

Angle dependence of matrix elements in X-ray bremsstrahlung isochromat spectroscopy

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

1991 J. Phys.: Condens. Matter 3 8503

(<http://iopscience.iop.org/0953-8984/3/43/016>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.159

The article was downloaded on 12/05/2010 at 10:40

Please note that [terms and conditions apply](#).

Angle dependence of matrix elements in x-ray bremsstrahlung isochromat spectroscopy

Ondřej Šipr

Institute of Physics, Czechoslovak Academy of Science, Cukrovarnická 10, 162 00 Praha 6, Czechoslovakia

Received 21 February 1991, in final form 28 May 1991

Abstract. Transition matrix elements for bremsstrahlung isochromat spectroscopy (BIS) are investigated. Contrary to formulae presented before, they are found to be dependent on the angle between the incident electron beam and the emitted bremsstrahlung radiation. The effect of using angle-dependent BIS matrix elements is demonstrated for the case of Cu.

1. Introduction

Bremsstrahlung isochromat spectroscopy (BIS) was recognized as a source of information on unoccupied electron states long ago. There is a generally accepted idea that the intensity of x-ray bremsstrahlung radiation which is emitted as a result of a deceleration of incident electrons inside a solid can be expressed as a weighted sum of partial densities of states (DOSS) n_i :

$$I \sim \sum_i |m_i|^2 n_i. \quad (1)$$

The main brake to making full use of the BIS technique was lack of knowledge of relevant matrix elements m_i . The effort to solve this problem has increased in recent years. It was recognized that matrix elements strongly depend on the isochromat energy $\hbar\omega$ [1–3]. The purpose of this paper is to demonstrate that another parameter, namely the angle ζ between the direction of the incident electron beam and the direction of the emission of detected x-ray photons, influences BIS matrix elements significantly.

The first expression for calculation of the BIS transition probability $\sigma_i \equiv |m_i|^2$ presented in equation (3) of [4] does not contain ζ at all. This seemed to indicate that the value of ζ is irrelevant to σ_i . However, as this paper shows in sections 2 and 3, equation (3) of [4] determines not the true transition probability but only a 'reduced' probability σ_i^{red} , which cannot be directly used for calculation of the BIS spectra. After proving this, it will be demonstrated in section 4 that using the true transition probabilities σ_i instead of σ_i^{red} results in experimentally observable effects. Finally, the dependence of σ_i on the angle ζ is pointed out.

2. Fundamental equations

If we neglect the inelastic energy losses of the incident electron prior to the bremsstrahlung transition, the intensity of the registered bremsstrahlung radiation can be supposed to be proportional to the probability of emission of a photon (of energy $\hbar\omega$) induced by deceleration of an electron from a high-energy state $|\psi_i\rangle$ (of energy E_i) to any low-energy state of energy $E = E_i - \hbar\omega$. First this probability w_{sc} for a single-crystal sample will be evaluated. On insertion of the Green function into the golden rule, it can be written as

$$w_{sc} = -\frac{2}{\hbar} \text{Im} \left(\sum_{\lambda=1,2} \iint d^3r d^3r' \langle \psi_i | K_\lambda^+ | r \rangle \langle r | G(E_i - \hbar\omega) | r' \rangle \langle r' | K_\lambda | \psi_i \rangle \right) \quad (2)$$

where K_λ is the Hamiltonian of the electromagnetic interaction (λ identifies the polarizations of the radiation). The muffin-tin form of the potential $V(\mathbf{r})$ is assumed so that $V(\mathbf{r}) = \sum_m V^m(\mathbf{r})$, $V^m(\mathbf{r}) \neq 0$ only for $|\mathbf{r} - \mathbf{R}^m| < |R_{MT}^m|$.

