concerning the interpretation of the very-high-frequency shell-model modes.

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Wavelength-Dependent Measurements of Extinction in an Extended-Face Crystal of Zinc Selenide

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Abstract

The effect of extinction on Bijvoet ratios is demonstrated. It is suggested that an observed anomaly in the wavelength dependence of ZnSe Bijvoet ratios is due to the Borrmann effect. It is shown that wavelength-dependent studies of extinction may be used to obtain extinction parameters from relative intensity measurements without resorting to a refined scale factor.

Introduction

The importance of the extinction problem derives from the common necessity of using available crystals which satisfy neither the perfection criteria of dynamical theory nor those of kinematic theory.

The most commonly used extinction theory is that first derived by Zachariasen (1967) from a set of transfer equations and later revised by Becker & Coppens (1974*a*,*b*). Various authors have discussed the shortcomings of Zachariasen's theory, the main criticisms being its kinematical nature and resulting inapplicability in the case of severe primary extinction (Werner, 1969; Lawrence, 1972), its neglect of the angle dependence of the effective path length through the crystal (Cooper & Rouse, 1970) and its failure in cases of severe extinction (Cooper & Rouse, 1970; Becker & Coppens, 1974*a*). Most tests of the validity of this theory known to us include a simultaneous refinement of the extinction parameter(s) and a scale factor (*e.g.* Zachariasen, 1968*a*; Cooper, Rouse & Fuess, 1973), notwithstanding the high correlation usually observed between these parameters (Lander & Mueller, 1970; Stevens & Coppens, 1975).

The ZnSe specimen used in this study has the cubic zinc-blende structure. The noncentrosymmetric nature of this structure and the presence of anomalous dispersion effects results in the manifestation of non-zero Bijvoet ratios, which has been discussed by McIntyre, Moss & Barnea (1980) (hereafter referred to as MMB) and corresponds to a breakdown of Friedel's law (Friedel, 1913).

The work described in this paper arose from the observation that measurements of Bijvoet ratios may be significantly affected by extinction [see Ramaseshan & Abrahams (1975) for discussions on this subject and Cole & Stemple (1962) and Fukamachi, Hosoya & Okunuki (1976) regarding the intensity ratio of Friedel-pair reflections]. In attempting to estimate the effects of extinction upon the Bijvoet ratios at various wavelengths, we found that we could derive values of extinction parameters without resorting to refined scale factors. However, we encountered a distinct region between the K absorption edges of zinc and selenium in which the derivation of consistent parameters proved impossible. We suggest that the systematic inconsistency in this region is due to an enhanced contribution from the Borrmann effect (Borrmann, 1941; Zachariasen, 1968*b*,*c*).

The most common method of obtaining values of the conventional extinction parameters r and g (the mean radius of the perfect-crystal domains and the quantity in the isotropic Gaussian distribution law describing the misalignment of the domains, respectively) is to carry out least-squares refinements of data obtained at two different wavelengths (λ). In so doing one obtains two

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values for the refined parameter r^* (the effective domain radius), from which r and g can be determined (Zachariasen, 1968*a*), where

$$r^* = r[1 + (r/\{\lambda g\})^2]^{-1/2}.$$

However, in light of the anomalous wavelength dependence of r^* which has been observed by Prager (1971) [see also Dawson (1975)], some values of r and g so obtained must, in the absence of further corroborative evidence, be treated with some suspicion. Cooper, Rouse & Fuess (1973) have emphasized the 'danger associated with the derivation of r and g values from data obtained at two wavelengths only' and also point out that the uncertainty in such values can be extremely large [see also Cooper & Rouse (1976)]. Least-squares refinements using data at several wavelengths require a large amount of time, for both data collection and analysis. Thus the possibility of deriving r and g values from accurate measurements of a limited number of scale-factor-independent Bijvoet ratios at several wavelengths is an attractive one.

The wavelength dependence of extinction effects remains, in spite of many attempts, largely untested (*e.g.* Marezio, 1966; Zachariasen, 1967; Prager, 1971; Dawson, 1975; Niimura, Tomiyoshi, Takahashi & Harada, 1975; Cooper & Rouse, 1976; Howard & Jones, 1977; Cooper, 1979). Most of the recent work, both theoretical and experimental, has been concerned with extinction effects at a single wavelength, with little regard for their wavelength dependence.

