

Anharmonic Temperature Factors, Anomalous-Dispersion Effects and Bonding Charges in Gallium Arsenide

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Abstract

The introduction of dispersion corrections in the generalized structure-factor expression for the zinc blende structure leads to the breakdown of Friedel's law for all even-index reflections, owing to bonding or anharmonicity in these crystals. A systematic and precise X-ray diffraction intensity measurement has been carried out using a spherical single crystal of gallium arsenide at 300 K. Least-squares refinement of the experimental data yields the Debye-Waller factors $B_{\text{Ga}} = 0.62$ (2), $B_{\text{As}} = 0.49$ (2) \AA^2 for the harmonic model and $B_{\text{Ga}} = 0.670$ (3), $B_{\text{As}} = 0.470$ (2) \AA^2 and individual anharmonic thermal factors $\beta_{\text{Ga}} = 3.15$ (59) $\times 10^{-18}$ and $\beta_{\text{As}} = 8.92$ (182) $\times 10^{-18}$ J \AA^{-3} for the anharmonic model. The residual index for the discrepancy between measured and calculated structure factors in the present work is $R = 1.237\%$ for the harmonic model and $R = 1.229\%$ for the anharmonic model. The present work reveals excellent agreement in both sign and magnitude of the Bijvoet inequalities for a large number of reflections. Covalent charge transfer has also been deduced from the experimental measurements on a few quasi-forbidden Bragg reflections showing a net transfer of charge from Ga to As.

Introduction

X-ray diffraction intensity data are usually interpreted assuming harmonic thermal vibration of atoms. However, the harmonic thermal vibration will be modified in a noncentrosymmetric crystal due to symmetry conditions. This gives rise to anharmonicity in the thermal vibrations of the atoms (McIntyre, Moss & Barnea, 1980). Several workers have studied the anharmonic thermal vibrations using neutron diffraction. However, some X-ray diffraction studies have also been reported in the literature as reviewed by McIntyre, Moss & Barnea (1980), who also evaluated the anharmonic temperature of ZnSe by X-ray diffraction from an extended-face crystal.

In all these studies, attempts to refine the individual anharmonic thermal factors were unsuccessful and an overall cubic anharmonic temperature factor only was evaluated. Recently, Mohanlal & Pathinetampadiyan (1990) have reported the refinement of individual anharmonic thermal parameters in

$\text{GaAs}_{0.065}\text{P}_{0.935}$. In the present work on GaAs a successful refinement of the individual anharmonic thermal parameters, using 968 measured reflections, has been carried out.

Some researchers have measured the charge density of GaAs using X-ray diffraction techniques. De Marco & Weiss (1964) found a net transfer of charge from Ga to As by measuring the intensity of the 200 Bragg reflection. Colella (1971) found that the measured values of 222 and $\bar{2}\bar{2}\bar{2}$ reflections were 66 and 86% higher than the calculated values, using free-atom scattering factors in GaAs. The fact that both experimental intensities are higher than the calculated value indicates a net transfer of charge from Ga to As. In the present work a large set of 318 quasi-forbidden reflections have been individually measured and then averaged to 22 non-equivalent reflections which were analysed for charge-transfer studies in GaAs. The measured structure factors (F_o), the calculated structure factors (F_c) using free-atom scattering factors (*International Tables for X-ray Crystallography*, 1974), individual Debye-Waller factors for Ga and As, individual anharmonic thermal factors together with the Bijvoet differences for both harmonic and anharmonic models (measured values compared with calculated values) are reported. The relevant theory for the analysis is discussed by McIntyre, Moss & Barnea (1980).

Experimental measurements

The original GaAs sample was in the form of a flat-plate single crystal. Small cubes were cut and ground in the form of spheres using a Nonius crystal spherizer. The spherical crystals were washed in acetone for removal of adhering powder and subjected to chemical polishing. Their quality and suitability for precise data collection were checked by Laue and oscillation X-ray patterns. The spherical sample chosen for the complete three-dimensional data collection was a crystal of radius 0.231 (3) mm, with a tolerance of about 1% for sphericity.