Arguments presented in [2, 4, 5] allow us to concentrate on a single muffin-tin sphere—particularly that muffin-tin sphere, near the centre of which the deceleration of the electron takes place ('single-site approximation'). We denote this muffin-tin sphere by index 0. Having this in mind and employing the multiple-scattering expansion of the Green function [6, 7], we can obtain finally [8]

$$w_{sc} = -\frac{2\pi^2 m^2}{\hbar^5 k^2} \text{Im} \left(\sum_\lambda \sum_{LL'} (\mu_L^{(\lambda)})^* \frac{\tau_{LL'}^{00}}{\sin \delta_l^0 \sin \delta_{l'}^0} \mu_L^{(\lambda)} \right). \quad (3)$$

The matrix element $\mu_L^{(\lambda)}$ is defined as

$$\mu_L^{(\lambda)} = \int d^3r Q_L^0(\mathbf{r}) K_\lambda(\mathbf{r}) \psi_i(\mathbf{r}) \quad (4)$$

where $Q_L^0(\mathbf{r})$ is a solution of the Lippmann–Schwinger equation:

$$Q_L^0(\mathbf{r}) = \sqrt{\frac{2}{\pi}} k j_l(kr) Y_L(\mathbf{r}) + \int d^3r' G_0(\mathbf{r}, \mathbf{r}') V^0(\mathbf{r}') Q_L^0(\mathbf{r}') \quad (5)$$

($G_0(\mathbf{r}, \mathbf{r}') \equiv \langle \mathbf{r} | G_0(E_i - \hbar\omega) | \mathbf{r}' \rangle$ is a free-electron Green function) and the scattering matrix $\tau_{LL'}^{00}$, satisfies the equation [9]

$$\tau_{LL'}^{mn} = t_L^m \delta^{mn} \delta_{LL'} + \sum_p \sum_{L''} t_L^m g_{LL''}^{m''} \tau_{L''L'}^{pn} \quad (6)$$

where

$$g_{LL'}^{mn} = -4\pi(1 - \delta_{mn}) i \frac{\pi m}{\hbar^2 k} \sum_{L''} i^{l''+l'-l} h_{l''}^{(+)}(k|\mathbf{R}^m - \mathbf{R}^n|) Y_{L''}(\mathbf{R}^m - \mathbf{R}^n) \\ \times \int d^2n Y_L(\mathbf{n}) Y_{L'}(\mathbf{n}) Y_{L''}(\mathbf{n}) \quad (7)$$

represents the free-electron propagator and

$$t_L^p = \int d^3r \sqrt{\frac{2}{\pi}} k j_l(kr) Y_L(\mathbf{r}) V^p(\mathbf{r}) Q_L^0(\mathbf{r}) \\ = -\frac{\hbar^2 k}{\pi m} \sin \delta_l^p \exp(i\delta_l^p) \quad (8)$$

is the scattering matrix of a scattering centre R^p . Note that $k = \sqrt{2mE}/\hbar$, $L = (lm)$ is a multi-index and $Y_L(r)$ denotes real spherical harmonics. According to [5, 10], the initial state $|\psi_i\rangle$ can be written as

$$\psi(r) = \frac{1}{(2\pi\hbar)^{3/2}} \sqrt{\frac{\pi}{2}} \frac{1}{k'} \sum_l 4\pi i^l \exp[i\delta_l(k')] R_{k'l}^0(r) \sum_m Y_{lm}(r) Y_{lm}(k') \tag{9}$$

where k' is the wavevector of the high-energy incident electron and $R_{k'l}^0(r)$ is the radial solution of the Schrödinger equation for the potential $V^0(r)$, normalized to the δ -function of the wavenumber k .

In order to get (3) into the desired form (1), it is necessary to express the DOS n_l in terms of the scattering matrix τ_{LL}^{00} . Starting from the 'definition' of the local DOS per Wigner-Seitz sphere (with radius r_{WS})

$$n^{WS} \equiv -\frac{1}{\pi} \text{Im} \left(\int_0^{r_{WS}} r^2 dr d\Omega G(r, r) \right) \tag{10}$$

and again using the multiple-scattering expansion of the Green function, the partial DOS n_l^{WS} can be introduced:

$$n_l^{WS} = -\frac{\pi m^2}{\hbar^4 k^2} \sum_m \text{Im} \left[\tau_{LL}^{00} \int_0^{r_{WS}} 4\pi r^2 dr \left(\frac{R_{kl}(r)}{\sin \delta_l^0} \right)^2 \right] \tag{11}$$

($R_{kl}(r)$ is the radial part of the wavefunction $Q_L^0(r)$, normalized to the δ -function of k), so that $n^{WS} = \sum_l n_l^{WS}$ (cf [11, 12]).

