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Determination of the Anharmonicity Constant of GaAs by Means of the Bijvoet Relation of the Weak (666) Reflection

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Abstract

As a result of the influence of anomalous dispersion the weak (hhh) and $(\bar{h}\bar{h}\bar{h})$ reflections of the zinc blende structure differ from each other. At large scattering vectors this difference, described by the Bijvoet relation B, depends solely on the size of the anharmonic force constant β. It can be determined by measuring B near the K-absorption edge of any constituent. This experiment was performed for the (666) and $(\bar{6}\bar{6}\bar{6})$ reflections of GaAs between $\lambda = 0.90$ and 0.97 Å using synchrotron radiation. Outside the extended X-ray absorption fine-structure spectroscopy region the integrated intensities decrease in a different manner with increasing λ for both reflections measured at 'umweganregung' free azimuthal positions. Under the assumption of $\beta_{Ga} = -\beta_{As}$ and using the measured wavelength dependence of B, the anharmonicity constant is evaluated to $\beta = -1.75\,(0.15) \times 10^{-17}$ J Å^{-3} which is nearly the same as that for germanium.

Introduction

Because of its technological importance GaAs is one of the most thoroughly investigated semiconductors. It crystallizes in the zinc blende structure and its chemical bond is dominated by the covalent overlap of bonding orbitals and the electronic charge exchange between the valence shells (covalent–ionic bond). Since most of the ground-state properties are due to the valence electron density (VED) of the material, the latter has been studied by various theoretical and experimental methods. However, various discrepancies still exist between the calculated VED and the experimental density determined by Fourier transformation of highly accurate X-ray structure amplitudes (Pietsch, Tsirelson & Ozerov, 1986). This is due to the restricted consideration of the complicated many-electron system by various theoretical approaches and by experimental limits. The accuracy of the experimental VED is presently restricted by an incomplete data set, which is known up to the copper limit $[q = 4\pi(\sin\theta/\lambda) \le 4\pi(0.64)$ Å$^{-1}]$, and by the limited knowledge of the anharmonicity correction (Pietsch, 1993). Because of the close proximity of gallium to arsenic in the Periodic Table the weak reflections of the type $h + k + l = 4n + 2$ (hkl – Miller indices, $n = 0, 1, 2...$) – which depend on the difference in scattering power of Ga and As – are very sensitive to the redistribution of valence electrons (bond charge) caused by the chemical bond. The weak scattering power of this type of reflection justifies the application of the kinematic scattering theory for the evaluation of the structure amplitude, $|F(hkl)|$, from the measured integrated intensity, $I(hkl)$ (Bilderback, 1975; Pietsch, 1981). Both the bond charge and the anharmonic

thermal vibration modify $|F(hkl)|$. Because of the influence of anomalous dispersion and in the case of $hkl \neq 0$ a difference between $|F(hkl)|$ and $|F(\overline{hkl})|$ is measured (Colella, 1971) which can be expressed by the so-called Bijvoet relation or Bijvoet difference

$$B(hkl) = \frac{F(hkl)F(hkl)^* - F(\overline{hkl})F(\overline{hkl})^*}{0.5[F(hkl)F(hkl)^* + F(\overline{hkl})F(\overline{hkl})^*]} \quad (1)$$

(McIntyre, Moss & Barnea, 1980). The q dependence differs for bond charge and anharmonicity contribution: for small q values B is dominated by the bond charge (Bilderback & Colella, 1976), whereas the influence of the anharmonicity increases with increasing q. For ionic materials or at large q the covalency can be neglected, and B can be used to determine the anharmonicity parameter β (McIntyre, Moss & Barnea, 1980). In the case of GaAs both the bond charge and the anharmonicity make an almost equal contribution to $q(442)$ (Pietsch, 1982). Neutron-scattering experiments are then required to determine β (Roberto, Battermann & Keating, 1974). An X-ray determination of β at high q values was performed by Merisalo & Järvinen (1978) for white tin and by Kumpat & Rossmanith (1990) for zinc. For GaAs only three experimental results are known to us (Table 1), two of which are of low accuracy only. [Bilderback (1975) did not give an error for his value.] The β parameters published by Mohanlal & Pathinettampadiyan (1990) and Saravanan, Mohanlal & Chandrasekaran (1992) were determined by least-squares fit including a full structure refinement. Compared with the reached accuracy given by Roberto, Battermann & Keating (1974) those β values are not significant.

