IOPscience iopscience.iop.org

Home Search Collections Journals About Contact us My IOPscience

Application of the reflection intensity of the Bijvoet pair to the determination of anomalous scattering factors for Ga

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1994 J. Phys.: Condens. Matter 6 1619

(http://iopscience.iop.org/0953-8984/6/9/004)

View the table of contents for this issue, or go to the journal homepage for more

Download details:
IP Address: 171.66.16.147
The article was downloaded on 12/05/2010 at 17:44

Please note that terms and conditions apply.

J. Phys.: Condens. Matter 6 (1994) 1619–1626. Printed in the UK

Application of the reflection intensity of the Bijvoet pair to the determination of anomalous scattering factors for Ga

Zhao Zongyan†, Han Jiahua†, Tomoe Fukamachi‡, Masami Yoshizawa‡, Kenji Ehara‡, Tetsuo Nakajima§ and Takaaki Kawamura‖

† Department of Physics, Anhui University, Hefei 230039, People's Republic of China
‡ Saitama Institute of Technology, Okabe, Saitama 369-02, Japan
§ Photon Factory, KEK (National Laboratory for High-Energy Physics), Oho, Tsukuba, Ibaraki 305, Japan
‖ Yamanashi University, Kofu, Yamanashi 400, Japan

Received 27 April 1993, in final form 9 November 1993

Abstract. This paper discusses how to use the integrated reflection intensity of the Bijvoet pair for a polar crystal to determine the anomalous scattering factors f'_{Ga} and f''_{Ga} for Ga near the Ga K absorption edge in GaAs. The values of f'_{Ga} and f''_{Ga} have been calculated from the integrated intensities of the $\pm(333)$ and $\pm(555)$ reflections by using the methods of the present paper. The agreement between calculations and theoretical values is fairly good. Furthermore, the x-ray absorption near-edge structure on the high-energy side near the K absorption edge has been given in the calculated values. Such a structure cannot be predicted by Sasaki's results.

1. Introduction

At present there is much activity in the study of anomalous scattering. There are several reasons for this continued interest. First of all, synchrotron radiation gives us almost ideal x-rays, particularly in its high parallelity, continuous wavelength and very high intensity over an energy region. This source is particularly useful for the study of anomalous scattering because it is possible to make the best use of anomalous scattering over a wide range of energy values for various kinds of atom. Secondly, the advent of the solid state detector has made it feasible to carry out energy-disperse diffractometry and to measure any reflection intensity at any energy, even in the energy region very near the absorption edge. Finally, there are many applications of anomalous scattering, such as determination of the phase of the crystal structure factor, measurement of the absolute configuration, and determination of the crystal polarity.

Therefore, the theoretical calculation [1–4] and experimental measurement [5–7] of anomalous scattering factors have attracted much attention. In this paper, we propose an intensity difference ratio method which first determines f'_{Ga} and f''_{Ga} on the high-energy side near the K absorption edge using the intensity ratio method, and then f'_{Ga} and f''_{Ga} on the low-energy side using the values from the high-energy side.

2. Theory

As is well known, the reflection intensity of x-rays from the (hkl) plane is proportional to the square of the structure factor amplitude $|F_h|$, namely

0953-8984/94/091619+08$19.50 © 1994 IOP Publishing Ltd

$$|F_h|^2 = \left| \sum_j^N (f_j^0 + f_j' + \mathrm{i} f_j'') \exp(2\pi \mathrm{i} h r_j) \right|^2 \tag{1a}$$

that is

$$|F_{\bar{h}}|^2 = \left| \sum_j^N (f_j^0 + f_j' - \mathrm{i} f_j'') \exp(-2\pi \mathrm{i} h r_j) \right|^2 \tag{1b}$$

where $h = (hkl)$, r_j is the position vector for the jth atom in the unit cell, n refers to the atomic number in the unit cell, f_j^0 is the normal atomic scattering factor, and f_j' and f_j'' the real and imaginary components, respectively, of the anomalous scattering factor. For a polar crystal, equation (1a) does not equal equation (1b), so we obtain [8]

$$\begin{aligned} |F_{h1}|^2/|F_{\overline{h1}}|^2 &= I_{h1}/I_{\overline{h1}} = R_{h1} \\ |F_{h2}|^2/|F_{\overline{h2}}|^2 &= I_{h2}/I_{\overline{h2}} = R_{h2} \end{aligned} \tag{2}$$