The equipment used for the diffraction measurements was a computer-controlled Nonius CAD-4 X-ray diffractometer, with Mo target X-ray tube, pyrolytic-graphite-crystal monochromator and scintillation detector installed at the Inorganic and

Table 1. Measured structure factors for six equivalent settings of the 800 reflections

hkl	F_o
800	69.99
080	70.32
008	70.44
800	71.94
008	70.31
080	70.53
Mean value of F_o	70.59 (63)
Standard deviation in F_o	0.89%

Physical Chemistry Department, Indian Institute of Science, Bangalore, India. To check the stability and reproducibility of the measurements, two monitor reflections were periodically measured after every 50 measured reflections. The standard deviations in the integrated measurements of these reflections ($\bar{1}\bar{1}\bar{5}$ and $1\bar{1}\bar{5}$) were found to be 0.9 and 0.91% respectively. The raw intensity data underwent Lorentz-polarization and absorption corrections (for spherical sample). An isotropic-extinction correction was also applied on the lines of Zachariassen (1967). The contribution of TDS to the scattering intensity was calculated on the basis of Nilsson (1957) using the elastic constants of Simmons & Wang (1971) and was found to be very low, but a TDS correction was made. The data were processed using least-squares refinement. The quantity minimized was $W(|F_o| - |kF_c|)^2$. The measured reflections can be classified into three categories as follows.

Type of reflection	F_c expression	Number of reflections measured	Remarks
$4n$	$4(f_{Ga} + f_{As})$	260	Used for least squares
$4n \pm 1$	$4(f_{Ga}^2 + f_{As}^2)^{1/2}$	708	Used for least squares
$4n + 2$	$4(f_{Ga} - f_{As})$	318	Averaged to 22 data and used for charge-transfer studies

All equivalent reflections were measured for each set of hkl and $\bar{h}\bar{k}\bar{l}$. The precision of measurements in the present work is indicated by the close internal agreement among the group of equivalent reflections of 800 as listed in Table 1.

Results

In comparison with earlier studies, the present experimental data consist of a very large number of reflections, with a good precision of measurement as seen from Table 1. The data were corrected for absorption and Lorentz-polarization (μR for Mo $K\alpha = 7.6$). The cell parameter obtained from the experimental data was in good agreement with the reported values.

The observed structure factors (F_o) of the reflections were compared in the least-squares refinement with the calculated structure factors (F_c) using

Table 2. Final values of parameters and R values

Parameter	Harmonic model	Anharmonic model
$B_{Ga} (\text{\AA}^2)$	0.62 (2)	0.670 (3)
$B_{As} (\text{\AA}^2)$	0.49 (2)	0.470 (2)
$\beta_{Ga} (10^{-18} \text{\AA}^{-3} \text{J})$	-	3.15 (59)
$\beta_{As} (10^{-18} \text{\AA}^{-3} \text{J})$	-	8.92 (182)
R (%)	1.237	1.229

Hartree-Fock atomic scattering factors for the free atoms Ga and As, with dispersion corrections taken from the values listed in *International Tables for X-ray Crystallography* (1974). The program included provision for refinement of scale factor, extinction (Zachariassen, 1967) and individual Debye-Waller factors. The thermal-diffuse-scattering effects calculated on the basis of Nilsson (1957) for the angular range of the present measurements on GaAs were found to be insignificant, being only about 0.11% even for the highest-angle reflection. The extinction effects observed in the present measurements were appreciable, being about 26% for the lowest-angle reflection and reducing to about 0.2% for the highest-angle reflection.

The least-squares refinement of the observed F_o and the postulated four-parameter model of the calculated F_c refined to 1.237% for the residual index defined by $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ for the harmonic model. In view of the good precision of the data collection and the low value of the residual index, an analysis of the present data was made for any possible anharmonicity features along the lines of Cooper, Rouse & Fuess (1973). In this anharmonic model two additional parameters, β_{Ga} and β_{As} , are introduced in the least-squares refinement. The refined values together with the standard deviations for these parameters are $\beta_{Ga} = 3.15 (59) \times 10^{-18}$ and $\beta_{As} = 8.92 (182) \times 10^{-18} \text{J \AA}^{-3}$. Now $R = 1.229\%$. The refined values are listed in Table 2 for both harmonic and anharmonic models. The measured structure factors and the calculated structure factors corrected for extinction and thermal effects for the anharmonic model are listed in Table 3.