The idea of the present work is to determine β from the Bijvoet relation at high q where the influence of the bond charge can be neglected. This has already been proposed by McIntyre, Moss & Barnea (1980). In addition, we try to measure B near the K-absorption edge of one of the constituents. Because of the change of anomalous dispersion close to the K edge B must vary with the wavelength. Both requirements can be fulfilled by measuring the (666) and ($\overline{666}$) reflections near the As K edge ($\lambda_K \simeq$ 1.0445 Å), using synchrotron radiation.

Structure-factor formalism

If the Ga atoms are chosen to occupy the (000)+ sites and the As atoms the ($\frac{1}{4},\frac{1}{4},\frac{1}{4}$)+ sites of the zinc blende structure the structure factors of the class $h + k + l = 4n + 2$ reflections can be written using the generalized structure-factor formalism introduced by Dawson (1967) and modified by Pietsch (1981) as

$$F(hkl) = F_r(hkl) + iF_i(hkl) \quad (2)$$

Table 1. *Anharmonicity parameters* β *for* GaAs *and* Ge ($\times 10^{-7}$ J Å^{-3})

β	Material	Reference
−2.3	GaAs	Bilderback (1975)
−0.8 (0.6)	GaAs	Mohanlal & Pathinettampadiyan (1990)
0.31 (0.06)	Ga	Saravanan et al. (1992)
0.89 (0.18)	As	
−1.75 (0.15)	GaAs	Present study
−2.11 (0.33)	Ge at 288 K	Roberto et al. (1974)
−1.78 (0.05)	Ge at 688 K	Roberto et al. (1974)

using

$$F_r = 4[(f_{Ga} + f'_{Ga})T_{h\,Ga} - (f_{As} + f'_{As})T_{h\,As}]$$
$$- 4(f''_{Ga}T_{anh\,Ga} - f''_{As}T_{anh\,As}) + S_r f_{BC}$$

$$F_i = 4[(f_{Ga} + f'_{Ga})T_{anh\,Ga} - (f_{As} + f'_{As})T_{anh\,As}]$$
$$- 4(f''_{Ga}T_{h\,Ga} - f''_{As}T_{h\,As}) + S_i f_{BC} \quad (2a)$$

for hkl reflections and

$$F_r = 4[(f_{Ga} + f'_{Ga})T_{h\,Ga} - (f_{As} + f'_{As})T_{h\,As}]$$
$$+ 4(f''_{Ga}T_{anh\,Ga} - f''_{As}T_{anh\,As}) + S_r f_{BC}$$

$$F_i = 4[(f_{Ga} + f'_{Ga})T_{anh\,Ga} - (f_{As} + f'_{As})T_{anh\,As}]$$
$$+ 4(f''_{Ga}T_{h\,Ga} - f''_{As}T_{h\,As}) - S_i f_{BC} \quad (2b)$$

for ($\overline{hkl}$) reflections. (2a) differs from (2b) in the signs of the individual terms. The f_{Ga} and f_{As} are the q-dependent atomic scattering factors (*International Tables for X-ray Crystallography*, 1974, Vol IV). $S_{r,i}f_{BC}$ is the structure-factor contribution of the bond charge. $f'(\lambda)$ and $f''(\lambda)$ describe the energy-dependent real and imaginary parts of the anomalous-dispersion correction which can be calculated using the quantum-mechanical formalism given by Cromer & Liberman (1970). Both quantities vary strongly near the K-absorption edge of the respective excited atom. On its high-energy side (XANES and EXAFS region) f' and f'' are modulated by the interaction of the exited photoelectron wave of the absorber with its nearest neighbours (Stern, Ma & Hanske-Petitpierre, 1992) which is not considered by Cromer & Liberman (1970).

Neglecting the bond charge, the difference between (hkl) and ($\overline{hkl}$) in (2a) and (2b) depends on the magnitude of the harmonic $T_{h,i}$ and anharmonic $T_{anh,i}$ temperature factors which are multiplied with $f'(\lambda)$ and $f''(\lambda)$. For the zinc blende structure the thermal displacement of the atoms can be approximated in terms of an anharmonic one-particle potential expanded up to the third order (Dawson, Hurley & Maslen, 1967)

$$V(xyz) = V_{o,i} + 0.5\alpha_i(x^2 + y^2 + z^2) + \beta_i xyz + \dots \quad (3)$$

where α_i describes the harmonic and β_i the anharmonic force constant. In this approximation the anharmonicity of the potential is solely directed along $\langle 111 \rangle$. The vibration amplitude is smaller

towards next nearest neighbours and larger in the direction opposite that of the bond. Using (3) the temperature factors can be expressed as

$$T_{h,i} = \exp[-q^2 kT/(2\alpha_i)] \qquad (4)$$

and

$$T_{anh,i} = (\beta_i/\alpha_i^3)(kT)^2(2\pi/a_0)hkl \qquad (5)$$

where k is the Boltzmann constant, T the absolute temperature and a_0 is the lattice parameter. The α_i's were taken from the literature (Bilderback, 1975; Pietsch, 1981).