The effect of extinction on the Bijvoet ratios

The effect of extinction upon the Bijvoet ratio (B) is clear from an inspection of its definition when the extinction factors y_{hkl} are included:

$$B = 2(I_{hkl}y_{hkl} - I_{\bar{h}\bar{k}\bar{l}}y_{\bar{h}\bar{k}\bar{l}})/(I_{hkl}y_{hkl} + I_{\bar{h}\bar{k}\bar{l}}y_{\bar{h}\bar{k}\bar{l}}), \quad (1)$$

where I_{hkl} is the kinematic intensity of a set of reflections (represented by the Miller indices hkl) which remain equivalent after allowance for dispersion effects. Since $y_{hkl} \neq y_{\bar{h}\bar{k}\bar{l}}$ in general, the effect due to extinction does not cancel out and as extinction is more severe for the stronger reflection this effect always results in a decrease in the magnitude of the Bijvoet ratio, with the sign remaining unchanged. The extent of the reduction, which depends both on the magnitude of the Bijvoet ratio and the severity of the extinction, is usually assumed to be negligible. That this is not so, even for moderate values of both, is illustrated in Fig. 1 with the aid of ZnSe data from MMB.

Fig. 1 shows a plot of observed and calculated Bijvoet ratios, B_{obs} and B_{calc} (including the calculated values of y_{hkl} and $y_{\bar{h}\bar{k}\bar{l}}$), each divided for convenience by B_{kin} [kinematically calculated; $y_{hkl} = y_{\bar{h}\bar{k}\bar{l}} = 1$ in (1)]. We note that the values of B_{obs} listed by MMB for the $311/31\bar{1}$ and $331/33\bar{1}$ pairs of reflections should read −3·8 and 6·4% respectively.

While one might well wish that the agreement between the calculated and experimental results were more convincing, Hamilton R factors, first calculated for all the ratios represented in Fig. 1 with unit weights, under the assumption that they are affected by extinction, and then on the assumption that they are not, were found to be 0·109 and 0·117, respectively. The resultant ratio of R factors corresponds to a rejection of the hypothesis that extinction does not affect B_{obs}/B_{kin} at the 1% significance level (Hamilton, 1965). In any case, the experimental error in the values of B_{obs}, estimated from differences between equivalent reflections, was about ±1·5% (MMB). We should note that we could find no specific reason for the large deviations of the two points marked by solid triangles and corresponding to the 331 and 533 reflections. The 331, in particular, was remeasured under conditions where the possibility of multiple diffraction and harmonic contamination of the incident beam were excluded; perhaps the 331 falls in a region where the effects due to extinction and bonding are comparable.

In any case, the point we wish to make is that neglect of extinction when interpreting Bijvoet ratios should by no means be automatic. Also, further measurements of the effect of extinction on Bijvoet ratios in noncentrosymmetric crystals with more severe extinction would be most desirable and may in certain instances constitute a sensitive test of extinction theory. It was with this in mind that we decided to investigate ZnSe at other wavelengths.

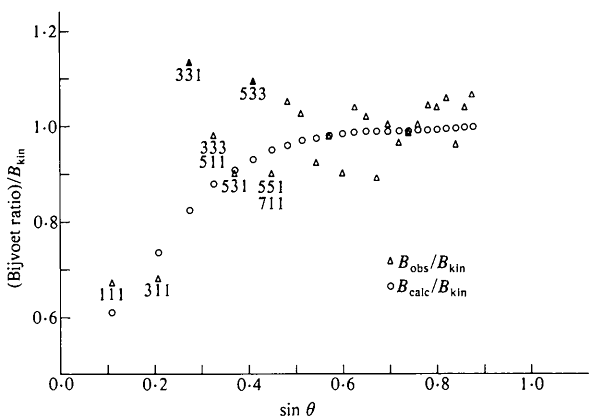

Fig. 1. The variation of observed and calculated Bijvoet ratios, each divided by the kinematically calculated B_{kin}, with sin θ (where θ is the Bragg angle). Miller indices for some of the low-angle data are indicated. In cases where more than one ratio occurs at the same value of sin θ, the average is plotted for clarity.