The introduction of anharmonicity in the structure-factor expressions leads to the Bijvoet inequality in the even reflections also (Table 3), in addition to the Bijvoet differences in the odd reflections, which are due to the introduction of dispersion corrections in the generalized structure-factor expressions.

Discussion

1. Analysis of the data for anharmonicity

The present experimental data consist of a very large number of reflections with good precision. Also, the residual index (R) value is very low. So, anharmonic thermal parameters are also included in

Table 3. Comparison of measured and calculated structure factors for GaAs for the anharmonic model

hkl	F_o	F_c	Y (Extinction)
111	154.871	154.514	0.732
$\bar{1}\bar{1}\bar{1}$	153.879	152.784	0.734
311	119.854	120.200	0.884
$\bar{3}\bar{1}\bar{1}$	120.654	121.886	0.887
331	102.295	102.520	0.933
$\bar{3}\bar{3}\bar{1}$	100.308	101.054	0.935
333	87.875	86.990	0.957
$\bar{3}\bar{3}\bar{3}$	88.096	88.266	0.958
511	88.466	88.197	0.957
$\bar{5}\bar{1}\bar{1}$	86.714	86.827	0.958
531	76.501	75.905	0.971
$\bar{5}\bar{3}\bar{1}$	77.148	77.040	0.971
533	68.366	67.974	0.979
$\bar{5}\bar{3}\bar{3}$	66.872	66.937	0.980
551	61.178	60.593	0.984
$\bar{5}\bar{5}\bar{1}$	59.728	59.623	0.985
711	59.987	59.655	0.984
$\bar{7}\bar{1}\bar{1}$	60.922	60.625	0.985
553	53.962	53.675	0.988
$\bar{5}\bar{5}\bar{3}$	54.560	54.602	0.989
731	54.783	54.444	0.988
$\bar{7}\bar{3}\bar{1}$	53.390	53.516	0.989
733	48.741	48.480	0.991
$\bar{7}\bar{3}\bar{3}$	49.417	49.382	0.991
751	44.283	44.039	0.993
$\bar{7}\bar{5}\bar{1}$	44.861	44.927	0.993
555	45.125	44.914	0.993
$\bar{5}\bar{5}\bar{5}$	43.887	44.021	0.993
753	41.140	41.127	0.994
$\bar{7}\bar{5}\bar{3}$	39.944	40.241	0.994
911	41.078	41.115	0.994
$\bar{9}\bar{1}\bar{1}$	40.210	40.233	0.994
931	37.049	37.020	0.995
$\bar{9}\bar{3}\bar{1}$	37.919	37.900	0.995
933	35.102	35.036	0.996
$\bar{9}\bar{3}\bar{3}$	34.111	34.154	0.996
755	34.313	34.496	0.996
$\bar{7}\bar{5}\bar{5}$	34.833	35.379	0.996
773	31.952	31.928	0.996
$\bar{7}\bar{7}\bar{3}$	32.826	32.811	0.996
951	32.583	32.567	0.997
$\bar{9}\bar{5}\bar{1}$	31.486	31.684	0.996
953	29.687	29.707	0.997
$\bar{9}\bar{5}\bar{3}$	30.420	30.590	0.997
11,1,1	27.450	27.596	0.997
$\bar{1}\bar{1},\bar{1},\bar{1}$	28.252	28.476	0.997
775	28.366	28.670	0.997
$\bar{7}\bar{7}\bar{5}$	27.156	27.775	0.997
10,4,2	40.268	40.317	0.995
$\bar{10},\bar{4},\bar{2}$	40.108	40.319	0.995
862	46.213	46.428	0.993
862	46.134	46.431	0.993
844	50.252	50.170	0.992
844	50.052	50.174	0.992
664	54.296	54.429	0.989
664	54.001	54.432	0.989
822	65.035	64.697	0.985
822	65.008	64.698	0.985
642	79.558	79.107	0.975
642	79.122	79.108	0.975
444	88.812	88.433	0.967
444	88.269	88.435	0.967
422	131.476	130.570	0.908
422	129.930	130.570	0.908
10,2,0	46.143	46.345	0.988
840	59.147	59.054	0.988
660	64.720	64.684	0.985
800	70.654	71.280	0.981
620	99.799	99.574	0.955
440	113.018	113.320	0.937
400	151.529	152.979	0.857
220	184.951	184.490	0.756