Incorporating of n_l^{WS} into (3) is possible in the case when the non-diagonal elements of the scattering matrix τ_{LL}^{00} are zero. This is exactly true for example in the case of cubic symmetric crystals for $l \leq 2$; however, practical calculations indicate that this condition is fulfilled within sufficient accuracy for higher l -numbers of interest, too. Hence, w_{SC} can be written as

$$w_{SC} = -\frac{2\pi^2 m^2}{\hbar^5 k^2} \sum_l \sum_m \left(\sum_\lambda (\mu_{lm}^{(\lambda)})^* \mu_{lm}^{(\lambda)} \right) \text{Im} \left(\frac{\tau_{lm,lm}^{00}}{\sin^2 \delta_l^0} \right). \tag{12}$$

Still it is necessary to remove the dependence of the term $\sum_\lambda (\mu_{lm}^{(\lambda)})^* \mu_{lm}^{(\lambda)}$ on the m -number.

3. Orientational averaging

The magnetic quantum number m describes the orientation of crystal axes with respect to a preferred direction, i.e. with respect to the direction of the incident electron beam in this case. Its significance can be suppressed by performing orientational averaging of the sample, which is equivalent to calculating the BIS spectrum for a polycrystal instead of for a single crystal. Realizing that

$$\begin{aligned} K_\lambda &= f\epsilon^{(\lambda)} \cdot r \\ &= (1/m\omega^2) f\epsilon^{(\lambda)} \cdot \nabla V^0(r) \end{aligned} \tag{13}$$

in the dipole approximation ($\epsilon^{(\lambda)}$ is a polarization vector and f is a normalization-dependent factor), $\mu_L^{(\lambda)}$ can be factorized as

$$\mu_L^{(\lambda)} = \sum_l \frac{f}{\hbar^{3/2}} \frac{1}{k'} i^l \exp[i\delta_l^0(k')] q_{ll} v_{lm,l}^{(\lambda)} \quad (14)$$

where the radial part is

$$\begin{aligned} q_{ll} &= \int r^2 dr R_{kl}(r) r R_{k'l'}^0(r) \\ &= \frac{1}{m\omega^2} \int r^2 dr R_{kl}(r) \frac{dV}{dr} R_{k'l'}^0(r) \end{aligned} \quad (15)$$

and the angular part (guaranteeing the dipole selection rule $l' = l \pm 1$) is

$$v_{lm,l'}^{(\lambda)} = \sum_{m'=-l}^l Y_{l'm'}(k') \int d^2n Y_{lm}(n) \epsilon^{(\lambda)} \cdot n Y_{l'm'}(n). \quad (16)$$

Oriental averaging of (12) is equivalent to integration over all those values of $\epsilon^{(\lambda)}$ which keep the angle ζ as well as the k' -direction fixed, followed by integration over all directions of k' —we denote it by $(1/8\pi^2) \int_{\text{ort}} d\epsilon^{(\lambda)} d^2k'$ (the factor $1/8\pi^2$ ensures the same normalization for both a single-crystal and a polycrystal sample). The probability of emission of a bremsstrahlung photon from a polycrystal sample is then

$$\begin{aligned} w_{\text{PC}} &= -\frac{2\pi^2 m^2 f^2}{\hbar^5 k^2} \frac{1}{\hbar^3 k'^2} \sum_l \sum_m \text{Im} \left(\frac{\tau_{LL}^{(0)}}{\sin^2 \delta_l} \right) \frac{1}{8\pi^2} \sum_{l'l''} i^{l'-l''} \exp[i\delta_{l'}(k')] \\ &\quad \times \exp[-i\delta_{l''}(k')] q_{ll} q_{l'l''} \frac{1}{8\pi^2} \sum_{\lambda} \int_{\text{ort}} d\epsilon^{(\lambda)} d^2k' v_{lm,l}^{(\lambda)} v_{lm,l''}^{(\lambda)}. \end{aligned} \quad (17)$$

