{Ga}})T_{c,\text{Ga}}T_{c,\text{As}}] \quad (2)$$

for $h+k+l=4n\pm 1$. $f'_{c,X}$ represents the sum of the centrosymmetric component of the atomic scattering factor ($f_{c,X}$) and the real anomalous-dispersion correction (f'_X) for atomic species X . f''_X is the imaginary anomalous-dispersion correction for atomic species X . $T_{c,X}$ is the centrosymmetric component of the temperature factor for atomic species X , given by

$$T_{c,X} = \exp(-B_X S^2/4), \quad (3)$$

where B_X is the Debye-Waller factor and $S = |\mathbf{S}| = 2\sin\theta/\lambda$, θ being the Bragg angle and λ the X-ray wavelength. $\tau_{a,\text{GaAs}}$ is given by

$$\tau_{a,\text{GaAs}} = (T_{a,\text{Ga}}/T_{c,\text{Ga}}) - (T_{a,\text{As}}/T_{c,\text{As}}), \quad (4)$$

where $T_{a,X}$ is the antisymmetric component of the temperature factor for atomic species X , given by

$$T_{a,X} = (B_X/4\pi a)^3 T_{c,X} \beta_X (hkl/k_B T), \quad (5)$$

where a is the lattice parameter, β_X is the cubic anharmonic parameter for atomic species X , k_B is the Boltzmann constant and T is the temperature. In the derivation of (1) and (2), bonding effects have been ignored and terms of order $T_{a,Ga} T_{a,As}$, $T_{a,Ga}^2$ and $T_{a,As}^2$ have been neglected. The temperature-factor expressions were obtained using the one-particle potential (OPP) approach. The classical form of the OPP temperature factor is valid here because GaAs is being studied at room temperature and the value of the Debye temperature, Θ_D , is comparable [264 (2) K, from Butt, Bashir & Nasir Khan (1993)].

Substitution of (5) in (4) gives

$$\tau_{a,GaAs} = -hkl B_{As}^3 \beta_{GaAs} / [(4\pi a)^3 k_B T], \quad (6)$$

where the effective cubic anharmonic parameter (Cooper, Rouse & Fuess, 1973) is given by

$$\beta_{GaAs} = \beta_{As} - (B_{Ga}/B_{As})^3 \beta_{Ga}. \quad (7)$$

In the preceding discussion, we have not considered the possibility of the presence of significant quartic anharmonic thermal vibrations. In fact, refinements were carried out with allowance made for such effects using the expressions appropriate to the $\bar{4}3m$ site symmetry given by Mair, Barnea, Cooper & Rouse (1974) [allowing for a factor of two missing from the denominator of one term – see Moss, McMullan & Koetzle (1980)]. The improvement resulting from the inclusion of quartic anharmonic effects proved, however, to be ‘not significant’ (Hamilton, 1964) and we do not discuss them further.

Experimental

The GaAs sample studied was supplied by American Xtal Technology and was polished, semi-insulating and undoped, with a resistivity of $4.5 \times 10^7 \Omega \text{ cm}$ and an etch-pit density of less than 1000 cm^{-2} . The orientation was nominally $(100) \pm 0.2^\circ$, the thickness was 3 mm and the diameter was approximately 33 mm.

All measurements were made on a computer-controlled Picker four-circle diffractometer with Mo $K\alpha$ radiation at 296 (1) K. The sample face was aligned to be perpendicular to the diffractometer φ axis to within 0.03° using a laser-alignment technique (Moss & Barnea, 1976). Least-squares analysis of Bragg-reflection peak positions (to get the orientation or UB matrix) yielded lattice-parameter values of $a = 5.660$ (1), $b = 5.648$ (2), $c = 5.647$ (2) Å and α

$= \beta = \gamma = 90.00$ (2)°, consistent with a small tetragonal distortion [the average value being 5.652 (1)]. The lattice-parameter value used for calculations was 5.6538 Å (Giesecke & Pfister, 1958). The measured peak positions for the 400 Bragg reflection at $\psi = 0, \pm 90$ and 180° (ψ being the azimuthal angle) yielded a miscut value of 0.03° , *i.e.* the sample is of (100) orientation within error. The absolute polarity of the sample was established by means of several Bijvoet-ratio measurements (see, for example, Mair, Prager & Barnea, 1971*b*; Freeman, Mair & Barnea, 1977) and is demonstrated later in this paper.

The integrated-intensity measurements were all made using $\omega/2\theta$ scans of width $0.62^\circ + 0.67^\circ \tan\theta$ in ω , with a step size of 0.005° in ω . The background was estimated by making stationary counts at the two extremes of the scan range. Each reflection was centred before measurement (with φ held fixed). A reference reflection was measured throughout the data collection and these measurements were used to scale the data (especially in the case of the X-ray generator current being changed, as was necessary to encompass the full diffracted-intensity range). The reference-reflection measurements also served to check on the efficacy of the applied dead-time corrections.

Multiple-diffraction effects are likely to be a problem, especially with Mo $K\alpha$ radiation. This is clearly demonstrated in Fig. 1, which shows (a) a complete ψ scan for the weak 200 reflection and (b) the corresponding simulation of (a) using the computer programs *UMWEG* of Prager (1971) (for peak positions) and *MDDSCRM* of Stevenson (1983) [which provides an approximate intensity calculation and uses the polarization corrections of Caticha-Ellis (1969)]. In an attempt to avoid multiple-diffraction effects, every reflection was measured at six different azimuthal positions (ψ and $\psi + 180^\circ$ for $\psi = 0$ and $\pm 1^\circ$) and the outlying pair of measurements discarded.* The excellent agreement obtained between integrated intensities for equivalent reflections (see next section) is testimony to the adequacy of the treatment of multiple-diffraction effects.

Certain restrictions were placed on χ to ensure that the glancing angle between the incident X-ray beam and the crystal surface was not too low.

Analysis and results

A total of 5058 integrated intensities were measured, not including reference reflections and reflections for which $h + k + l = 4n + 2$, which are discussed later (we

* For some of the higher-angle reflections, these symmetric or near-symmetric positions were not accessible owing to angle restrictions on ω . Consequently, six other azimuthal positions (not paired), sometimes quite asymmetric, were selected in these cases and the two outlying measurements discarded.

initially discuss the refinement of a data set excluding the reflections for which $h+k+l=4n+2$ because these reflections are, in GaAs, very weak and require the inclusion of bonding effects in the analysis. Lorentz polarization and absorption effects* were corrected for at this stage, the latter using $\mu = 328 \text{ cm}^{-1}$.

Extinction effects must be expected to be very severe in the GaAs sample owing to its high degree of perfection. Stevenson (1993) demonstrated the use of an empirical extinction correction that accounted

* For most reflections, it was not strictly necessary to correct for absorption because of the values of ψ chosen (see Mair, Prager & Barnea, 1971*a,b*). However, some high-angle reflections had to be measured at values of ψ for which the $\psi+180^\circ$ position was inaccessible (see previous section).