Table 4. Observed and calculated Bijvoet ratios B

hkl	$100 \times \frac{\Delta I_{\text{obs}}}{\langle I_{\text{obs}} \rangle}$	$100 \times B_{\text{cal}}$	
		Harmonic	Anharmonic
111	+0.77	+2.25	+2.25
311	-1.03	-2.79	-2.79
331	+3.75	+2.88	+2.88
333	-2.38	-2.92	-2.91
511	+3.89	+2.92	+2.92
531	-1.59	-2.98	-2.97
533	+4.38	+3.08	+3.07
551	+4.75	+3.25	+3.23
711	-2.54	-3.25	-3.23
553	-2.15	-3.46	-3.42
731	+5.15	+3.46	+3.44
733	-1.75	-3.73	-3.69
751	-2.45	-4.04	-3.99
555	+5.53	+4.04	+4.02
753	+5.93	+4.38	+4.36
911	+3.95	+4.38	+4.34
931	-4.37	-4.76	-4.69
933	+6.13	+5.16	+5.09
755	-2.35	-5.16	-5.05
773	-4.17	-5.57	-5.46
951	+5.65	+5.57	+5.49
953	-4.45	-5.99	-5.86
11,1,1	-6.53	-6.39	-6.28
775	+8.79	+6.39	+6.34
10,4,2	+0.67	0.0	+0.01
862	+0.95	0.0	+0.013
844	+0.97	0.0	+0.014
664	+1.09	0.0	+0.011
822	+0.36	0.0	+0.003
642	+1.12	0.0	+0.003
444	+1.23	0.0	+0.005
422	+2.37	0.0	+0.000
		$\Sigma = -3.28$	$\Sigma = -2.851$

the refinement process resulting in values $\beta_{\text{Ga}} = 3.15 (59) \times 10^{-18}$ and $\beta_{\text{As}} = 8.92 (182) \times 10^{-18} \text{ J } \text{Å}^{-3}$. To test the statistical significance of the anharmonic thermal parameter, Hamilton's (1965) test was carried out for the following two hypotheses: (1) all atoms have individual thermal parameters only; (2) with individual thermal parameters for the atoms and also individual anharmonic thermal parameters for the atoms. The R -factor ratio was found to be 1.0065, with a significance level < 0.005 indicating the presence of anharmonicity in GaAs. Furthermore, in structures of this type anharmonic thermal vibrations will lead to Bijvoet inequalities for the even reflections (h, k, l all even but $\neq 0$) as was verified experimentally by McIntyre, Moss & Barnea (1980) for ZnSc for a large number of such even reflections. In the present work on GaAs as listed in Table 4, appreciable Bijvoet inequalities exist, justifying the presence of small anharmonicity in GaAs. It must further be pointed out that the introduction of these additional anharmonic parameters has slightly affected the Debye-Waller factors as seen from Table 2.

2. Anomalous dispersion effects

In ZnS-type structures, anharmonic thermal vibrations will lead to Bijvoet inequalities for the even reflections (h, k, l even but $\neq 0$). The inclusion of

Table 5. *Experimental and theoretical values of the Debye-Waller factor of GaAs at room temperature*