Introducing polar coordinates of the unit k' -vector, namely

$$k' = \begin{pmatrix} \cos \varphi \sin \theta \\ \sin \varphi \sin \theta \\ \cos \theta \end{pmatrix} \quad (18)$$

the polarization vectors of the BIS radiation can be chosen for example as

$$\epsilon^{(1)} = \begin{pmatrix} \cos \varphi \cos \theta \cos \delta - \sin \varphi \sin \delta \\ \sin \varphi \cos \theta \cos \delta + \cos \varphi \sin \delta \\ -\sin \theta \cos \delta \end{pmatrix} \quad (19)$$

$$\epsilon^{(2)} = \begin{pmatrix} -\cos \varphi \cos \theta \sin \delta \cos \zeta - \sin \varphi \cos \delta \cos \zeta + \cos \varphi \sin \theta \sin \zeta \\ -\sin \varphi \cos \theta \sin \delta \cos \zeta + \cos \varphi \cos \delta \cos \zeta + \sin \varphi \sin \theta \sin \zeta \\ \sin \theta \sin \delta \cos \zeta + \cos \theta \sin \zeta \end{pmatrix} \quad (20)$$

(note that $\epsilon^{(1)} \perp k'$, $\epsilon^{(1)} \perp \epsilon^{(2)}$, $\delta \in (0, 2\pi)$) represents the degree of freedom connected

with the rotation of the sample around the k' -vector direction) and the expression $\sum_{\lambda} \int_{\text{ort}} d\epsilon^{(\lambda)} d^2k' v_{lm,l'}^{(\lambda)} v_{lm,l''}^{(\lambda)}$ can be written as

$$\sum_{\lambda} \int_{\text{ort}} d\epsilon^{(\lambda)} d^2k' v_{lm,l'}^{(\lambda)} v_{lm,l''}^{(\lambda)} = \sum_{\lambda} A_{(lm)(lm)l'l''}^{(\lambda)} \tag{21}$$

$$A_{(lm)(l'm')l'l''}^{(\lambda)} = \int_0^{2\pi} d\varphi \int_0^{\pi} \sin \theta d\theta \int_0^{2\pi} d\delta v_{lm,l'}^{(\lambda)} v_{l'm',l''}^{(\lambda)} \tag{22}$$

where $v_{lm,l'}^{(\lambda)}$ is defined by (16) and k' and $\epsilon^{(\lambda)}$ by (18)–(20).

In order that equation (11) could be inserted into (17), $\sum_{\lambda} \int_{\text{ort}} d\epsilon^{(\lambda)} d^2k' v_{lm,l'}^{(\lambda)} v_{lm,l''}^{(\lambda)}$ must not depend on the quantum number m . The present author cannot demonstrate this independence analytically. However, the ‘matrix’ $A_{(lm)(l'm')l'l''}^{(\lambda)}$ was tested numerically for many values of the angle ζ for l as high as 11 (i.e. even for much higher l -values than those which are required for practical BIS calculations; see, e.g., [10] or [13]) and found to be diagonal in both l, l' and m, m' as well as independent of m within the numerical accuracy of the calculation (the relative error was found to be less than 10^{-14} for a 64-bit internal representation of real-type variables). This indicates that the assumption of independence of $\sum_{\lambda} \int_{\text{ort}} d\epsilon^{(\lambda)} d^2k' v_{lm,l'}^{(\lambda)} v_{lm,l''}^{(\lambda)}$ on m is true and hence it will be presupposed in the rest of this paper. The fact that it was not proven rigorously does not affect the validity of the results presented in section 4, since the independence of $A_{(lm)(lm)l'l''}^{(\lambda)}$ on m was tested for every particular calculation.

Having all this in mind, we can denote

$$\frac{1}{8\pi^2} \sum_{\lambda} \int_{\text{ort}} d\epsilon^{(\lambda)} d^2k' v_{lm,l'}^{(\lambda)} v_{lm,l''}^{(\lambda)} = p_{l,l',l''}(\zeta) \tag{23}$$

and write finally

$$w_{\text{PC}} = \sum_l \sigma_l n_l^{\text{WS}} \tag{24}$$

where n_l^{WS} is determined by (11) and

$$\sigma_l = \frac{2\pi f^2}{\hbar^4 k'^2} \frac{1}{[s_l(k)]^2} \sum_{l',l''} i^{l'-l''} \exp[i\delta_{l'}(k')] \exp[-i\delta_{l''}(k')] q_{ll'} q_{ll''} p_{l,l',l''}(\zeta) \tag{25}$$

the Wigner–Seitz normalization factor being

$$s_l(k) = \left(\int_0^{r_{\text{WS}}} 4\pi r^2 dr [R_{kl}(r)]^2 \right)^{1/2} \tag{26}$$

When no sharp (e.g. plasmon) peaks occur in the electron-energy-loss spectrum, w_{PC} can be compared with the experimental BIS intensity directly [9]; otherwise including energy losses by convolution of w_{PC} with an electron-energy-loss function is necessary [14].