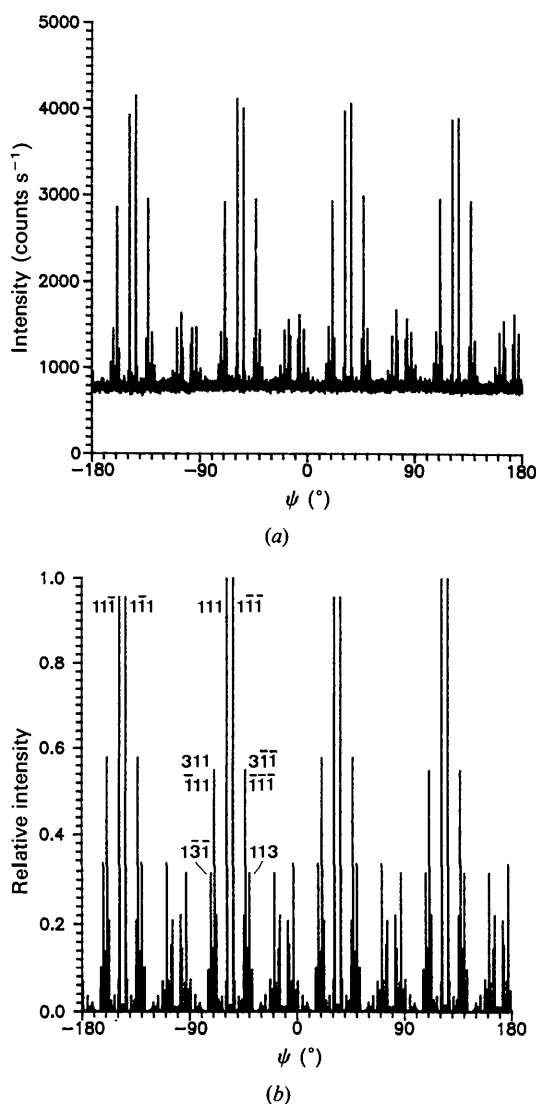


Fig. 1. (a) a complete ψ scan for the weak Mo $K\alpha$ 200 reflection and (b) the corresponding simulation.

for the effect's dependence on the degree of asymmetry involved. In the present work, this ψ dependence of extinction was corrected for, using the same formulae in such a way that the contribution of extinction to a given measurement should then be that corresponding to the symmetric position ($\psi=0$ or 180°). The correction for extinction was then included in the least-squares refinement in the normal manner. Since the most extinguished reflections are at low angles where measurements were made very close to or at the symmetric positions, this correction is not expected to be large. Inclusion of this correction did, however, result in slightly better agreement between equivalent reflections and a non-trivial reduction of the weighted R factor and goodness-of-fit parameter.

Averaging over azimuthal positions yielded a total of 843 integrated intensities and averaging over equivalent reflections left data for 146 independent Bragg reflections. The agreement between equivalent reflections was excellent, the average deviation in integrated intensity of a reflection from the mean value for its equivalent-reflection group being 0.75% and the average coefficient of variation [σ_{pop}/I , where σ_{pop} is the standard deviation for the integrated intensity I from population statistics (agreement between equivalent reflections)] being 0.0092.

TDS contributions to measured integrated intensities, although fairly small for GaAs (which is quite 'hard' in an elastic constant sense), still have a significant effect on refined temperature-parameter values (Stevenson & Harada, 1983). Anisotropic one-phonon (acoustic) TDS effects were corrected for with the program of Sakata, Stevenson & Harada (1983) and the elastic constants of Cottam & Saunders (1973).

The quantity minimized in the least-squares refinement of data was

$$M = \sum_{i=1}^{146} w_i (|F_{oi}| - |F_{ci}|)^2, \quad (8)$$

where F_{oi} and F_{ci} are the observed and calculated structure factors, respectively, for the i th observation and w_i is the weight given to $(|F_{oi}| - |F_{ci}|)$. It should be pointed out that $|F_{oi}|$ and $|F_{ci}|$ include extinction effects, i.e. $|F_{ci}| = |F|y^{1/2}$, where y is the calculated extinction factor. The variances ($w_i = \sigma_i^{-2}$) contain contributions from counting statistics and population statistics and an estimated error in the extinction corrections of 3% of $(1-y)$. In calculating structure-factor magnitudes, we used the relativistic Hartree-Fock (spherical) atomic scattering factors of Doyle & Turner (1968), the anomalous scattering factors of Cromer & Liberman (1970), and the anomalous-scattering-factor corrections of Kissel & Pratt (1990). The parameters refined were: B_{Ga} , B_{As} ,

a scale factor s , β_{GaAs} and the mean radius of the perfect-crystal domains r (for extinction correction).

The extinction correction employed here is essentially that of Zachariasen (1967). In the present study, we are most interested in thermal-vibration effects, which are most noticeable at high angles where extinction is small, and bonding effects in a few very weak $4n+2$ reflections where extinction is again small. Stevenson & Barnea's (1983*a,b*) investigation of extinction effects in an extended-face crystal of ZnSe suggest that an appropriate form of Zachariasen's (1967) effective domain radius r^* is

$$r^* = r \sin 2\theta, \quad (9)$$

where the $\sin 2\theta$ factor is a correction suggested by Becker & Coppens (1974). Given certain assumptions (in regard to the nature of secondary-extinction effects), it can be shown that (9) is appropriate even in the case of severe primary-extinction effects, as are likely for the GaAs sample (see also Pryor & Sanger, 1970). A least-squares refinement of all 146 independent Bragg reflections including allowance for extinction [(9)] and cubic anharmonic thermal vibrations resulted in the parameter values given in Table 2. We note first the excellent fit and the appropriateness of the weighting scheme, as indicated by the values of the weighted R factor and the goodness-of-fit parameter GFIT. The values of the two Debye-Waller factors are in good accord with those of SMC and of Barnea, McIntyre & Moss (1974) and Bublik & Gorelik (1977) (see Table 1).† The value of r is quite large (*cf.* Table 4 of Stevenson & Barnea, 1983*a*), as expected for such a perfect sample. We should note three points with regard to the extinction correction. First, the value of R for a refinement identical except for the noninclusion of the ψ dependence of extinction, was 0.697%, *i.e.* the fit was somewhat worse. Secondly, the value of R for a refinement in which $r^* = r$, rather than using (9), was 1.026%, clearly endorsing our use of (9) and consistent with the findings of Stevenson & Barnea (1983*b*) for the extended-face crystal of ZnSe [McIntyre, Moss & Barnea's (1980) data]. Finally, since it is one of our main aims to obtain accurate values for the thermal parameters, we carried out least-squares refinements

† We should point out at this stage that a refinement carried out from different starting values for the parameters yielded the following final parameter values: $B_{\text{Ga}} = 0.47$ (1) \AA^2 , $B_{\text{As}} = 0.67$ (1) \AA^2 , $s = 5.35$ (3), $r = 5.2$ (2) μm and $\beta_{\text{GaAs}} = -0.22$ (4) $\times 10^{-18} \text{ J \AA}^{-3}$, with $R = 0.665\%$ and GFIT = 1.059. On the basis of the two R -factor values, the fits are essentially indistinguishable, *i.e.* we cannot state that one is significantly better than the other. The most obvious difference between the two refined-parameter sets is that the values of B_{Ga} and B_{As} are almost interchanged [a similar effect has been observed for the wurtzite-type structure $\beta\text{-AgI}$ – see, for example, Piltz & Barnea (1987)]. Our decision on which refined-parameter set to accept is justified later in the paper in the context of another refinement.