Assuming $\beta_{Ga} = -\beta_{As}$ the expected wavelength dependence of the (666) and ($\overline{666}$) reflections and the variation of the Bijvoet relation *versus* λ are shown in Fig. 1 between $\lambda = 0.9$ and 1.08 Å, neglecting the possible influence of the EXAFS modulation. $B(\lambda)$ reaches its maximum between $\lambda = 1.01$ and 1.02 Å.

Experimental details

The measurements were performed on a Huber four-circle goniometer at the HASYLAB beamline D3 (Kupčik, Wendschuh-Josties, Wolf & Wulf, 1986; Wulf, Almen & Wendschuh-Josties, 1991). The wavelength was tuned by a silicon (111) double-crystal monochromator to an accuracy better than $\delta\lambda = 0.001$ Å. The normalized intensities $I(666)$ and $I(\overline{666})$ were measured from [111] and [$\overline{111}$] cut single-crystal wafers (A and B surface) having nearly the same thickness of about 0.350 mm. In both cases the wafer dimension was much larger than the irradiated sample area of about 1 × 1 mm. Within the angular limits of the diffractometer ($2\theta \leq 145°$) the (666) reflection was measureable up to $\lambda \leq 1.0$ Å. The range between $\lambda = 0.9$ and 1.0 Å was chosen for

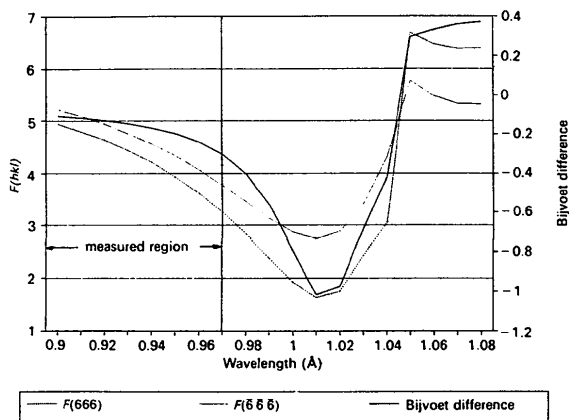measurement. For each wavelength ω scans were performed for a range of ψ values (ψ scan) in order to find regions free from *umweganregung* (Fig. 2). A nearly linear decrease in $I(666)$ and $I(\overline{666})$ was found between $\lambda = 0.9$ and ~0.97 Å (Fig. 3) which corresponds to the expected behaviour shown in the left-hand portion of Fig. 1. Because of the initial influence of the EXAFS modulations the scattering power did not follow expectations at larger wavelengths, thus the range above 0.95 Å was neglected in further interpretation (see below).

Results

The standard deviations of the measured $I(666)$ and $I(\overline{666})$ are in the 1% region of each λ. In order to enhance the accuracy of the evaluated $B(\lambda)$ the $I(\lambda)$ for both reflections were approximated by straight lines. The experimental conditions for both wafers were the same and for both reflections the kinematic
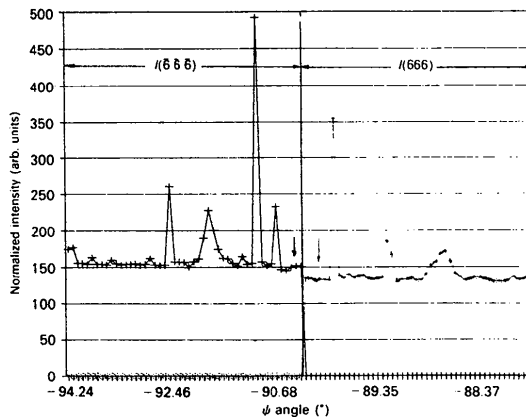

Fig. 2. The intensities $I(666)$ and $I(\overline{666})$ measured by ψ scans at $\lambda = 0.9$ Å. The arrows indicated the regions of measurement.