where F_{h1}, and $F_{\overline{h1}}$, and F_{h2}, $F_{\overline{h2}}$, denote the structure factors of two sets of Bijvoet pairs, I_{h1}, $I_{\overline{h1}}$, and I_{h2}, $I_{\overline{h2}}$, are the corresponding reflection intensities. If the reflection intensities of the Bijvoet pair near the K edge for a polar crystal were measured, the atomic anomalous scattering factors generally can be derived from equation (2). This is called the intensity ratio method. For GaAs there are only $\pm(111)$, $\pm(333)$ and $\pm(555)$ Bijvoet pair reflections near the Ga K absorption edge. According to the precision of the present measurement, the $\pm(333)$ and $\pm(555)$ Bijvoet pair reflections were used in the determination of anomalous scattering factors for Ga. Thus, we can write (2) as follows:

$$\begin{aligned} & f_{\mathrm{Ga}}'^2 + f_{\mathrm{Ga}}''^2 + 2\{[(f_{\mathrm{Ga}}^0 - f_{\mathrm{As}}'') - R_3(f_{\mathrm{Ga}}^0 + f_{\mathrm{As}}'')]/(1 - R_3)\} f_{\mathrm{Ga}}' \\ &\qquad + 2\{[(f_{\mathrm{As}}^0 + f_{\mathrm{As}}') + R_3(f_{\mathrm{As}}^0 + f_{\mathrm{As}}')]/(1 - R_3)\} f_{\mathrm{Ga}}'' \\ &\qquad + \{(f_{\mathrm{Ga}}^{02} + f_{\mathrm{As}}^{02} + f_{\mathrm{As}}'^2 + f_{\mathrm{As}}''^2) + 2[(f_{\mathrm{As}}^0 f_{\mathrm{As}}' - f_{\mathrm{Ga}}^0 f_{\mathrm{As}}'') \\ &\qquad - R_3(f_{\mathrm{As}}^0 f_{\mathrm{As}}' + f_{\mathrm{Ga}}^0 f_{\mathrm{As}}'')]/(1 - R_3)\} = 0 \\ & f_{\mathrm{Ga}}'^2 + f_{\mathrm{Ga}}''^2 + 2\{[(f_{\mathrm{Ga}}^0 + f_{\mathrm{As}}'') - R_5(f_{\mathrm{Ga}}^0 - f_{\mathrm{As}}'')]/(1 - R_5)\} f_{\mathrm{Ga}}' - 2\{[(f_{\mathrm{As}}^0 + f_{\mathrm{As}}') \\ &\qquad + R_5(f_{\mathrm{As}}^0 + f_{\mathrm{As}}')]/(1 - R_5)\} f_{\mathrm{Ga}}'' + \{(f_{\mathrm{Ga}}^{02} + f_{\mathrm{As}}^{02} + f_{\mathrm{As}}'^2 + f_{\mathrm{As}}''^2) \\ &\qquad + 2[(f_{\mathrm{As}}^0 f_{\mathrm{As}}' + f_{\mathrm{Ga}}^0 f_{\mathrm{As}}'') - R_5(f_{\mathrm{As}}^0 f_{\mathrm{As}}' - f_{\mathrm{Ga}}^0 f_{\mathrm{As}}'')]/(1 - R_5)\} = 0 \end{aligned} \tag{3}$$

where $R_3 = I_{333}/I_{\bar{3}\bar{3}\bar{3}}$, $R_5 = I_{555}/I_{\bar{5}\bar{5}\bar{5}}$.

Absorption on the low-energy side near the edge is very faint, therefore the values of the intensity ratios R_3 and R_5 approach unity with a decrease in energy of the incident x-rays. Some of the results calculated from equation (2) or (3) might yield considerable errors sometimes. If the values of f_{Ga}' and f_{Ga}'' on the low-energy side are given by the method of Pendellösung fringes due to x-ray resonant scattering [9] and the dispersion relation [10], respectively, the above-mentioned problem can be resolved. Unfortunately, to determine the experimental data, one has to use different experimental observation methods and theoretical calculation methods. We, therefore, proceed as follows.