Experimental

X-ray measurements were carried out with a large as-grown single crystal of cubic ZnSe mounted on a eucentric goniometer head and previously used by MMB. Parker (1971) describes the method of growth and the physical properties of this crystal, whose extended face was a very smooth 100 growth face in the shape of a truncated 11 × 13 mm rectangle. The advantages of using the extended-face-crystal technique (Mair, Prager & Barnea, 1971*b*; Freeman, Mair & Barnea, 1977) for accurate measurement of Bijvoet ratios have been expounded by Mair, Prager & Barnea (1971*a*). The intensities were measured on a Philips PW1100/20 computer-controlled four-circle diffractometer powered by a stabilized Philips PW1130/90 generator and using a NaI(Tl) scintillation detector in conjunction with pulse-height analysis.

Integrated intensities were obtained in an ω–2θ scan of width 3° θ starting 1·5° θ below the peak maximum. Background was measured from stationary counts at both limits of the scan. The measurements were carried out at 292 (2) K.

All but the most insignificant multiple diffraction effects were avoided by rotating the crystal about the scattering vector of a given reflection (azimuthal scan) and finding a position in which the Bragg intensities showed no irregularities (Prager, 1971; Post 1976). All measurements were carried out in two aspects (generally asymmetric) and averaged, a procedure which provides an experimental correction for absorption (Mair, Prager & Barnea, 1971*a*). The Bragg intensities were measured in positions no more than 2° in azimuth from the symmetric aspects. Mathieson (1975) has shown that the inclusion of surface-layer effects for extended-face crystals in the formula for the integrated intensity requires an additional factor of the form

$$\exp\{-\mu' t[\operatorname{cosec}(\theta+\alpha)+\operatorname{cosec}(\theta-\alpha)]\},$$

where μ' is the effective absorption coefficient for the surface layer of thickness t and α is the angle between the crystal surface and the crystal plane in question, as viewed by the incident beam. In the present work, α is always small in comparison with θ and this additional factor can be approximated by

$$\exp\{-2\mu' t \operatorname{cosec}\theta\},$$

which, although worth considering for the integrated intensity, does not enter the expression for the Bijvoet ratio.

The X-radiation for this experiment was supplied by Ag, Mo and Cu tubes used in conjunction with a graphite (002) flat-crystal monochromator and three incident-beam collimators (of diameters 0·3, 0·5 and 0·8 mm). Using both the characteristic K lines and the *Bremsstrahlung*, we selected a set of 21 wavelengths in the range from 0·561 to 1·542 Å. The lower-wavelength limit was selected to ensure that the Bragg angles for the reflections of interest in this study were not too small, since this could result in anomalies in the measured intensities due to surface effects (the diffractometer angle χ was restricted for the same reason). When using *Bremsstrahlung* the adjustment of the tower angle, to maximize the diffracted intensity of some strong reflection, is more difficult. This contributes to the error associated with the quoted wavelength of the incident radiation which is in any case larger than that for characteristic radiation. The optimized tower angles for the characteristic radiations were used to obtain the tower angles for the desired wavelengths of *Bremsstrahlung*. Measurements taken in the vicinity of the K absorption edges of Zn and Se (1·283 and 0·9798 Å, respectively) provided a sensitive test of the accuracy of wavelength determinations. The estimated maximum error in the wavelength determination is 1%.

Bremsstrahlung used was always obtained with a tube whose characteristic K lines were not in the vicinity of the desired wavelength. Some measurements of Bijvoet ratios were obtained with *Bremsstrahlung* from two different tubes and/or with different generator settings in order to check consistency, which was satisfactory, *i.e.* agreement was obtained within the estimated standard deviations. Various generator settings were used throughout the data collection and, wherever possible, were chosen so as to eliminate any harmonic contamination of the incident beam (Mair, Prager & Barnea, 1971*b*).

The measured intensities of a particular reflection from different parts of the extended face of our specimen varied by considerably less than 1%. This implies that the possible inhomogeneity of the perfection of our crystal specimen (Gay & Hirsch, 1953; Boehm, Prager & Barnea, 1974) is not significant.