Fig. 1. The expected λ dependence of $|F(666)|$ and $|F(\overline{666})|$ and of the Bijvoet relation near the As K edge. The part indicated at the left-hand side was investigated in the present work. The thermal parameters were taken from the literature (Bilderback, 1975).
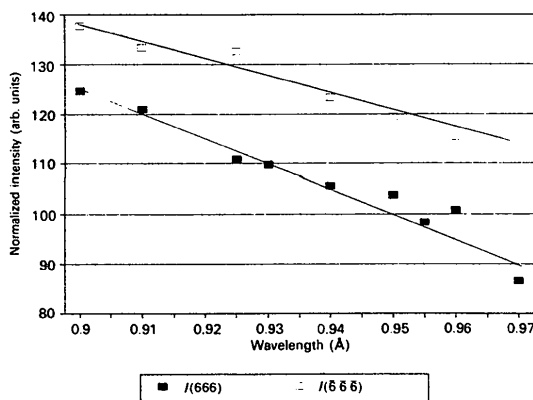

Fig. 3. The intensities $I(666)$ and $I(\overline{666})$ taken from regions free from *umweganregung* between $\lambda = 0.9$ and 0.97 Å. The straight lines were obtained by regression of the measured values.

limit is fulfilled. Thus [cf. equation (1)]:

$$B(\lambda) = \frac{I(666\lambda) - I(\overline{666}\lambda)}{0.5[I(666\lambda) + I(\overline{666}\lambda)]}. \tag{6}$$

The evaluated B values are shown in Fig. 4. They are determined using pairs of experimental $I(hkl\lambda)$ and the value from the fitted straight line. From the range between $\lambda = 0.90$ and 0.95 Å the anharmonicity constant evaluates to $\beta = -1.75\,(0.15) \times 10^{-17}$ J Å^{-3}.

Discussion

Unfortunately it was not possible to evaluate the Bijvoet relation at the most sensitive wavelengths in the range between $0.95 \leq \lambda \leq 1.05$ Å. This was because of the instability of the storage ring and the influence of the EXAFS modulations on $|F(hkl)|$ which can in fact be expected up to about 800 eV above the As K edge. In addition, Cromer & Liberman's f' and f'' were used for data evaluation which cannot be expected to be valid in the EXAFS region.

However, the accuracy of the determined anharmonicity parameter is much better than that given in previous publications (Table 1). It is similar to the value determined for germanium by means of neutron scattering by Roberto, Battermann & Keating (1974). The anharmonicity of GaAs is almost the same as that of Ge. This is not surprising taking the predominant covalent-bonding character into account. The influence of the ionic charge transfer is

smaller than 0.1 electrons per bond (Harrison, 1973; Pietsch, 1985). An increase of the anharmonicity scaled by β/α^3 (5) can be expected for more ionic materials in which the closed-shell character dominates. This has indeed been found for ZnX where X = S, Se, Te (McIntyre, Moss & Barnea, 1980). Different anharmonic parameters of the cation and anion were only evaluated in the case of the $A^I B^{VII}$ compounds near the zinc blende to NaCl phase transition by Harada (1976) for CuBr and by Valvoda & Ječný (1978) for CuCl. It is impossible, however, to distinguish between β_{Ga} and β_{As} with the present method. This might be accomplished by additional measurements of the class of $h + k + l = 4n + 1$ reflections. Unfortunately, the influence of the anharmonicity on the integrated intensity is several orders of magnitude smaller than for the class $4n + 2$ reflections and the expected B value is smaller than the experimental accuracy.

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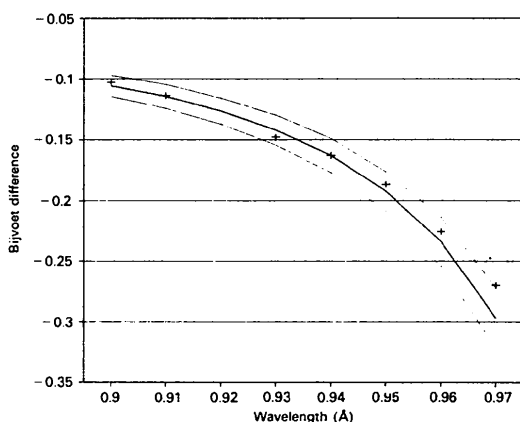WULF, R., ALMEN, H. & WENDSCHUH-JOSTIES, M. (1991). HASYLAB Jahresber. pp. 483–484.

Fig. 4. The Bijvoet relations derived from the experimental values of Fig. 3. The crosses indicate the measured values. The solid line represents the expected variation for $\beta = -1.75 \times 10^{-17}$ J Å^{-3}. The dotted lines are given for $\beta = -1.60$ and -1.90×10^{-17} J Å^{-3}, respectively.