Table 2. Refined parameter values from least-squares analysis of 146 independent Bragg reflections (anharmonic model)

Parameter	Value
B_{Ga}	0.63 (1) \AA^2
B_{As}	0.48 (1) \AA^2
s	5.21 (3)
r	4.6 (2) μm
β_{GaAs}	-0.6 (1) $\times 10^{-18} \text{ J \AA}^{-3}$
R	0.668%
GFIT	1.069

Table 3. Data for Bragg reflections with $h + k + l = 4n + 2$, based on the refined parameter values in Table 2

h	k	l	$ F_{oi} $	$ F_{ci} $	y_i	$\sigma_i/ F_{oi} $	α_i	B_{oi} (%)	B_{ci} (%)
2	0	0	6.62	5.49	0.995	0.042	0.001		
2	2	2	6.10	5.46	0.995	0.019	0.003		
2	2	-2	5.28	5.48	0.995	0.008	0.003	28.6	-0.5
4	2	0	6.44	6.48	0.994	0.012	0.006		
4	4	2	6.92	7.20	0.993	0.012	0.011		
4	4	-2	6.99	7.22	0.993	0.011	0.011	-2.0	-0.5
6	0	0	7.70	7.21	0.993	0.033	0.011		

with various numbers of the most extinguished reflections removed and found that the changes in all parameter values were considerably less than the original e.s.d.'s (the new e.s.d.'s were, in general, somewhat larger). For example, this was true when all reflections with $y < 0.7$ (of which there were 31) were removed from the refinement.

The value of β_{GaAs} in Table 2 accords well with values obtained for other zinc blende materials (see Table 6 of Stevenson, Gao, Pain & Wieluński, 1991). Although the effect of anharmonicity is not very large for GaAs, in terms of the change in integrated intensity, it is still significant. In order to make such a statement more quantitative: the value of R for a refinement in which β_{GaAs} was constrained to be zero (*i.e.* a harmonic model) was 0.730% (other parameter values were unchanged, as were e.s.d.'s). Applications of Hamilton's (1965) R -factor significance tests shows that the improvement resulting from the inclusion of anharmonicity is 'highly significant' (Hamilton, 1964). An attempt to refine both cubic anharmonic parameters separately was unsuccessful in that the resulting R value was 0.664%, which does not represent a significant improvement in the fit. The two anharmonic parameters were found to have a severe correlation* (correlation coefficient 0.93). This experience is in accord with those of other authors [see, for example, Moss, McMullan & Koetzle (1980) for ZnS].

* On the subject of correlations, we should point out that a severe correlation also occurs between s and r . This correlation is not unexpected (see, for example, Lander & Mueller, 1970; Stevens & Coppens, 1975).

Barnea, McIntyre & Moss (1974) obtained a value for a cubic anharmonic parameter ($=|\beta_{\text{Ga}}| = |\beta_{\text{As}}|$) of $0.22(15) \times 10^{-18} \text{ J } \text{Å}^{-3}$. In order to convert this value to one that we can compare directly with our β_{GaAs} value, we assume that $\beta_{\text{Ga}} = -\beta_{\text{As}}$ (see Moss, McMullan & Koetzle, 1980). This approximation reflects the fact that the tetrahedral arrangements of the four nearest-neighbour atoms surrounding each species are inversely related, *i.e.* β_{Ga} and β_{As} must have opposite signs if the atoms are to vibrate away from their nearest neighbours. We further assume that β_{Ga} is positive so that β_{GaAs} is negative [all known values of this effective cubic anharmonic parameter for zinc blende structures are indeed negative – see Table 6 of Stevenson, Gao, Pain & Wieluński (1991)]. Barnea, McIntyre & Moss's (1974) cubic anharmonic parameter value thus becomes $-0.8(7) \times 10^{-18} \text{ J } \text{Å}^{-3}$. Clearly, the size of the latter e.s.d. makes comparison rather meaningless but the values agree. SMC have quoted individual values of β_{Ga} and β_{As} from their least-squares analysis, which yield a value for β_{GaAs} of $-0.2 \times 10^{-18} \text{ J } \text{Å}^{-3}$. Unfortunately, the e.s.d. for this value is much larger than the magnitude of the value itself (by more than an order of magnitude). This situation stems from the fact that both of SMC's anharmonic parameter values are positive (*cf.* above discussion) and so the expression for β_{GaAs} [(7)] becomes a difference between two relatively close positive numbers whose magnitude is large compared with their difference. SMC do not discuss any other anharmonic models. In a very recent paper, Pietsch, Paschke & Eichhorn (1993) have determined an accurate value for the GaAs cubic anharmonic parameter by means of Bijvoet-ratio measurements for the weak $666/66\bar{6}$ reflections using different wavelengths (near the GaAs *K*-absorption edges) at a synchrotron source. Their quoted value (of β_{As} , with $\beta_{\text{Ga}} = -\beta_{\text{As}}$ assumed) is $-1.75(15) \times 10^{-17} \text{ J } \text{Å}^{-3}$, which we believe should actually read $-1.75(15) \times 10^{-19} \text{ J } \text{Å}^{-3}$ [the germanium β values of Roberto, Batterman & Keating (1974), quoted for comparison in Table 1 of Pietsch, Paschke & Eichhorn (1993) are certainly of this order]. Use of this latter value in (7) yields a value for β_{GaAs} of $-0.55(5) \times 10^{-18} \text{ J } \text{Å}^{-3}$, in excellent agreement with the present value.

In order to make a direct comparison between the least-squares fits of the present work and of SMC, the values of the residual index for this work as defined by SMC have been calculated. For the harmonic model, the value is 0.761% (0.580% if weights are included); for the anharmonic model, it is 0.736% (0.538% if weights are included). These values are considerably less than those of SMC and the ratio of residual indices for harmonic to anharmonic models is 1.034 (1.078 if weights are

included), indicating a much greater significance of anharmonicity in the present analysis than was reported by SMC, where the ratio of residual indices was only 1.007. The author does not understand the claim made by SMC indicating '... a significance level <0.005...', unless they have based their number of degrees of freedom on the number of reflections before averaging equivalents.

Inclusion of $h+k+l=4n+2$ reflections

Table 3 lists observed and calculated structure-factor magnitudes for seven independent $4n+2$ Bragg reflections. These data were collected in experimental conditions identical to those already described. The calculated structure-factor magnitudes are based on the parameter values listed in Table 2. The observed and calculated structure-factor magnitudes include extinction effects and should be divided by $\gamma^{1/2}$ if the corresponding kinematic quantity is required. Table 3 also includes the extinction factors (which are, of course, very close to unity here), $\sigma_i/|F_{oi}|$, TDS correction factors (α 's) and the observed and calculated Bijvoet ratios [see McIntyre, Moss & Barnea (1980) for detailed discussion of Bijvoet ratios in materials with the zinc blende structure].