On comparison of (25) with equation (3) of [4], it can be seen that the latter equation determines not the true transition probability σ_l but only a ‘reduced transition probability’

$$\sigma_l^{\text{red}} = \frac{\omega^4}{k'^2} \frac{1}{[s_l(k)]^2} \sum_{l',l''} \exp[i\delta_{l'}(k')] \exp[-i\delta_{l''}(k')] q_{ll'} q_{ll''} \delta_{l',l \neq 1} \tag{27}$$

provided that the high-energy radial wavefunction of [4] is normalized as it is in [12] or

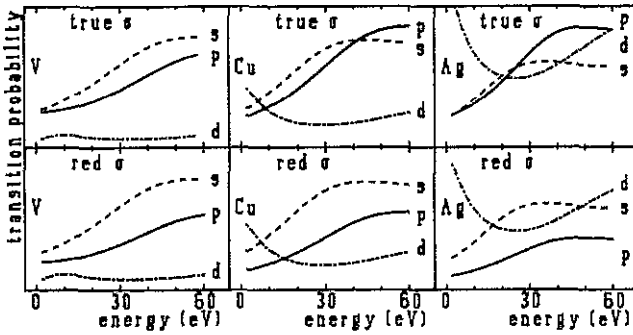


Figure 1. BIS transition probability σ_l together with reduced transition probability σ_l^{red} for metallic V, Cu and Ag ($\zeta = 40^\circ$; isochromat energy, 1487 eV).

[15]. The fundamental difference between σ_l in (25) and σ_l^{red} in (27) consists in the omission of the ζ -dependent factor $i^{l'-l} p_{l,l',r}(\zeta)$ in σ_l^{red} . This difference does not depend on the precise form of the normalization of the high-energy wavefunction.

4. Numerical examples

In order to demonstrate the effect of this difference, figure 1 shows the transition probabilities σ_l together with the reduced transition probabilities σ_l^{red} for three metals for the 1487 eV isochromat (an additional factor was introduced into (27) in order to obtain both σ_l and σ_l^{red} on the same scale). The angle ζ was taken to be 40° , which is roughly the value at which the experimental spectra in [4] or [13] were measured [16]. It is evident that σ_l^{red} does not provide the correct weights of particular l -symmetries.

In spite of that, BIS spectra calculated using σ_l^{red} instead of σ_l agree with experiment fairly well [3, 4]. This can be caused partly by the fact that the partial DOS for different l may be quite similar to each other and partly by the fact that the oscillations of the total BIS spectral curve can be dominated rather by the most significantly oscillating l -component than by the component which gives the highest absolute contribution. Nevertheless, the difference between σ_l and σ_l^{red} can be observed experimentally, as is demonstrated for the case of the BIS spectrum of Cu; figure 2 shows experimental BIS oscillations (i.e. the raw BIS spectrum in [13] subtracted by a smooth curve) together with two theoretical BIS spectra calculated according to (24), using both σ_l and σ_l^{red} . The partial DOS data were provided by Zeller (see, e.g., [13] for details of DOS calculations); the radial parts of the matrix elements $q_{ll'}$ were calculated by the method presented in [17]. Both theoretical spectra were broadened by a convolution with the same energy-dependent Lorentzian [18].

Although the overall shapes of both theoretical spectra are similar, a significant difference arises in the structure of the broad peak at about 9–14 eV. While use of σ_l^{red} implies that the subpeak at 9.5 eV is higher than the subpeak at 13.5 eV, the correct theoretical spectrum (obtained using σ_l) as well as the experiment clearly show that the first subpeak is lower than the second subpeak.