The internal consistency of the measured integrated Bragg intensities was judged by the agreement between symmetrically equivalent reflections, each having been measured several times in two aspects. The average deviation of an intensity from the mean value of the set of measurements to which it belonged was less than 2% and consistent with a small degree of anisotropy in the extinction (not of sufficient magnitude to warrant further consideration). Long-term fluctuations in the system were monitored by remeasuring certain reference reflections at regular intervals throughout the data collection. These fluctuations proved to be insignificant.

Analysis

The calculated Bijvoet ratios were formed by substituting absolute values of calculated structure factors ($|F|$'s) and extinction factors in the following equation:

$$B=\frac{2(|F_{hkl}|^2y_{hkl}-|F_{\bar h\bar k\bar l}|^2y_{\bar h\bar k\bar l})}{(|F_{hkl}|^2y_{hkl}+|F_{\bar h\bar k\bar l}|^2y_{\bar h\bar k\bar l})}. \qquad (2)$$

Trial calculations revealed that the inclusion of bonding (Moss, 1977) and anharmonic effects (MMB) in the calculated structure factors had an insignificant effect on the calculated Bijvoet ratios of interest here and so only harmonic temperature factors were included. These were calculated using the lattice parameter a = 5·6670 Å (ASTM file, 1953) and the temperature parameters B_{Zn} = 1·021 (4) and B_{Se} = 0·743 (6) Å^2 (MMB). MMB corrected their intensity data for the effects of one-phonon thermal diffuse scattering (TDS) prior to least-squares analysis and so the refined values of the temperature parameters have not been artificially reduced, as is the case in the absence of such corrections. The observed integrated intensities in this study were not corrected for TDS effects because such corrections do not significantly affect the values of the observed Bijvoet ratios.

The relativistic Hartree–Fock spherical X-ray atomic scattering factors of Doyle & Turner (1968) were used in the structure factor calculations. The wavelength-dependent anomalous dispersion corrections (especially the imaginary correction f''), necessary for structure factor calculation, are of course of particular importance in this study. It is noted that the wavelengths at which Bijvoet ratios were measured are not so close to the K absorption edges as to be affected by extended X-ray absorption fine structure (EXAFS) (with the possible exception of the measurements at 1·250 Å which is less than 300 eV above the Zn absorption edge). Anomalous dispersion corrections were calculated in two ways. The first method employs Hönl's equations (Hönl, 1933*a*,*b*; Barnea, 1966), which include only effects due to K-shell electrons and so are better suited to light elements where effects due to other shells are less important. Zn and Se are both relatively light elements with L absorption edges quite removed from the region of interest. Hönl's equation for f'' is only valid for wavelengths less than that of the K absorption edge. The second method for calculating the dispersion corrections is that described by Barnea (1966). The value of f'' was obtained from a formula expressing the direct proportionality between f'' and the mass absorption coefficient, values of which were calculated using the photoelectric cross sections of Veigele (1973). The value of the real dispersion correction f' was then obtained using this f'' value and both of Hönl's equations.

There are small systematic discrepancies between the values obtained for f' and f'' by the two methods described above. However, the second method yields the values in best agreement with those of Cromer & Liberman (1970) and Hazell (1967) for $K\alpha_1$ and $K\beta$ radiations, respectively, and it was these values which were used in the analysis. The f' and f'' values from the second method were supplemented by f' values from the first for wavelengths greater than that of the corresponding K absorption edge, the Bijvoet ratios being, in any case, relatively insensitive to f'.

Calculated values of the wavelength-dependent linear absorption coefficients, required for the calculation of the extinction factors, were compared using three different sources: (i) photoelectric cross sections from *International Tables for X-ray Crystallography* (1974); (ii) mass absorption coefficients from *International Tables for X-ray Crystallography* (1962); (iii) photoelectric cross sections from Veigele (1973). The linear absorption coefficients from (ii) and (iii) are in good agreement, but those from (i) show systematic discrepancies below the absorption edges. Finally, values calculated using (iii) and ranging from 174·3 cm^{-1} (0·561 Å) to 747·0 cm^{-1} (1·250 Å) were chosen for the analysis.