The most obvious discrepancies in Table 3 are that the observed structure-factor magnitude for the 200 reflection is considerably [20 (5)%] larger than the calculated value and that the observed Bijvoet-ratio value for the $222/22\bar{2}$ reflections [29 (4)%] is very different from the calculated value (the relatively large e.s.d.'s reflecting the difficulty of such measurements). The agreement between experiment and theory is quite reasonable for the other reflections, given the difficulties associated with the measurement of such weak reflections. The discrepancies noted above are consistent with the findings of De Marco & Weiss (1964), who reported a 16 (3)% increase of the 200 structure-factor magnitude relative to the calculated value, and with the $222/22\bar{2}$ Bijvoet ratio reported by Barnea, McIntyre & Moss (1974) (17%). Clearly, there is considerable disagreement with the results reported by SMC for the $4n+2$ reflections (see also *Introduction*), where the observed structure-factor magnitudes were of the order of 100% or more larger than the calculated values for all $4n+2$ reflections measured, and the $222/22\bar{2}$ Bijvoet ratio was $-5(6)\%$. The results presented in Table 3 are consistent with the presence of bonding-electron-density redistribution effects in the GaAs sample and more specifically with a net transfer of electron charge from gallium to arsenic [see, for example, Walter & Cohen (1971) and later discussion].

The Bijvoet ratios for reflections with $h+k+l=4n+2$ (or $4n$) are zero in the absence of anharmonic

thermal vibrations and bonding effects (see McIntyre, Moss & Barnea, 1980). In the presence of cubic anharmonic thermal vibrations alone, the $222/22\bar{2}$ GaAs Bijvoet ratio is expected to be very slightly negative for Mo $K\alpha$ radiation. The measured value in Table 3 is thus a very significant manifestation of the presence of bonding effects. The weighted R factor for the full set of 153 independent Bragg reflections, including those with $h+k+l=4n+2$, increases to 0.831% (from 0.668%), using the parameter values in Table 2. Moss (1977) has derived the appropriate expressions for the atomic scattering factor, reflecting the symmetry of the sites for the zinc blende structure. There is a term, which is added to the free-atom (spherical) scattering factor, corresponding to a spherical expansion or contraction of the bonded atom relative to an isolated atom. There is also an expression for the antisymmetric component of the atomic scattering factor, corresponding to nearest-neighbour bonding. The inclusion of these expressions introduces four bonding parameters: α_0 and C_0 (both zeroth order) and α_3 and C_3 (both third order). A least-squares refinement of the full data set was carried out including these four bonding parameters. The values of α_0 and α_3 were assumed to be the same for the two atomic species and the values of C_0 and C_3 were assumed to be equal in magnitude for the two atomic species but opposite in sign (see Moss, 1977). These parameters were initially set to the values used by Moss (1977) for the analysis of integrated-intensity data from the isoelectronic zinc blende compound ZnSe. A severe correlation between α_3 and C_3 (correlation coefficient 0.99) precluded their simultaneous refinement. Consequently, α_3 was fixed at the ZnSe value (3.0 \AA^{-1}). The resulting refined parameter values are given in Table 4 (if the value at which α_3 is fixed is changed, the other refined parameter values remain essentially unchanged, except, as expected, for C_3).

The values of B_{Ga} , B_{As} (also listed in Table 1), β_{GaAs} , s and r in Table 4 have not changed significantly from those in Table 2, although the e.s.d.'s for B_{Ga} and B_{As} are considerably reduced in Table 4. In the earlier anharmonic refinement of 146 independent Bragg reflections, we mentioned an ambiguity involving two refined parameter sets, the most obvious difference being the interchange (essentially) of the values of B_{Ga} and B_{As} . The question as to whether we expect $B_{\text{Ga}} > B_{\text{As}}$ or $B_{\text{Ga}} < B_{\text{As}}$ is not easily answered. Simplistically, we may postulate that, since arsenic has the greater mass, $B_{\text{Ga}} > B_{\text{As}}$. However, the difference in atomic mass here is rather small and there are in any event many counter examples [see, for example, Keffer, Hayes & Bienenstock (1968) for PbTe]. Huiszoon & Groenewegen (1972) and Scheringer (1973) have discussed possible conditions for which the heavier

Table 4. Refined parameter values from least-squares analysis of 153 independent Bragg reflections (anharmonic model including bonding effects)

The values of C_0 and C_3 quoted are for gallium, the values for arsenic being constrained to have equal magnitude and opposite sign.

Parameter	Value
B_{Ga}	0.622 (3) \AA^2
B_{As}	0.483 (5) \AA^2
s	5.22 (3)
r	4.6 (2) μm
β_{GaAs}	$-0.6 (1) \times 10^{-18} \text{ J \AA}^{-3}$
α_0	4.0 (3) \AA^{-1}
C_0	-0.05 (2)
C_3	1.6 (3)
R	0.683%
GFIT	1.083

atomic species might have the larger B value, the former concluding that it might happen when $T > \Theta_D$; the latter that it is more likely to occur for large unit cells and when the atomic masses are close. In the present case, T is comparable with Θ_D and, although the atomic masses are quite close, the unit cell is not particularly large. It is thus difficult to make a prediction for GaAs. However, for the refinement of 153 independent Bragg reflections just mentioned (and including bonding effects), the ambiguity is resolved, *i.e.* even if the starting values for the parameters are set to those mentioned in the earlier footnote (with $B_{\text{Ga}} < B_{\text{As}}$), the least-squares refinement results in the parameter values given in Table 4. Fig. 2 shows R -factor maps corresponding to (a) the earlier refinement of 146 independent Bragg reflections including cubic anharmonicity but not bonding effects and (b) the refinement of 153 independent Bragg reflections including cubic anharmonicity and bonding effects. These maps were calculated by carrying out least-squares refinements point by point for fixed values of B_{Ga} and B_{As} . For Fig. 2(b), the bonding parameters were all held fixed at the values given in Table 4 (and $\alpha_3 = 3.0 \text{ \AA}^{-1}$), *i.e.* only s , r and β_{GaAs} were refined in calculating Figs. 2(a) and (b). In Fig. 2(a), there are clearly two distinct minima [*cf.* Fig. 1 of Piltz & Barnea (1987) for β -AgI] of very nearly equal depth, the results in Table 2 corresponding to the solid diamond and the results mentioned in the earlier footnote to the solid triangle. Fig. 2(b) quite clearly has only one minimum, marked by the solid diamond and corresponding to the results in Table 4. The open triangle in Fig. 2(b) marks the position of the minimum mentioned in the earlier footnote. The R -factor map obtained if α_0 , C_0 and C_3 are also allowed to vary has more structure, this being attributed to the greater number of refined parameters involved (six instead of three) and their interactions. This R -factor map does possess the second minimum (with $B_{\text{Ga}} <$

B_{As}), but it is very much shallower than the minimum with $B_{Ga} > B_{As}$. Experiences with *false minima* are not uncommon (see, for example, Donohue & Goodman, 1967) but the present situation with GaAs serves as a timely reminder. While R -factor maps such as in Fig. 2 are quite demanding of computer time, refinements should at least be carried out from a number of different sets of starting values for refined parameters.