Finally, figure 3 displays the relative magnitude of the Cu transition probabilities σ_l with respect to $\sigma_{l=1}$ for three values of ζ . It demonstrates that the angle ζ may be crucial

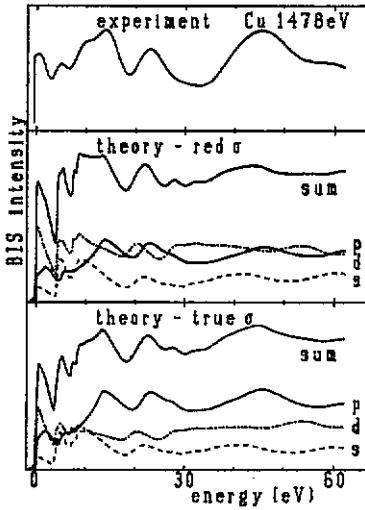


Figure 2. BIS spectrum of Cu for 1487 eV isochromat energy. The experimental data are from [14]; the theoretical spectra ($\zeta = 40^\circ$) were calculated for identical partial DOSs but different transition probabilities.

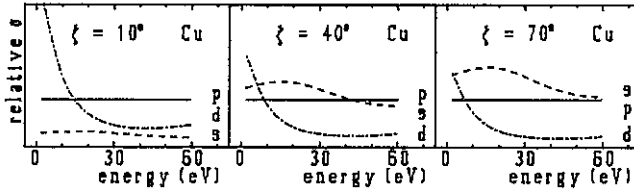


Figure 3. The quotient σ_l/σ_1 for Cu (isochromat energy, 1487 eV) for three values of the angle ζ .

for the ratio between transition probabilities σ_l and hence for the significance of particular l -components in the BIS spectrum.

5. Conclusions

The overall agreement of BIS spectra computed using reduced transition probabilities σ_l^{red} with experiment indicates that the l -selectiveness of BIS spectra is not very high. Nevertheless, the transition probabilities σ_l may play a more significant role in materials with a strongly l -dependent partial DOS.

Moreover, the ζ -dependence of σ_l indicates that the angle ζ is a parameter which is characteristic of each experimental BIS spectrum, in a similar way to the isochromat energy $\hbar\omega$. One can imagine that relative weights of particular l -symmetries could be changed using different angles ζ , in a similar manner to which they can be changed using different isochromat energies.

Acknowledgments

This work was stimulated by the author's visit to Institut für Festkörperforschung des Forschungszentrums Jülich. The author would like to thank R Zeller for the permission

to use his band-structure results and W Speier for the provision of experimental data. Thanks are also due to J Vackář for the provision of the computer code calculating the radial part of matrix elements.

References

- [1] Chu C and Best P E 1979 *Phys. Rev. B* **19** 3414
- [2] Šimůnek A, Vackář J and Sobczak E 1988 *Phys. Rev. B* **38** 8515
- [3] Speier W 1988 *J. Phys. C: Solid State Phys.* **21** L1183
- [4] Speier W, Fuggle J, Durham P, Zeller R, Blake R and Sterne P 1988 *J. Phys. C: Solid State Phys.* **21** 2621
- [5] Winter H, Durham P J and Stocks G M 1984 *J. Phys. F: Met. Phys.* **14** 1047
- [6] Faulkner J and Stocks G M 1980 *Phys. Rev. B* **21** 3222
- [7] Zeller R 1987 *J. Phys. C: Solid State Phys.* **20** 2347
- [8] Šipr O, Vackář J and Šimůnek A 1991 *Phys. Rev. B* **44** 4832
- [9] Durham P J, Pendry J B and Hodges C H 1982 *Comput. Phys. Commun.* **38** 159
- [10] Šimůnek A, Šipr O and Vackář J 1989 *Phys. Rev. Lett.* **63** 2076
- [11] Gyorfyy B L and Stott M J 1973 *Band Structure Spectroscopy of Metals and Alloys* ed J Fabian and L M Watson (New York: Academic) p 385
- [12] Durham P J 1988 *X-ray Absorption* ed D C Kroningsberger and R Prins (New York: Wiley) p 53
- [13] Speier W, Zeller R and Fuggle J 1985 *Phys. Rev. B* **32** 3597
- [14] Hoekstra H, Speier W, Zeller R and Fuggle J 1986 *Phys. Rev. B* **34** 5177
- [15] Durham P J 1981 *J. Phys. F: Met. Phys.* **11** 2475
- [16] Speier W 1990 private communication
- [17] Vackář J, Šimůnek A and Šipr O 1991 *Comput. Phys. Commun.* **66** 259
- [18] Müller J, Jepsen O and Wilkins J 1982 *Solid State Commun.* **42** 365