Overall value \bar{B}_{GaAs}	Individual values		Method and reference
	B_{Ga}	B_{As}	
0.560 (1)	0.62 (2)	0.49 (2)	Present work; XRD; single-crystal sphere (harmonic model)
0.560 (1)	0.670 (3)	0.470 (2)	Present work; XRD; single-crystal sphere (anharmonic model)
0.906	0.916	0.924	X-ray; powder (a)
0.418	0.418	0.418	Theoretical (b)
0.411	0.411	0.411	Theoretical (c)
-	0.65	0.70	Theoretical (d)
0.765	-	-	Theoretical (e)
0.774	-	-	Neutron diffraction, powder (f)
0.595 (10)	-	-	Reflection profile (g)
0.550	-	-	Photographic (h)

References: (a) Sirota & Olekhovich (1961, 1962); (b) Vetelino, Gaur & Mitra (1972); (c) Talwar & Agarwal (1974); (d) Reid (1983); (e) Banerjee & Varshini (1969); (f) Arnold & Nereson (1963); (g) Matsushita & Hayashi (1977); (h) Uno, Okano & Yukino (1970).

dispersion corrections in the structure-factor calculations for the present structure gives rise to the breakdown of Friedel's law for all odd-index reflections. Colella (1971), Barnea, McIntyre & Moss (1974) and Bilderback & Colella (1976) have observed Bijvoet differences in low-angle reflections, due to bonding in different ZnS-type structures. McIntyre, Moss, Boehm & Barnea (1975) and Valvoda & Jecny (1978) have reported Bijvoet differences for high-angle reflections where anharmonic effects are appreciable for ZnSe and CuCl respectively.

The observed Bijvoet ratio is defined as

$$\Delta I / \langle I \rangle = (I_{hkl} - I_{\bar{h}\bar{k}\bar{l}}) / \frac{1}{2}(I_{hkl} + I_{\bar{h}\bar{k}\bar{l}}).$$

In Table 4, the observed Bijvoet ratios are compared with the calculated (extinction-corrected) values for both harmonic and anharmonic models. The agreement between the calculated and observed Bijvoet ratios is found to be good, in both sign and magnitude, for all the reflections. The Bijvoet ratios of reflections with the same $(\sin \theta) / \lambda$ values are generally different. That difference is inherent when anharmonicity is included in the structure-factor expressions as can be seen from the equations due to McIntyre, Moss & Barnea (1980).

3. Comparison of Debye-Waller factors

The present Debye-Waller factors for individual atoms of GaAs are compared with other reported values in Table 5. From the experimentally measured values in this table, only the work of Matsushita & Hayashi (1977) seems comparable to the present work, whereas the others have employed either photographic or powder techniques. Matsushita & Hayashi

(1977) employed flat-plate samples in an asymmetric Bragg reflection geometry using Cu $K\alpha$ X-radiation and generally observed about 15 to 20" for the full width at half maximum (FWHM) of the reflection profile on their three-crystal spectrometers, indicating 'near' perfect behaviour of the crystal samples used. For the sample preparation in the present work the 'mosaic' crystal model (*International Tables for X-ray Crystallography*, 1974) together with extinction corrections are more appropriate.

It is well known that the intensities in X-ray diffraction are proportional to $|F|$ for the ideally perfect non-absorbing crystals and to $|F|^2$ for the ideally mosaic crystals. It is interesting that despite the extreme ends of the models adopted in the two cases the isotropic overall Debye-Waller factor at 293 K reported by Matsushita & Hayashi (1977) [$\bar{B} = 0.595 (10) \text{ \AA}^2$] is in reasonable agreement with the present work [$\bar{B} = 0.560 \text{ \AA}^2$]. Some theoretically calculated values are also listed in Table 5.

4. Charge transfer in GaAs

In the III-V* semiconductor compound GaAs the structure factor of Bragg reflections of type $h + k + l = 4n + 2$ is $F_c = 4(f_{\text{Ga}} - f_{\text{As}})$ and arises from the difference between the atomic scattering factors of Ga and As atoms. These reflections are in general weak and considered as 'quasi-forbidden' reflections. They contain information concerning the bonding charges in the crystal and hence are of interest. The core contribution can be accurately evaluated using Hartree-Fock free-atom wave functions. Since the core charge densities are very similar for Ga and As, a large fraction of the measured intensities is contributed by valence electrons. Therefore, any departure from spherical symmetry of the valence electrons is expected to produce appreciable effects on the measured intensities.