For a GaAs crystal, on subtraction of $|F_{\bar{h}}|^2$ from $|F_h|^2$, we obtain the equation

$$|F_h|^2 - |F_{\bar{h}}|^2 = \pm 64[f_{\mathrm{Ga}}''(f_{\mathrm{As}}^0 + f_{\mathrm{As}}') - f_{\mathrm{As}}''(f_{\mathrm{Ga}}^0 + f_{\mathrm{Ga}}')] \tag{4}$$

where $h = (hhh)$, $\bar{h} = (\bar{h}\bar{h}\bar{h})$, and (+) and (−) refer to ±(333) and ±(555), respectively.

The reflection intensities are expressed as

$$I_h = K|F_h|^2/\mu = K'|F_h|^2/(f''_{\mathrm{Ga}} + f''_{\mathrm{As}}) \tag{5}$$

where K and K' are the proportional coefficients and μ is the absorption coefficient. We make use of the expression

$$\begin{aligned}[f''_{\mathrm{Ga1}}(f^0_{\mathrm{As}} + f'_{\mathrm{As1}}) - f''_{\mathrm{As1}}(f^0_{\mathrm{Ga}} + f'_{\mathrm{Ga1}})]/[f''_{\mathrm{Ga2}}(f^0_{\mathrm{As}} + f'_{\mathrm{As2}}) - f''_{\mathrm{As2}}(f^0_{\mathrm{Ga}} + f'_{\mathrm{Ga2}})] \\ = \Delta I_1(f''_{\mathrm{Ga1}} + f''_{\mathrm{As1}})/\Delta I_2(f''_{\mathrm{Ga2}} + f''_{\mathrm{As2}})\end{aligned} \tag{6}$$

where $\Delta I = I_h - I_{\bar{h}}$, and the subscripts 1 and 2 denote the results for the low- and the high-energy sides, respectively, near the edge. Using the results on the high-energy side obtained from (3) we find the anomalous scattering factors f'_{Ga1} and f''_{Ga1} on the low-energy side near the K absorption edge from equation (6). Because f' and f'' are independent of $(\sin\theta)/\lambda$ for the Bijvoet pair [11], angle correction factors are neglected. The present calculations of f'_{Ga1} and f''_{Ga1} based on equation (6) are carried out using two methods.

(1) Making use of the intensities obtained by the different two sets of $\pm(hkl)$ reflections, we can write the relevant equations and obtain f'_{Ga1} as well as f''_{Ga1} thereby.

Using the intensities of a set of $\pm(hkl)$ reflections, such as ±(333), first evaluate

$$A_0 = f''_{\mathrm{Ga2}}(f^0_{\mathrm{As}} + f'_{\mathrm{As2}}) - f''_{\mathrm{As2}}(f^0_{\mathrm{Ga}} + f'_{\mathrm{Ga2}})$$

$$B_0 = \Delta I_2(f''_{\mathrm{Ga2}} + f''_{\mathrm{As2}})$$

$$A_{11} = (f^0_{\mathrm{As}} + f'_{\mathrm{As1}})/A_0 - \Delta I_1/B_0$$

$$A_{12} = -f''_{\mathrm{As1}}/A_0$$

$$C_1 = f''_{\mathrm{As1}}(f^0_{\mathrm{Ga}}/A_0 + \Delta I_1/B_0)$$

and then A_{21}, A_{22} and C_2 by making use of another set of $\pm(hkl)$, such as the ±(555) reflections similarly. We thus obtain

$$\begin{aligned}A_{11}f''_{\mathrm{Ga1}} + A_{12}f'_{\mathrm{Ga1}} = C_1 \\ A_{21}f''_{\mathrm{Ga1}} + A_{22}f'_{\mathrm{Ga1}} = C_2.\end{aligned} \tag{7}$$

Then the values of f'_{Ga1} and f''_{Ga1} can be determined from (7).

(2) Using each result on the high-energy side near the absorption edge, first evaluate f''_{Ga1} and then f'_{Ga1}.