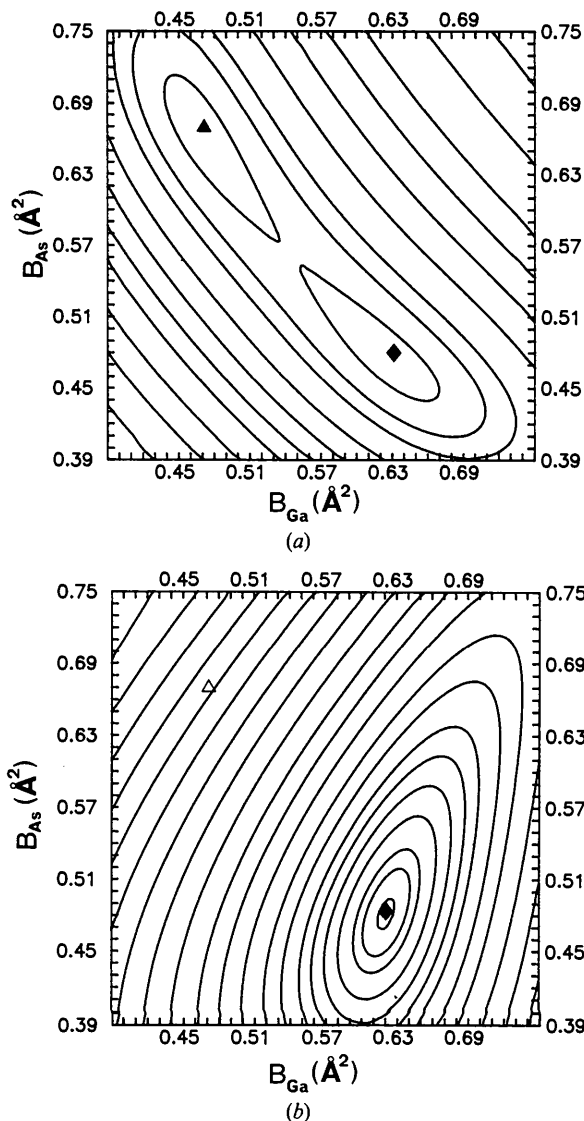


Fig. 2. R -factor maps corresponding to (a) refinement of 146 independent reflections including cubic anharmonicity but not bonding effects and (b) refinement of 153 independent reflections including cubic anharmonicity and bonding effects. The contour levels are 0.7, 0.8, 0.9, 1.1, 1.3, 1.5, 1.7, 2.0, 2.3 and 2.7% for (a) and (b) and, additionally, 3.1, 3.5, 4.0, 4.5, 5.0, 5.5, 6.0, 6.5, 7.0, 7.5 and 8.0% for (b). The positions of the symbols are described in the text.

The resolution of the ambiguity reflected in Fig. 2(a), as shown in Fig. 2(b), is directly attributable to the inclusion of the 'quasiforbidden' $4n+2$ reflections in the refinement and the associated allowance for bonding effects in the analysis. The fact that the structure-factor magnitudes for these reflections are *essentially* only nonzero because of the difference between the gallium and arsenic atomic scattering factors makes their inclusion in the refinement extremely important. The significant reduction of the e.s.d.'s for B_{Ga} and B_{As} (compare results in Tables 2 and 4; the correlation coefficient between B_{Ga} and B_{As} decreases from 0.82 to 0.45) is also a manifestation of the above-mentioned improvement.

The values of B_{Ga} and B_{As} result in a value for the mass-weighted average, \bar{B} , of 0.550 (4) \AA^2 and a value for Θ_D of 292 (2) K (*cf.* Butt, Bashir & Nasir Khan, 1993). Stevenson & Harada (1983) derived the following approximation for Debye-Waller factors:

$$B_{lm} = 8k_B T \langle (A^{-1})_{lm} \rangle q'_{ZB} \ln 2, \quad (10)$$

where $\langle (A^{-1})_{lm} \rangle$ is the average value of an element of a 3×3 symmetric tensor determined from the elastic constants and the direction cosines of the wave vector [A is Christoffel's elasticity matrix – see, for example, Cady (1964)], and q'_{ZB} is the radius of a sphere of equivalent volume to an extended* Brillouin zone. There are two methods of evaluating $\langle (A^{-1})_{lm} \rangle$ (see Stevenson, 1983). The first method (I) is to restrict the waves considered to those travelling in certain directions (see, for example, Harada & Pedersen, 1968; Hewat, 1972); the second and more accurate method (II) is to evaluate the resulting surface integral numerically (see, for example, Sakata & Harada, 1976). Stevenson (1983) has compared these two methods for a number of materials with a range of softnesses (as indicated by elastic constants), including GaAs. In the case of a material as 'hard' as GaAs, there is little difference between the two methods. In cases where method I can be used, the values of the elements of A^{-1} should in general be calculated directly and averaged over the directions considered, rather than any general formulae being relied on, as these are quite cumbersome in all but very specific cases, for example:

$$\langle (A^{-1})_{11} \rangle = p(5, -1) / [p(3, 0)p(1, -1)], \quad (11)$$

for cubic materials that satisfy the isotropy condition

* The first Brillouin zone is extended to the second or higher zone, depending on the number of atoms per primitive unit cell, to include the contribution of optic modes. In the present case of a face-centred cubic lattice, the primitive-cell volume is $a^3/4$ and the volume of the first Brillouin zone is $32\pi^3/a^3$. Since there are two atoms per primitive unit cell, the volume of the extended Brillouin zone becomes twice that of the original zone and $q'_{ZB} = 2(6\pi^2)^{1/3}/a$.

(where the elastic constants C_{ij} are related by $2C_{44} = C_{11} - C_{12}$) and

$$\langle(A^{-1})_{11}\rangle = \frac{1}{13} \left[\frac{4}{p(0,1)} + \frac{13}{p(1,0)} + \frac{8p(1,1)}{p(1,-1)p(1,3)} - \frac{24p(0,1)}{p(1,0)p(1,6)} \right], \quad (12)$$

for cubic materials that satisfy the Cauchy relation ($C_{12} = C_{44}$), where

$$p(\varepsilon, \eta) = \varepsilon C_{11} + \eta C_{12}. \quad (13)$$

For GaAs, $C_{12}/C_{44} = 0.909$ and so the Cauchy relation is approximately satisfied and (12) yields $\langle(A^{-1})_{11}\rangle = 1.81 \times 10^{19} \text{ \AA}^3 \text{ J}^{-1}$, in excellent agreement with Stevenson's (1983) values. Equation (10) thus yields a value for B_{11} of 0.57 \AA^2 , in excellent agreement with the experimental value of \bar{B} .

The ratio of R factors without (0.804%) and with (0.683%) the inclusion of bonding effects is 1.177, indicating that the improvement resulting from the inclusion of bonding effects is 'highly significant' (Hamilton, 1964). Table 5 lists the data for all 153 independent Bragg reflections corresponding to this refinement. The calculated *kinematic* structure-factor magnitudes vary between 185.4 (220 reflection) and 5.3 (22 $\bar{2}$ reflection). We note that the extinction effects are very severe at low angles and the lowest-angle reflections are overcorrected, as was the case for ZnSe (Stevenson & Barnea, 1983*b*). The weighting scheme ensures that the importance of such reflections in the least-squares analysis is downgraded. The observed and calculated Bijvoet ratios are in excellent agreement and confirm the assignment of absolute polarity. (The average e.s.d. for the observed Bijvoet ratios is 1.6%.) The observed and calculated 200 structure-factor magnitudes and 222/22 $\bar{2}$ Bijvoet ratios are now in excellent agreement and there has been no significant deterioration of the agreement for any other data. It should also be pointed out that non-symmetry-related reflections occurring at the same Bragg angle can have different structure-factor magnitudes in the presence of significant anharmonic thermal vibrations and/or bonding effects (see, for example, the 997 and 11,9,3 reflections in Table 5).