De Marco & Weiss (1964) have indicated a net transfer of charge from Ga to As. For the 200 reflection of InSb, Bilderback & Colella (1976) and Colella (1971) have found an increase of 29% in intensity when compared with the calculated value, leading to a charge transfer from In to Sb. In the present work, the 200 reflection of GaAs is found to be 111% larger than the expected value, which can only be interpreted as due to a charge transfer from Ga to As. If there is a transfer of charge from As to Ga, then according to the structure-factor expression for the 200 reflection of GaAs the observed intensity must be less than the calculated one. For reflection 200, the measured structure factors of all equivalent reflections are listed in Table 6 and the standard deviation for internal agreement among all the equivalent reflections was found to be small (2.5%). So the above

* 3-5 in IUPAC (1988) nomenclature.

Table 6. *The internal agreement among all the equivalent settings for the 200 reflection for GaAs*

<i>hkl</i>	F_o
200	10.04
$\bar{2}00$	9.82
020	10.25
$0\bar{2}0$	10.47
002	9.74
$00\bar{2}$	10.17
Mean value of F_o	10.08 (25)
Standard deviation in F_o	2.48%

Table 7. *A comparison of measured (F_o) and calculated (F_c) structure factors of a few $4n+2$ -type reflections*

<i>hkl</i>	$(\sin \theta)/\lambda$ (\AA^{-1})	F_o	F_c	% increase of F_o over F_c
200	0.1772	10.08 (25)	4.78	111 (3)
420	0.3962	10.77 (35)	4.98	116 (4)
600	0.5317	10.85 (26)	5.54	96 (2)
640	0.6389	10.34 (39)	5.16	101 (4)
820	0.7307	9.57 (35)	4.42	117 (4)
860	0.8861	7.67 (30)	2.96	159 (5)
10,0,0	0.8861	6.11 (10)	2.96	106 (2)
10,4,0	0.9544	7.84 (30)	2.38	229 (9)
442	0.5317	12.19 (35)	5.54	120 (4)
622	0.5878	11.55 (30)	5.42	113 (3)
644	0.7307	9.57 (31)	4.42	117 (4)
662	0.7725	11.55 (30)	4.03	187 (5)
666	0.9209	8.32 (43)	2.66	213 (11)
864	0.9544	7.63 (39)	2.38	220 (11)
222	0.3070	9.06 (22)	4.25	113 (3)
$\bar{2}\bar{2}\bar{2}$	0.3070	9.30 (18)	4.25	120 (3)
442	0.5317	12.24 (35)	5.54	121 (4)
$\bar{6}\bar{2}\bar{2}$	0.5878	10.81 (47)	5.42	99 (4)
644	0.7307	9.26 (30)	4.42	110 (4)
$\bar{6}\bar{6}\bar{2}$	0.7725	11.05 (39)	4.03	174 (6)
$\bar{6}\bar{6}\bar{6}$	0.9209	8.32 (30)	2.66	213 (8)
864	0.9544	7.28 (39)	2.38	206 (11)

large increase in the observed structure factor can only be due to the transfer of charge from Ga to As. Considering Bragg reflections 222 and $\bar{2}\bar{2}\bar{2}$, Colella (1971) found an increase of 66 and 86% in intensity when compared with the calculated value for these reflections. In the present work, the measured structure factors were found to be larger than their calculated values by 113 (3) and 120 (3)% respectively, as shown in Table 7, indicating a small anharmonicity in GaAs.

The measurements of all the $4n+2$ -type reflections show a net transfer of charge from Ga to As and our observations are in agreement with the earlier observations (De Marco & Weiss, 1964; Colella, 1971). For the 200 reflection the increase in intensity in the present work is 111% whereas that obtained by De Marco & Weiss (1964) is only 16%. Such a large difference cannot be due to Debye-Waller factor or extinction, which are both small for this low-angle weak quasi-forbidden reflection. The possibility of multiple diffraction having contributed to a large increase in intensity of 200 in the present work is readily ruled out since it is well known that multiple

reflection is very sensitive to angular settings of the crystal, whereas the mean value of the structure factors for the 200 reflection as seen from Table 6 at six different settings have yielded consistent values with a small standard deviation.