The polarity of the crystal and hence the proper indexing of reflections was determined from the signs of a small set of measured Bijvoet ratios (Mair, Prager & Barnea, 1971*b*).

An inadequacy in the extinction theory

The data from a wavelength-dependent study of the 311/31$\bar{1}$ Bijvoet ratio, together with the calculated kinematic values, is presented in Fig. 2 (initially we ignore the triangles). The errors associated with the measured quantities (in most instances of the same size as the points or smaller) are based on differences between intensities of equivalent reflections (population statistics) or counting statistics, whichever is larger. The sense of the systematic discrepancies between the observed and calculated Bijvoet ratios is consistent with the presence of extinction. However, the magnitude of the discrepancies in the region between the

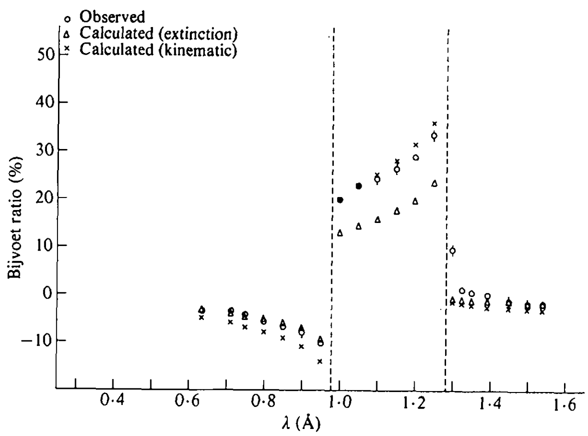

Fig. 2. The variation of the 311/31$\bar{1}$ Bijvoet ratio with wavelength. The dashed vertical lines represent the K absorption edges of Se and Zn.

absorption edges seems anomalous in that extinction is expected to have its largest effects on the Bijvoet ratios in this region. The large discrepancy between the observed and calculated Bijvoet ratios for 1·300 Å radiation reflects the acute dependence of the Bijvoet ratio on wavelength in this vicinity (an error in the determination of the wavelength of less than 1% is consistent with the observed value).

In the light of the above findings an attempt was made to allow for the effect of extinction in the calculated $311/31\bar{1}$ Bijvoet ratios. This was done by solving, for two observations at a time, the simultaneous equations in r and g which result when it is assumed that the difference between the observed and calculated Bijvoet ratios is due entirely to extinction. There was at this stage no definite indication of whether ZnSe could be classified as type I or type II (Zachariasen, 1967) and so the extinction theory used initially was based on the general secondary extinction formulae, where primary extinction is assumed to be negligible, of Zachariasen (1967):

$$y_{hkl} = (1 + 2p_2 x_s/p_1)^{-1/2} \quad (3)$$

$$p_n = (1 + \cos^{2n} 2\theta)/2 \quad (4)$$

$$x_s = r^* Q_0 \bar{T}/\lambda \quad (5)$$

$$Q_0 = r_c^2 \lambda^3 |F_{hkl}|^2/(V^2 \sin 2\theta) \quad (6)$$

for an unpolarized incident beam, where $\bar{T}$ is the mean path length through the crystal, r_c is the classical electron radius and V is the unit-cell volume. A $\sin 2\theta$ factor originally omitted from the expression for the diffraction cross section in a perfect crystallite (Becker & Coppens, 1974*a*,*b*) was also included, by replacing r by $r \sin 2\theta$ in r^*. The authors are not aware of any studies involving extended-face crystals, in which the inclusion of this factor in the extinction formulae has been tested. Indeed, there are very few studies of extinction in extended-face imperfect crystals. [One of the main consequences of the additional $\sin 2\theta$ factor is that the differentiation between type I and type II crystals becomes less distinct for severe extinction.] It is worth noting that Tomiyoshi, Yamada & Watanabe (1980) have shown that extinction correction in white-beam diffraction agrees with that in monochromatic-beam diffraction.

The selection of several pairs of observations enables one to test the consistency of the derived values of extinction parameters and the ability of the extinction theory to account for the wavelength dependence. Table 1 lists typical values of r and g obtained in the manner described above, with and without the $\sin 2\theta$ factor. In some cases only approximate solutions could be found for the simultaneous equations. The corresponding calculated Bijvoet ratios are all within 5% of the observed values. Table 2 contains details of the observations used in Table 1 together with the calculated Bijvoet ratios using the average values of the extinction parameters in Table 1.