Generally, the values of f'_{Ga} on the two sides of the K absorption edge have symmetry, especially near the absorption edge. So f''_{Ga1} obtained from (6) can be expressed as

$$f''_{\mathrm{Ga1}} = \{(\Delta I_1 f''_{\mathrm{As1}})/[\Delta I_2(f''_{\mathrm{Ga2}} + f''_{\mathrm{As2}})]\}B(f)/[(f^0_{\mathrm{As}} + f'_{\mathrm{As1}}) - \{\Delta I_1/[\Delta I_2(f''_{\mathrm{Ga2}} + f''_{\mathrm{As2}})]\}C(f)] \tag{8}$$

where

$$B(f) = [f''_{\mathrm{Ga2}}(f^0_{\mathrm{As}} + f'_{\mathrm{As2}}) - f''_{\mathrm{As2}}(f^0_{\mathrm{Ga}} + f'_{\mathrm{Ga2}})] + f''_{\mathrm{As1}}(f^0_{\mathrm{Ga}} + f'_{\mathrm{Ga1}})$$

$$C(f) = [f''_{\mathrm{Ga2}}(f^0_{\mathrm{As}} + f'_{\mathrm{As2}}) - f''_{\mathrm{As2}}(f^0_{\mathrm{Ga}} + f'_{\mathrm{Ga2}})].$$

By substitution of the values of f'_{Ga2} for f'_{Ga1} of the symmetry energy point, the values of f''_{Ga1} for each energy are obtained from (8) [12]. The values of the f'_{Ga1} corresponding energy point thus may be evaluated by making use of the above-mentioned f''_{Ga1} as well as the dispersion relation [10]. In the foregoing discussion the differences between the temperature factors of the Bijvoet pair have been neglected.

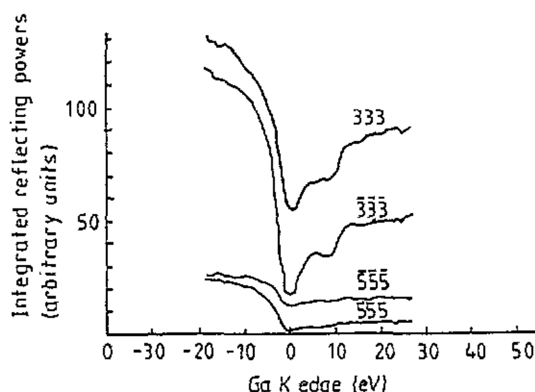

Figure 1. Integrated reflecting powers of the ±(333) and ±(555) Bijvoet pairs from GaAs near the Ga K absorption edge in the Bragg case.

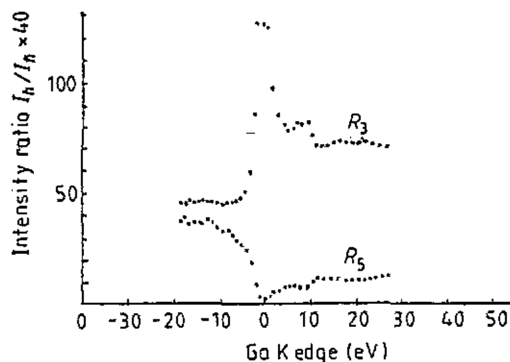

Figure 2. Reflection intensity ratios R_3 and R_5, from the ±(333) and ±(555) Bijvoet pairs of GaAs near the Ga K absorption edge in the Bragg case.

3. Results of the experimental determination and calculation

The integrated intensities of the ±(333) and ±(555) reflections for a perfect GaAs crystal were measured by the four-circle diffractometer equipped with a solid state detector at the Saitama Institute of Technology, Japan, and the Photon Factory, KEK, Tsukuba, Japan. The incident x-rays with π polarizations were chosen by a Matsushita Si monochromator from (333) reflections. In these measurements, the background has been subtracted. The measured values shown in figure 1 were standardized. The ordinates were multiplied by a suitable proportional coefficient. The R_3- and the R_5-values which are multiplied by 40.0 are shown in figure 2. The values of f^0_{Ga}, f^0_{As} and the unit-cell parameter for GaAs shown in table 1 were used in the calculation. Because variations in f'_{As} and f''_{As} near the Ga K absorption edge were small, their values were derived from the theoretical results of Sasaki [13] by the use of interpolation. Then the values of f'_{Ga} and f''_{Ga} for each energy were determined from (3), while the above values of f'_{As} and f''_{As} were used. Generally, equation (3) has two solutions for f'_{Ga} and f''_{Ga}, one of which can be chosen because of its physical significance. The values for f'_{Ga} and f''_{Ga} thus obtained are shown in figure 3 as