Fig. 3 shows the dependence on β_{GaAs} of calculated Bijvoet ratios for Mo $K\alpha$ 666/66 $\bar{6}$, 886/88 $\bar{6}$ and 10,8,8/10,8, $\bar{8}$ reflections (all having $h+k+l = 4n+2$). The calculations have, justifiably, assumed that bonding effects are negligible for such reflections. The calculated values in Fig. 3 corresponding to the refined value of β_{GaAs} are indicated by asterisks and all Bijvoet ratios are, as expected, zero for $\beta_{\text{GaAs}} = 0$. These three Bijvoet ratios (and

Table 5. Data for the full set of 153 independent GaAs Bragg reflections

The analysis includes cubic anharmonic thermal vibrations and bonding effects.

h	k	l	$ F_{o1} $	$ F_{c1} $	y_i	$\sigma_i/ F_{o1} $	α_i	$B_{oi}(\%)$	$B_{ci}(\%)$
1	1	1	93.43	90.19	0.325	0.031	0.001		
1	1	-1	92.53	89.68	0.328	0.031	0.001	1.9	1.1
2	2	0	100.81	99.18	0.286	0.037	0.002		
3	1	1	79.29	78.14	0.421	0.023	0.003		
3	1	-1	80.18	78.77	0.416	0.023	0.003	-2.2	-1.6
4	0	0	90.15	90.57	0.345	0.030	0.004		
3	3	1	72.06	71.99	0.483	0.017	0.005		
3	3	-1	71.17	71.36	0.489	0.017	0.005	2.5	1.8
4	2	2	84.74	83.52	0.402	0.024	0.007		
4	2	-2	84.09	83.52	0.402	0.024	0.007	1.5	0.0
3	3	3	64.27	65.15	0.553	0.013	0.008		
3	3	-3	64.86	65.77	0.547	0.014	0.008	-1.8	-1.9
5	1	1	65.27	65.85	0.547	0.014	0.008		
5	1	-1	64.20	65.22	0.552	0.013	0.008	3.3	1.9
4	4	0	77.24	77.29	0.455	0.021	0.010		
5	3	1	59.36	59.81	0.608	0.011	0.011		
5	3	-1	60.24	60.42	0.603	0.011	0.011	-2.9	-2.0
6	2	0	72.05	71.64	0.505	0.016	0.013		
5	3	3	55.32	55.53	0.651	0.010	0.014		
5	3	-3	54.37	54.92	0.657	0.010	0.014	3.5	2.2
4	4	4	66.83	66.46	0.550	0.013	0.016		
4	4	-4	66.87	66.46	0.550	0.013	0.016	-0.1	0.0
5	5	1	51.42	51.10	0.693	0.007	0.017		
5	5	-1	50.47	50.50	0.698	0.007	0.017	3.7	2.4
7	1	1	50.31	50.52	0.698	0.007	0.017		
7	1	-1	51.09	51.12	0.692	0.008	0.017	-3.1	-2.4
6	4	2	62.06	61.71	0.590	0.012	0.019		
6	4	-2	62.06	61.71	0.590	0.012	0.019	0.0	0.0
5	5	3	46.74	46.57	0.733	0.006	0.021		
5	5	-3	47.66	47.18	0.727	0.007	0.021	-3.9	-2.6
7	3	1	47.41	47.12	0.728	0.007	0.021		
7	3	-1	46.57	46.50	0.733	0.006	0.021	3.6	2.6
8	0	0	57.21	57.37	0.626	0.011	0.023		
7	3	3	43.07	42.97	0.762	0.006	0.024		
7	3	-3	43.87	43.60	0.757	0.006	0.024	-3.7	-2.9
6	6	0	54.56	53.43	0.658	0.009	0.026		
8	2	2	53.58	53.43	0.658	0.009	0.026		
8	2	-2	53.46	53.43	0.658	0.008	0.026	0.4	0.0
7	5	1	39.75	39.74	0.788	0.005	0.028		
7	5	-1	40.59	40.39	0.782	0.005	0.028	-4.2	-3.2
5	5	5	40.42	40.28	0.783	0.005	0.028		
5	5	-5	39.49	39.63	0.789	0.005	0.028	4.6	3.2
8	4	0	49.94	49.88	0.686	0.008	0.030		
7	5	3	37.73	37.45	0.804	0.005	0.031		
7	5	-3	36.83	36.78	0.810	0.005	0.031	4.9	3.6
9	1	1	37.65	37.51	0.803	0.006	0.031		
9	1	-1	36.85	36.85	0.809	0.005	0.031	4.3	3.6
6	6	4	46.66	46.67	0.711	0.007	0.033		
6	6	-4	46.74	46.67	0.711	0.007	0.033	-0.4	0.0
9	3	1	34.19	34.32	0.828	0.005	0.035		
9	3	-1	35.10	35.00	0.822	0.005	0.035	-5.3	-3.9
8	4	4	44.46	43.80	0.734	0.006	0.037		
8	4	-4	44.55	43.79	0.734	0.006	0.037	-0.4	0.0
7	5	5	32.10	32.14	0.843	0.005	0.038		
7	5	-5	32.92	32.83	0.837	0.005	0.038	-5.0	-4.3
7	7	1	32.81	32.70	0.838	0.005	0.038		
7	7	-1	31.93	32.00	0.845	0.005	0.038	5.4	4.3
9	3	3	32.39	32.68	0.839	0.005	0.038		
9	3	-3	31.44	31.98	0.845	0.005	0.038	5.9	4.4
8	6	2	40.93	41.22	0.755	0.006	0.041		
8	6	-2	40.94	41.21	0.755	0.006	0.041	0.0	0.0
10	2	0	40.92	41.21	0.755	0.006	0.041		
7	7	3	29.84	30.09	0.859	0.005	0.042		
7	7	-3	30.77	30.80	0.852	0.005	0.042	-6.2	-4.7
9	5	1	30.71	30.69	0.853	0.005	0.042		
9	5	-1	29.89	29.97	0.859	0.005	0.042	5.4	4.8
9	5	3	28.15	28.26	0.872	0.005	0.046		
9	5	-3	28.94	28.99	0.866	0.005	0.046	-5.6	-5.1
10	4	2	36.44	36.80	0.793	0.006	0.048		
10	4	-2	36.40	36.80	0.793	0.006	0.048	0.2	0.0

Table 5 (cont.)