Table 1. *Typical values of the extinction parameters, r and g, obtained as described in the text with and without the additional* $\sin 2\theta$ *factor (A and B respectively)*

The first column gives the numbers of the observations used, as detailed in Table 2. Values preceded by a tilde (~) are approximate solutions.

Observations used	A: r (μm)	A: g (mrad⁻¹)	B: r (μm)	B: g (mrad⁻¹)
2 & 3	2·94	20·3	2·49	18·7
1 & 6	3·60	67·3	~4·1	~27
2 & 5	2·52	33·1	~2·5	~25
1 & 2	~3·7	~24	2·14	26·1
2 & 6	~3·5	~29	~3·2	~26
3 & 5	~3·1	~22	~3·3	~20
2 & 4	~2·5	~15	~2·1	~15
1 & 5	~4·8	~23	~3·5	~22
Average	3·3 (8)	29 (16)	2·9 (7)	23 (4)

Table 2. *The observed Bijvoet ratios used in Table 1 to determine values of the extinction parameters*

The kinematically calculated Bijvoet ratios are listed, together with values calculated using the average extinction parameters from Table 1.

Observation No.	$h\,k\,l$	λ (Å)	B_{obs} (%)	B_{kin} (%)	B_{calc} (%)$-A$	B_{calc} (%)$-B$
1	3 1 1	0·711	−3·8 (1)	−6·1	−3·9	−3·8
2	3 1 1	1·542	−1·8 (2)	−3·2	−1·8	−1·8
3	5 3 1	0·711	−5·6 (3)	−6·7	−5·4	−5·5
4	5 5 1	0·711	6·9 (4)	7·3	6·4	6·5
5	5 5 1	1·150	−44·4 (2·0)	−52·4	−43·8	−44·8
6	7 3 1	1·150	−47·5 (1·2)	−56·8	−49·5	−50·4

In carrying out the above-mentioned calculations we found that values of r and g could be obtained from two sufficiently different wavelengths in Fig. 2 provided that neither belonged to the region between the absorption edges; otherwise, such a calculation resulted in two simultaneous equations for which no satisfactory solutions existed. This inconsistency is reflected in Fig. 2 by the calculated Bijvoet ratios with extinction effects included, represented by triangles. The extinction factors were calculated using the average extinction-parameter values in Table 1 ($\sin 2\theta$ factor included). These calculated Bijvoet ratios are seen to be in better agreement with the observed ratios outside the absorption edges, but between these absorption edges the agreement is very much worse. It would thus seem that the previous agreement between the observed and calculated (kinematic) Bijvoet ratios between the absorption edges was largely fortuitous.

Attempts made to account for the inconsistency between the absorption edges included:

1. Allowance for primary extinction (Zachariasen, 1967), with and without the $\sin 2\theta$ factor. [The

resulting values of the extinction parameters were quite erratic (especially g) and yielded extinction corrections which were predominantly primary in nature (hence the difficulty encountered in determining g). These corrections were incapable of resolving the inconsistency in Fig. 2.]

2. The assumption that the ZnSe specimen is of type I or type II. [For the observations in Table 2 we obtained $g = 18$ (6) mrad^{-1} (type I), $r = 2{\cdot}3$ (1·0) µm (type II with sin 2θ factor) and $r = 1{\cdot}8$ (9) µm (type II without sin 2θ factor). These parameter values are not greatly different from those in Table 1. None of these extinction models was able to resolve the inconsistency in Fig. 2.]

3. Consideration of a possible angular dependence of the extinction factor (Cooper & Rouse, 1970), to no avail.

4. Estimating the changes required to the values of the imaginary dispersion corrections. [These would have had to differ from theoretically calculated values by about 30% (the amount by which f''_{Zn} would have to increase and f''_{Se} decrease). This was extremely unlikely, as was the need for large changes of the imaginary dispersion correction of a given atom over the absorption-edge region of the other atom. Such changes would in fact result in poorer agreement of theory and experiment between the absorption edges for other data, presented later.]