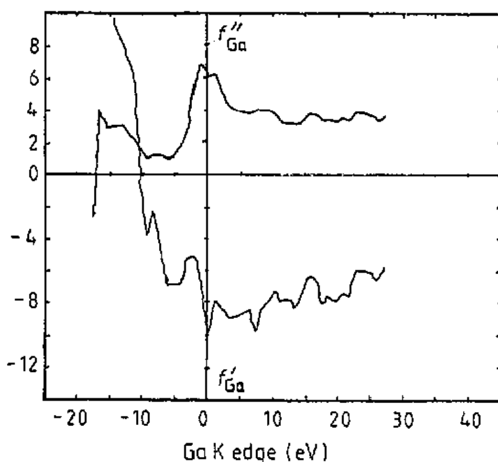

Figure 3. The values of f'_{Ga} and f''_{Ga} obtained from the intensity ratio method.

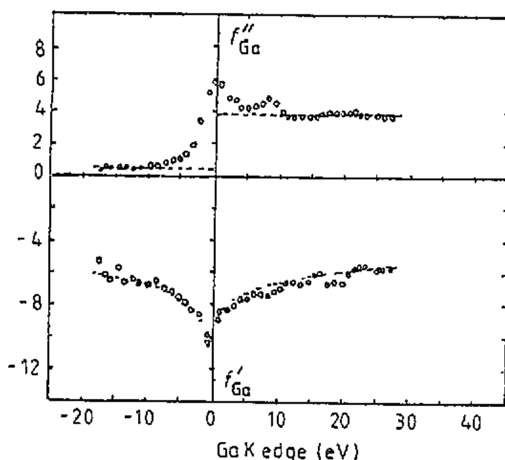

Figure 4. The values of f'_{Ga} and f''_{Ga} obtained from (7): – – –, theoretical values obtained by Sasaki.

full curves. As seen in figure 3, the curves near the edge are steeper on the low-energy than on the high-energy side. The errors in the calculated values of f'_{Ga1} and f''_{Ga1} are so large that they affect the results seriously. Therefore, we evaluate values of f'_{Ga} and f''_{Ga} on the low-energy side by using (7) and (8) again, these are shown in figures 4 and 5. For comparison, Fukamachi's [14] observational results which he obtained by another method shown in figure 6.

4. Discussion

(1) The advantage of the present method is the use of the relative quantity of the reflection

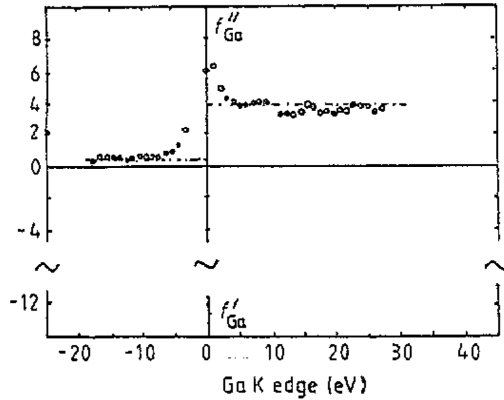

Figure 5. The values of f''_{Ga} obtained from (8): – – –, theoretical values obtained by Sasaki.

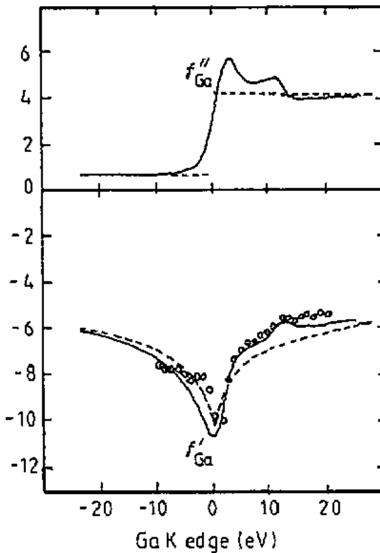

Figure 6. The values of f'_{Ga} and f''_{Ga} obtained from [14]: ——, upper curve, values of f''_{Ga} measured using the absorption coefficient μ; ——, lower curve, calculated values of f'_{Ga} based on the dispersion relation using the upper f''_{Ga}; ○, measured values.

intensity for the Bijvoet pair. Difficulties in the measured absolute quantity of reflection intensity are thus avoided.