<i>h</i>	<i>k</i>	<i>l</i>	<i>F_{oi}</i>	<i>F_{ci}</i>	<i>y_i</i>	$\sigma_i/ F_{oi} $	α_i	<i>B_{oi}</i> (%)	<i>B_{ci}</i> (%)
7	7	5	27.29	27.17	0.880	0.005	0.050		
7	7	-5	26.45	26.42	0.887	0.005	0.050	6.3	5.6
11	1	1	26.52	26.55	0.885	0.006	0.050		
11	1	-1	27.31	27.30	0.879	0.006	0.050	-5.8	-5.6
8	8	0	35.49	34.90	0.811	0.005	0.052		
9	5	5	25.82	25.72	0.892	0.005	0.053		
9	5	-5	24.99	24.95	0.898	0.005	0.053	6.5	6.1
9	7	1	24.94	25.10	0.897	0.005	0.053		
9	7	-1	25.87	25.86	0.891	0.006	0.053	-7.3	-6.0
11	3	1	25.79	25.82	0.891	0.005	0.053		
11	3	-1	25.04	25.05	0.897	0.006	0.053	5.9	6.0
8	6	6	32.87	33.17	0.828	0.005	0.056		
8	6	-6	32.92	33.16	0.828	0.005	0.056	-0.3	0.0
10	6	0	32.80	33.17	0.828	0.005	0.056		
9	7	3	24.30	24.41	0.903	0.005	0.057		
9	7	-3	23.50	23.63	0.909	0.005	0.057	6.7	6.5
11	3	3	23.76	23.77	0.908	0.006	0.057		
11	3	-3	24.46	24.54	0.902	0.006	0.057	-5.8	-6.4
8	8	4	31.49	31.58	0.845	0.005	0.060		
8	8	-4	31.52	31.57	0.845	0.005	0.060	-0.2	0.0
12	0	0	32.12	31.58	0.845	0.005	0.060		
11	5	1	22.56	22.52	0.918	0.005	0.061		
11	5	-1	23.38	23.30	0.913	0.005	0.061	-7.1	-6.8
7	7	7	22.71	22.66	0.917	0.005	0.061		
7	7	-7	23.64	23.43	0.912	0.005	0.061	-8.0	-6.7
10	6	4	29.94	30.11	0.860	0.005	0.063		
10	6	-4	29.92	30.10	0.860	0.005	0.063	0.1	0.0
12	2	2	29.79	30.10	0.860	0.005	0.063		
12	2	-2	29.78	30.10	0.860	0.005	0.063	0.1	0.0
9	7	5	21.46	21.50	0.927	0.005	0.065		
9	7	-5	22.36	22.28	0.921	0.005	0.065	-8.3	-7.1
11	5	3	22.20	22.07	0.923	0.005	0.065		
11	5	-3	21.34	21.28	0.928	0.005	0.065	7.9	7.2
9	9	1	21.27	21.06	0.931	0.006	0.069		
9	9	-1	20.39	20.28	0.936	0.008	0.069	8.5	7.6
10	8	2	27.50	27.45	0.888	0.005	0.071		
10	8	-2	27.49	27.44	0.888	0.005	0.071	0.1	0.0
9	9	3	19.43	19.44	0.943	0.008	0.073		
9	9	-3	20.30	20.21	0.938	0.008	0.073	-8.8	-7.8
11	5	5	19.50	19.45	0.943	0.008	0.073		
11	5	-5	20.34	20.22	0.938	0.008	0.073	-8.4	-7.8
11	7	1	20.21	20.08	0.939	0.008	0.073		
11	7	-1	19.34	19.30	0.943	0.008	0.073	8.8	7.9
13	1	1	20.36	20.11	0.939	0.008	0.073		
13	1	-1	19.39	19.33	0.943	0.008	0.073	9.7	7.9
12	4	4	26.32	26.24	0.900	0.005	0.075		
12	4	-4	26.29	26.23	0.900	0.005	0.075	0.2	0.0
9	7	7	19.16	19.02	0.946	0.008	0.076		
9	7	-7	18.37	18.25	0.951	0.008	0.076	8.4	8.4
11	7	3	18.54	18.52	0.949	0.008	0.076		
11	7	-3	19.33	19.28	0.945	0.008	0.076	-8.3	-8.1
13	3	1	18.37	18.44	0.950	0.008	0.076		
13	3	-1	19.34	19.21	0.945	0.008	0.076	-10.3	-8.2
12	6	2	25.05	25.08	0.910	0.005	0.079		
12	6	-2	25.07	25.08	0.910	0.005	0.079	-0.2	0.0
9	9	5	18.04	18.18	0.952	0.008	0.080		
9	9	-5	17.16	17.41	0.956	0.008	0.080	10.1	8.6
8	8	8	24.16	23.99	0.919	0.005	0.083		
8	8	-8	24.17	23.98	0.919	0.005	0.083	-0.1	0.1
11	7	5	17.56	17.38	0.957	0.008	0.084		
11	7	-5	16.75	16.62	0.961	0.008	0.084	9.5	8.9
13	5	1	17.52	17.49	0.957	0.008	0.084		
13	5	-1	16.68	16.74	0.960	0.008	0.084	9.8	8.8
10	8	6	23.18	22.95	0.927	0.005	0.086		
10	8	-6	23.12	22.94	0.927	0.005	0.086	0.5	0.1
11	9	1	16.03	16.04	0.964	0.008	0.088		
11	9	-1	16.86	16.77	0.960	0.008	0.088	-10.1	-8.9
13	5	3	15.93	16.07	0.964	0.008	0.088		
13	5	-3	16.70	16.81	0.960	0.008	0.088	-9.5	-8.9
12	8	0	22.01	21.95	0.933	0.005	0.090		
9	9	7	15.43	15.48	0.966	0.008	0.091		
9	9	-7	16.11	16.19	0.963	0.008	0.091	-8.7	-9.0
11	9	3	15.79	15.91	0.964	0.008	0.091		
11	9	-3	15.08	15.19	0.967	0.008	0.091	9.2	9.3

Table 5 (cont.)

<i>h</i>	<i>k</i>	<i>l</i>	<i>F_{oi}</i>	<i>F_{ci}</i>	<i>y_i</i>	$\sigma_i/ F_{oi} $	α_i	<i>B_{oi}</i> (%)	<i>B_{ci}</i> (%)
10	10	4	20.83	21.00	0.938	0.005	0.093		
10	10	-4	20.82	20.99	0.938	0.005	0.093	0.1	0.1
2	0	0	6.61	6.55	0.993	0.042	0.001		
2	2	2	6.09	6.10	0.994	0.019	0.003		
2	2	-2	5.27	5.28	0.996	0.008	0.003	28.6	28.5
4	2	0	6.43	6.32	0.994	0.012	0.006		
4	4	2	6.91	7.02	0.993	0.012	0.011		
4	4	-2	6.97	7.00	0.993	0.011	0.011	-2.0	0.7
6	0	0	7.68	7.01	0.993	0.033	0.011		

others)* are quite sensitive to the value of β_{GaAs} and so accurate measurements of these quantities are of particular interest. In the present work, it was not possible to measure accurately these Bijvoet ratios because of the low integrated intensities involved. However, with a more intense X-ray source [rotating-anode generator or synchrotron source (with care taken to avoid harmonic contamination in some circumstances)] such measurements, at room temperature, are quite possible (Pietsch, Paschke & Eichhorn, 1993). When such measurements are made, great care should be taken to avoid multiple-diffraction effects.

* The choice of reflections is dictated by several criteria: the reflections should have $h+k+l=4n+2$ (not $4n$) because the integrated intensities for Bijvoet-pair reflections with $h+k+l=4n$ are, in general, much larger (without a corresponding increase in their difference) - see (1) and equations (5a) and (5b) of McIntyre, Moss & Barnea (1980); the reflections should be reasonably high angle so that the Bijvoet ratio is relatively large and so that there is no significant contribution from bonding effects; the magnitude of the product of h, k and l should be large so that $|\tau_{\alpha, \text{GaAs}}|$ is large - see (6).

