Experimental f'' of As at 170, 200, 250 and 300 K from the Bijvoet pairs of GaAs

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Abstract. Anomalous dispersion effects lead to the modification of the measured X-ray structure factors. In this work, we have determined the imaginary part of the anomalous dispersion correction terms (f'') of arsenide atom (As), through the X-ray data collected using spherical single crystal of GaAs, at various temperatures, i.e. 170, 200, 250 and 300 K. It is stressed that more measurements of f'' of the elements are needed to confirm the theoretical calculations.

Keywords. X-ray; anomalous dispersion; III–V compound semiconductor; GaAs.

1. Introduction

X-ray anomalous scattering techniques are very useful for structural studies as well as other physical properties of crystalline systems. It is obvious that for precise analysis of the collected X-ray intensity data, values of the dispersion correction terms f' and f'' are essential. The correction factors are available in literature (Int. Tables 1974) for almost all the elements, but the reliability of most of these factors are still to be verified through precise X-ray measurements (Srinivasan 1972). Two of the authors have studied the f'' of silicon from the experimental measurement of linear absorption coefficients (Srinivasan *et al* 1995).

The present work deals with the evaluation of the imaginary component of the anomalous dispersion correction term f'' using precise X-ray data measured at 170, 200, 250 and 300 K for GaAs. The data were collected using a AFC-5R automatic diffractometer installed at the Department of Applied Physics, Tohoku University, Japan. The sample used was a perfect sphere of radius about 0.1 mm. For the low temperature measurements, liquid nitrogen was used as coolant. The sample was mounted on a thin glass capillary rod and covered with a thin walled capillary tube to avoid the vibrations of the sample due to dry air supplied during the low temperature measurements. The structure factor data were refined to get the harmonic and anharmonic thermal parameters, charge transfer values etc. Further, electron density distribution of the atoms in these materials have been mapped using

the maximum entropy method (MEM) technique (Kajitani *et al* 2001). The final structure factors were used in the evaluation of f'' of As using the measured and calculated Bijvoet ratios.

2. Refinement

The experimental intensities were reduced into the structure factors after correction for L_p factor and absorption effects. The structure factors were used in the refinement routine. The weak reflections whose $F_{\text{obs}}(\mathbf{k}) < 3 S(\mathbf{k})$ were omitted from the refinement process. The refinable parameters in these routines are the scale, extinction, individual harmonic and anharmonic thermal parameters, the charge transfer parameter etc. These parameters and the electron density distributions are reported elsewhere (Kajitani *et al* 2001).

The basic methodology for the analysis of f'' of atoms has been reported by Engel and Sturm (1975). Using this approach, the f''_{As} has been determined experimentally using the observed Bijvoet differences of the paired reflections.

3. f'' of arsenide

If a structure contains only two types of atoms (heavy (H) and light (L)), the contribution of the imaginary component of the dispersion correction term to the structure factor depends on (Ramaseshan and Abrahams 1975),

$$f''_{\text{eff}} = f''_{\text{H}} - f''_{\text{L}} \frac{f_{\text{H}}}{f_{\text{L}}}. \quad (1)$$

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The f_{eff}'' corresponds to the effective anomalous scattering factor of the heavy atom H with respect to the light atom L. Here f is the real part of the scattering factor. The Bijvoet difference of a reflection hkl is defined as

where

$$Q = \frac{|F_{hkl}|}{|F_{\bar{h}\bar{k}\bar{l}}|}.$$

$$B = (Q - 1)/(Q + 1),$$

(2)

For a known structure, the structure factors are calculated using suitable values of f_{eff}'' . Then the experimental

Table 1. The observed and calculated Bijvoet ratios and the correction factor, X, for GaAs at 170 K.

<i>h</i>	<i>k</i>	<i>l</i>	<i>F</i> ₋ (obs)	<i>F</i> ₋ (cal)	<i>F</i> ₊ (obs)	<i>F</i> ₊ (cal)	<i>B</i> (obs)	<i>B</i> (cal)	<i>X</i>
5	5	7	38.52	36.56	39.47	43.3	4.86	33.51	0.144894
3	5	7	45.56	49.02	44.07	41.7	-6.64	-32.08	0.207133
1	5	7	47.94	45.18	49.45	52.78	6.24	30.84	0.20215
3	3	7	52.19	49.17	53.49	57.07	4.9	29.58	0.165652
1	3	7	58.71	62.02	57.78	53.79	-3.18	-28.28	0.112488
1	1	7	64.03	59.43	65.36	67.99	4.12	26.76	0.153888
5	5	5	48.77	52.66	47.92	45.04	-3.54	-31.01	0.11408
3	5	5	57.13	53.89	58.5	62.11	4.75	28.19	0.168619
3	3	5	71.79	75.07	70.04	66.14	-4.93	-25.19	0.19553
1	3	5	79	74.53	80.21	83.83	3.02	23.41	0.128848
3	3	3	88.06	84.94	90.06	94.64	4.49	21.56	0.208481

Average X value: 0.1637.

Table 2. The observed and calculated Bijvoet ratios and the correction factor, X, for GaAs at 200 K.