(2) As seen in figure 3, the values of f'_{Ga1} and f''_{Ga1} obtained from the intensity ratio method are not very good within the limits of less than -10 eV. In the intensity difference ratio method, we make the best use of the enormous values of f''_{Ga2} on the high-energy side of the Ga K absorption edge and the large intensity difference between the Bijvoet pair reflections (hhh) and $(\overline{hhh})$. This enables us to reduce the relative error of our measurement. Therefore, f'_{Ga1} and f''_{Ga1} obtained from (7) and (8) shown in figures 4 and 5 show comparatively good correspondence to the theoretical values.

Table 1. Numerical values used for atomic scattering factors and other quantities.

Lattice constants of GaAs	
$a = b = c$	5.6534 Å
$\alpha = \beta = \gamma$	90°
Atomic positions	
Ga	$(0,0,0), (0,\frac{1}{2},\frac{1}{2}), (\frac{1}{2},0,\frac{1}{2}), (\frac{1}{2},\frac{1}{2},0)$
As	$(\frac{1}{4},\frac{1}{4},\frac{1}{4}), (\frac{1}{4},\frac{3}{4},\frac{3}{4}), (\frac{3}{4},\frac{1}{4},\frac{3}{4}), (\frac{3}{4},\frac{3}{4},\frac{1}{4})$
Normal atomic scattering factors	
Reflection used, $\pm(333)$	
f^0_{Ga}	16.4850
f^0_{As}	18.0820
Reflection used, $\pm(555)$	
f^0_{Ga}	9.9898
f^0_{As}	11.2174

(3) Because the intensity differences of the Bijvoet pair reflections (hhh) and $(\bar{h}\bar{h}\bar{h})$ were mainly caused by f''_{Ga}, the present method is more effective for the determination of f''_{Ga} than of f'_{Ga}.

(4) The x-ray absorption near-edge structure (XANES) on the high-energy side, which is just the same as Durham's [15] XANES and the fine structure in [14], has been given in our calculated results. This structure cannot be predicted by Sasaki's theoretical results. The theoretical results for f'_{Ga} and f''_{Ga} are different from the measured values in the present paper for f'_{Ga} and f''_{Ga} on the high-energy side near the Ga K absorption edge within roughly 30 eV of the edge. These should not be interpreted as incorrect theoretical results or experimental determinations in the present paper. The answer is that the XANES can be measured, but the data cannot be well described by the theory (see e.g. [13–15]). The theoretical calculations of f' and f'' were evaluated using a model of an isolated hydrogen-like ion. Because of the absence of the local environment of the electron and bond structure, these theoretical results are no longer true for the lattice structure. The results on f' and f'' are improved if the band theory is used in the calculations. However, there is still a difference between theoretical values and experimental determination values [14, 15]. This means that we do not find a proper wavefunction to describe the electron motion in GaAs. Thus the results of the present paper provide an incentive for improving the theory and practical application.

References

[1] Waller I 1927 *Z. Phys.* **51** 213
[2] Parratt L G and Hempstead C F 1954 *Phys. Rev.* **94** 1593
[3] Hönl H 1933 *Ann. Phys.* **18** 626; 1933 *Z. Phys.* **84** 11
[4] Cromer D T and Liberman D 1970 *J. Chem. Phys.* **53** 1891
[5] James R W 1954 *The Optical Principles of the Diffraction of X-rays* (London: Bell) ch 4
[6] Kato N and Takeda T 1977 *J. Cryst. Soc. Japan* **19** 95
[7] Hosoya S and Yamagishi T 1966 *J. Phys. Soc. Japan* **21** 2638
[8] Cole H and Stemple N R 1962 *J. Appl. Phys.* **33** 2227
[9] Yoshizawa M, Fukamachi T, Ehara K, Kawamura T, Nakajima T and Zhao Z 1990 *Photon Factory Activity Report* 8 p 123
[10] Fukamachi T, Hosoya S, Kawamura T and Okunuki M 1977 *Acta Crystallogr.* A **33** 54
[11] Hazell A C 1975 *Anomalous Scattering* ed S Ramaseshan and S C Abrahams (Copenhagen: Munksgaard) p 41
[12] Sakamaki T, Hosoya S, Tagai T, Ohsumi K and Satow Y 1984 *J. Appl. Crystallogr.* **17** 219

[13] Sasaki S 1989 *KEK Report* 88-14
[14] Fukamachi T 1977 *J. Cryst. Soc. Japan* **19** 51
[15] Durham P J, Pendry J B and Hodges C H 1981 *Solid State Commun.* **38** 159