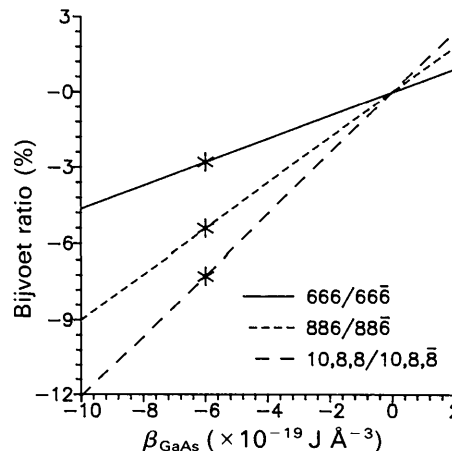


Fig. 3. Graph showing the dependence of certain Mo $K\alpha$ Bijvoet ratios (with $h+k+l=4n+2$) on the effective cubic anharmonic parameter β_{GaAs} . The asterisks mark the values for the β_{GaAs} value determined in the present work.

Discussion

The interpretation of the observed GaAs structure-factor magnitudes with respect to bonding effects is crucially dependent on the calculated atomic scattering factors used in the analysis. The direction of the transfer of electron charge obtained from piezoelectric measurements on GaAs (see, for example, Zerst & Boroffka, 1963) and Fourier synthesis of the charge distribution (see, for example, Attard, Mifsud, Sant & Sultana, 1969) is from arsenic to gallium, in contrast to the present study. On the other hand, linear-combination-of-atomic-orbitals (LCAO) calculations (Coulson, Rèdei & Stocker, 1962) and K -absorption-edge measurements (Kantelhardt & Waidelich, 1969) are in agreement with the present study. It is therefore appropriate that we discuss this matter further.

In this section, we discuss the analysis of the GaAs results in terms of three sets of atomic scattering factors: (i) the relativistic Hartree–Fock (RHF) scattering factors of Doyle & Turner (1968), which have been used for the present work thus far; (ii) the Thomas–Fermi–Dirac (TFD) scattering factors of Thomas & Umeda (1957); (iii) the relativistic Dirac–Slater (RDS) scattering factors of Cromer & Waber (1965). In the case of the RHF and RDS scattering factors, nine parameter values determined by curve-fitting procedures have been supplied for each atom (see Vand, Eiland & Pepinsky, 1957), *i.e.* there are analytical approximations in terms of Gaussian functional forms. Thomas & Umeda (1957) supply values for the TFD scattering factors at 31 discrete values of $S/2$, from 0.00 to 1.50 in steps of 0.05 \AA^{-1} , but not analytical approximations. It was thus necessary to carry out least-squares fits to this data, for neutral Ga and As atoms, to obtain values for the nine parameters in the conventional analytical approximation. The 31 data points for each atom were weighted according to the scheme of Forsyth & Wells (1959), so that the best fit was obtained near $S/2 = 0.50 \text{ \AA}^{-1}$. The fits obtained in this way were excellent and are comparable with the fits obtained when the analytical approximations given by Doyle & Turner (1968) and Cromer & Waber (1965) were compared with their respective tabulated scattering-factor values [the maximum (weighted) residuals were 0.152 and 0.054% of $f_{c,\text{Ga}}(0) = Z = 31.000$ and $f_{c,\text{As}}(0) = Z = 33.000$, respectively, *cf.* the corresponding values 0.076 and 0.054% for the data of Doyle & Turner (1968), and 0.072 and 0.046% for the data of Cromer & Waber (1965)].

Least-squares refinements corresponding to the results presented in Tables 4 and 5 were performed for both the TFD and RDS scattering factors. For the TFD scattering factors, the resulting fit was very much worse than for the RHF scattering factors, the

values of R and GFIT 1.524% and 2.410, respectively. In the case of the RDS scattering factors, the resulting fit was much better ($R = 0.708\%$ and GFIT = 1.117) but still significantly worse than for the RHF scattering factors [the refined-parameter values were: $B_{\text{Ga}} = 0.620(3) \text{ \AA}^2$, $B_{\text{As}} = 0.456(5) \text{ \AA}^2$, $s = 5.03(3)$, $r = 4.1(2) \text{ \mu m}$, $\beta_{\text{GaAs}} = -0.7(1) \times 10^{-18} \text{ J \AA}^{-3}$, $\alpha_0 = 4.2(3) \text{ \AA}^{-1}$, $C_0 = -0.05(2)$ and $C_3 = 1.6(3)$].

If we consider the presence of bonding effects in the GaAs data purely in terms of net transfer of electron charge Q from gallium to arsenic (which is an oversimplification of the true situation*), (1) can be rewritten, for $h+k+l=4n+2$, with Q subtracted from $f'_{c,\text{Ga}}$ and added to $f'_{c,\text{As}}$ wherever they appear. f represents an average atomic scattering factor per electron and can be given by (Attard, 1968)

$$f = (f_{c,\text{As}} - f_{c,\text{Ga}})/2. \quad (14)$$

The modified form of (1) can be written as a quadratic equation in Q , one solution being of unreasonably large magnitude (*e.g.* $Q \approx -2$ electrons for the 200 reflection). The other solution is presented in Table 6 for the 200, 222 and $22\bar{2}$ reflections and for RHF, TFD and RDS scattering factors. The fact that the Q values for the TFD scattering factors are negative is in accord with Attard's (1968) analysis of the Mo $K\alpha$ 200 reflection result of De Marco & Weiss (1964). However, in the light of the above-mentioned least-squares fits for the full data set, we regard the Q values for the RHF and RDS scattering factors as being more reasonable. In the case of the 222 and $22\bar{2}$ reflections, both of the additional atomic scattering factor terms associated with bonding (see earlier discussion) are nonzero, whereas for the 200 reflection the antisymmetric component (involving α_3 and C_3 and corresponding to nearest-neighbour bonding) is zero, *i.e.* only the term involving α_0 and C_0 and associated with spherical expansion or contraction of the bonded atom relative to an isolated atom is nonzero. It is thus a straightforward matter to use the refined values of α_0 and C_0 (see Table 4) to estimate the value of Q associated with the 200 reflection. The value so obtained is 0.21(9), in excellent agreement with the corresponding value given in Table 6. Our findings thus favour the conclusion that the direction of net electron-charge transfer is from gallium to arsenic, in accordance with the electronegativity principle.

* The fact that the observed structure-factor magnitudes for the 200 and 222 reflections are larger than those values calculated without the inclusion of bonding effects, while that for the $22\bar{2}$ is smaller, is testimony to this being an oversimplification. In the case of the isoelectronic zinc blende compound ZnSe, a similar situation arises in that McIntyre, Moss & Barnea (1980) observed the integrated intensity for the 200 reflection to be 20% larger than calculated, while those for the 222 and $22\bar{2}$ are 2 and 10% lower, respectively.

Table 6. Calculated values of Q , the electron charge transfer from gallium to arsenic, based on observed structure-factor magnitudes in Table 3 ($4n+2$ Bragg reflections)

The Q values in the second column are obtained using the RHF scattering factors of Doyle & Turner (1968), those in the third column using the TFD scattering factors of Thomas & Umeda (1957), and those in the fourth column using the RDS scattering factors of Cromer & Waber (1965).

hkl	D & T (1968)	T & U (1957)	C & W (1965)
200	0.22 (5)	-0.09 (4)	0.18 (5)
222	0.16 (3)	-0.25 (2)	0.12 (3)
222	-0.02 (1)	-0.41 (1)	-0.06 (1)
Average	0.12 (3)	-0.25 (2)	0.08 (3)

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