<i>h</i>	<i>k</i>	<i>l</i>	<i>F</i> ₋ (obs)	<i>F</i> ₋ (cal)	<i>F</i> ₊ (obs)	<i>F</i> ₊ (cal)	<i>B</i> (obs)	<i>B</i> (cal)	<i>X</i>
5	5	7	37.94	36.54	39.03	43.35	5.68	33.85	0.167747
3	5	7	44.97	48.83	43.77	41.4	-5.43	-32.71	0.165935
1	5	7	47.97	45.1	48.76	52.76	3.26	31.15	0.104519
3	3	7	52.14	49.16	53.48	57.12	5.05	29.76	0.16972
1	3	7	58.6	61.96	57.11	53.67	-5.16	-28.54	0.180816
1	1	7	63.64	59.39	64.76	68	3.5	26.91	0.130073
5	5	5	48.53	52.45	47.3	44.72	-5.12	-31.58	0.162004
3	5	5	57.58	53.94	58.29	62.2	2.46	28.3	0.086976
1	5	5	64.44	67.92	63.76	59.29	-2.13	-26.99	0.07892
3	3	5	72.24	75	70.24	66.02	-5.63	-25.37	0.222044
1	3	5	79.28	74.57	81	83.89	4.3	23.47	0.183141
1	1	5	90.48	94.63	88.31	84.89	-4.85	-21.63	0.224276
3	3	3	89.43	85.04	91.27	94.76	4.08	21.57	0.189311

Average X value: 0.15888.

Table 3. The observed and calculated Bijvoet ratios and the correction factor, X, for GaAs at 250 K.

<i>h</i>	<i>k</i>	<i>l</i>	<i>F</i> ₋ (obs)	<i>F</i> ₋ (cal)	<i>F</i> ₊ (obs)	<i>F</i> ₊ (cal)	<i>B</i> (obs)	<i>B</i> (cal)	<i>X</i>
1	7	7	35.86	41.01	35.58	35.07	-1.57	-31.02	0.050607
3	5	7	42.1	46.82	41.6	40.24	-2.39	-30.1	0.079366
1	5	7	45.4	43.66	46.3	50.57	3.92	29.2	0.134377
3	3	7	50.3	47.6	51.07	54.87	3.02	28.26	0.106889
1	3	7	56.19	59.83	55.05	52.16	-4.09	-27.26	0.150024
1	1	7	60.55	57.77	62.15	65.84	5.19	25.99	0.199597
5	5	5	46.03	50.45	45.16	43.51	-3.83	-29.37	0.130496
3	5	5	54.82	52.27	56.18	59.92	4.91	27.16	0.180694
1	5	5	62.19	65.8	60.74	57.73	-4.71	-26.02	0.180854
3	3	5	69.37	72.97	68.44	64.47	-2.71	-24.65	0.109857
1	3	5	76.96	72.9	78.62	81.85	4.26	23.05	0.184948

Average X value: 0.13706.

Table 4. The observed and calculated Bijvoet ratios and the correction factor, X , for GaAs at 300 K.

h	k	l	F_- (obs)	F_- (cal)	F_+ (obs)	F_+ (cal)	B (obs)	B (cal)	X
5	5	7	35.85	40.38	35.04	34.98	-4.54	-28.5	0.159468
3	5	7	40.81	39.71	42.2	45.85	6.68	28.55	0.233778
1	5	7	45.92	49.64	44.81	43.15	-4.93	-27.83	0.17697
3	3	7	50.39	53.92	49.05	47.04	-5.40	-27.12	0.199062
1	3	7	54.63	51.47	55.67	58.78	3.78	26.43	0.142939
7	1	7	34.66	34.72	35.67	40.15	5.74	28.86	0.198876
1	1	7	62.2	64.8	61.34	57.04	-2.78	-25.35	0.109467
5	5	5	44.7	42.89	45.61	49.42	4.04	28.12	0.143579
3	5	5	55.58	58.96	54.43	51.67	-4.18	-26.25	0.15918
1	5	5	60.72	56.97	61.65	64.73	3.04	25.41	0.119749
3	3	5	67.35	63.62	68.81	71.86	4.28	24.24	0.17649
1	3	5	78.02	80.82	76.43	72.09	-4.13	-22.75	0.181629
1	1	5	86.54	82.51	88.43	91.78	4.33	21.21	0.204083
3	3	3	88.03	91.88	86.27	82.63	-4.04	-21.16	0.190968

Average X value: 0.17116.

Table 5. Evaluated and reported values of f'' of Arsenide.

Temperature (°K)	f''
170	2.041
200	2.032
250	1.988
300	2.056
*Reported value	2.007

*Int. Tables for X-ray Crystallography (1974).

Bijvoet differences are used to find the ratio $X = B_{\text{Ex}}/B_{\text{Th}}$. This X provides the correction for the f''_{eff} used for the calculation of B_{Th} . If f''_{L} is considered known, f''_{H} can be evaluated using (1).

The refined X-ray structure factors of GaAs at 170, 200, 250 and 300 K were used for the determination of the observed and calculated Bijvoet differences. The correction factors, X , have been listed in tables 1–4. The values of the imaginary part of the anomalous dispersion correction terms determined from the present work are listed in table 5 together with reported/calculated values.

4. Results and discussion

As evidenced from tables 1–4 the values of the correction factor, X , are consistently good for all the temperatures. In the evaluation of X values, some low angle reflections have been omitted because there is a possibility that the effects of bonding and charge transfer might affect those reflections and hence the X value for those reflections will be biased. The X values are very small, for example, the average values of X factor are 0.163, 0.159, 0.137 and 0.171 at 170, 200, 250 and 300 K, respectively. These values indicate the corrections to be applied to the effec-

tive f'' are very very small. Because, the atomic numbers of Ga and As are nearly equal and hence the dispersive scattering by these atoms will be almost same. Hence arsenide which is slightly heavy has been taken as the heavy atom in the expression for the evaluation of f'' . If one of the atoms is much lighter than the other, for example, as in InP, then one would expect that the correction factor would be very large approaching unity (Saravanan *et al* 1992).

The f'' values are given in table 5 along with the value reported for room temperature from literature (Int. Tables 1974). The present values are reasonably good. The room temperature value is in good agreement with the reported value. It is noted that the f'' values decrease with temperature up to 250 K. Further investigation is being carried out to determine the temperature dependence of f'' of arsenide.

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