In Table 7 a comparison of measured F_o values and calculated structure factors (F_c) is made for a few $4n+2$ -type reflections and the increase in the F_o values is in accord with charge transfer from Ga to As.

Concluding remarks

The structure-factor expression for the non-centrosymmetric ZnS-type structure leads to the breakdown of Friedel's law for all odd-index reflections with the introduction of dispersion corrections, for all even non-zero low-angle reflections, mostly due to bonding, and high-angle reflections, mostly due to anharmonic thermal vibration.

Bijvoet ratios for the same $(\sin \theta)/\lambda$ values are generally different to anharmonicity.

It is customary to neglect any anharmonic effects in the usual data collection and analysis of the data. But when precision and internal consistency of the measured data are very high, anharmonicity must be taken into account for the interpretation of the data and there is no reason to omit the anharmonic effect although it is very small.

The large increase in the measured structure factors over the calculated structure factors for the $4n+2$ -type reflections reveal a net transfer of charge from Ga to As. If we assume that charge is transferring from cation to anion then the measured structure factors for InP, GaP *etc.* (where the atomic number of the cation is larger) would be less than the calculated structure factor.

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Combining *MAGEX* with Random Phases

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Abstract

An algorithm is described which combines the magic-integer concept with that of representing a large number of phases by random numbers. The process, called *MAGEX89*, is more economical than previous magic-integer approaches and in a number of tests its performance compares favourably with those of other commonly used methods of solving small structures.

Introduction

The magic-integer concept, introduced by White & Woolfson (1975), was utilized in a number of direct-method approaches to structure solution culminating in *MAGEX* (Hull, Viterbo, Woolfson & Zhang, 1981; Zhang & Woolfson, 1982) which was an option in earlier versions of *MULTAN*. In the original *MAGEX* procedure a number, q , of reflexions had their phases represented (in cycles) by

$$\varphi_j = m_j x \pmod{1}, \quad j = 1, 2, \dots, q, \quad (1)$$

where the m_j are integers based on the Fibonacci series. The relationships which linked the combination of these reflexions with those defining the origin and enantiomorph ($O+E$) became the foundation for a one-dimensional Fourier series, the ψ map, with space variable x . Peaks in the ψ map, translated into phases by (1), gave plausible starting points for phase extension. There was also a facility for carrying out multiple-pathway phase extension from each starting set of phases by further use of the ψ -map concept.

Although the general use of *MAGEX* has declined, in favour of the *RANTAN* approach (Yao, 1981) or

SAYTAN (Debaerdemaeker, Tate & Woolfson, 1985, 1988) we have continued to develop the idea and would claim that, at least for small structures (≤ 100 independent atoms, say), what we have produced, *MAGEX89*, compares favourably in effectiveness and efficiency with other available methods.

MAGEX89

In the procedure *MAGEX89* we have combined the magic-integer concept with that of representing a large number of phases by random numbers. The algorithm we use to select the starting-set reflexions is that given by Zhang, Luo, Chen & Yao (1989). The $O+E$ reflexions are chosen to have values of E and α_{est} as large as possible where

$$\alpha(\mathbf{h})_{\text{est}} = \sum_k \kappa(\mathbf{h}, \mathbf{k}) \frac{I_1\{\kappa(\mathbf{h}, \mathbf{k})\}}{I_0\{\kappa(\mathbf{h}, \mathbf{k})\}}, \quad (2)$$

where $\kappa(\mathbf{h}, \mathbf{k})$ is the usual direct-methods κ value and $I_1(x)$ and $I_0(x)$ are modified Bessel functions. A further 5–25 reflexions for the starting set are chosen so as to satisfy the following criteria as well as possible:

(i) these reflexions must be strongly linked with $O+E$ so that the origin and enantiomorph are strongly defined by the phases of the complete starting set;

(ii) they should have values of E and α_{est} as large as possible.

These extra starting-set reflexions, q in number, have their phases allocated by (1) with multiple starting sets generated using random values in the range