The failure of Zachariasen's (1967) theory to account for severe extinction effects has been witnessed by a number of authors. The deviations between theory and experiment which accompany this breakdown of the theory are usually characteristic, for spherical crystals, of an underestimation of extinction (Cooper & Rouse, 1970; Becker & Coppens, 1974*a*). Lawrence (1972) has reported the overestimation of severe primary-extinction effects in a large parallel-sided crystal of LiF when using Zachariasen's (1967) theory. The discrepancy between theory and experiment in Fig. 2 is also characteristic of an overestimation of extinction effects.

The fact that the anomaly occurs substantially only in regions where the values of the linear absorption coefficient are large suggested to us that the effect is absorption dependent. The only manner known to us in which the absorption could still enter into our measurements appeared to be through the Borrmann effect (Borrmann, 1941; Borie, 1966), first incorporated into extinction theory by Zachariasen (1968*b*,*c*).

Inclusion of the Borrmann effect

The Borrmann effect results in an enhancement of integrated intensities [or an apparent decrease in extinction, as shown by Zachariasen (1968*b*,*c*)] in proportion to the structure factor and normal linear absorption coefficient. Both factors, the high absorption coefficients and large differences between the absolute values of the structure factors for hkl and $\bar{h}\bar{k}\bar{l}$ reflections (due to large differences in f'' values), are indeed most significant between the absorption edges. This would render the disagreement of the observed Bijvoet ratios and conventional extinction theory largest in this region: the large values of the normal absorption coefficient (μ_0) enhance the Borrmann effect while the large differences between f''_{Zn} and f''_{Se} make this disagreement most conspicuous.

In seeking other evidence corroborating our hypothesis, we measured the wavelength dependence of the $551/55\bar{1}$ Bijvoet ratio. In this case the Borrmann effect is expected to be less pronounced because the structure factors are smaller. Fig. 3, showing these results, confirms that this expectation is realized. The discrepancy between theory and experiment for the case of 1·300 Å radiation has been discussed in conjunction with Fig. 2. Consistent values of r and g could be obtained from any appropriate pairs of wavelengths in Fig. 3 and these were also in good accord with those derived from the $311/31\bar{1}$ data outside the absorption edges in Fig. 2 [two of the measurements in Fig. 3, as listed in Table 2, were used in the derivation of the extinction parameter values presented in Table 1]. Comparison of theory and experiment between the absorption edges in Fig. 3 shows only a slight systematic discrepancy, consistent with the diminishing role of the Borrmann effect.

The low-angle Mo $K\alpha$ data for ZnSe published by MMB also shows a discrepancy between theory and experiment, attributed to the inadequacy of the extinction model used. Here the conventional extinction correction (Zachariasen, 1967) resulted in the calculated intensities being systematically lower than those observed, *i.e.* extinction was overestimated for the most severely extinguished reflections. The observed and calculated Bijvoet ratios of MMB show no evidence of a systematic discrepancy, as confirmed by the $311/31\bar{1}$

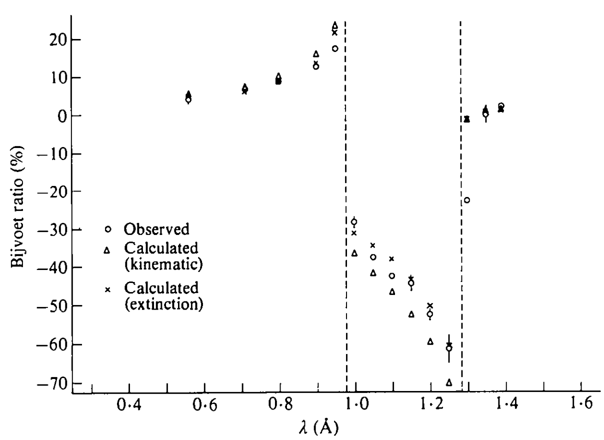

Fig. 3. The variation of the $551/55\bar{1}$ Bijvoet ratio with wavelength.

and 551/55$\bar{1}$ Bijvoet ratios in Figs. 2 and 3, respectively, for Mo $K\alpha$ (λ = 0·711 Å) radiation. This is associated with the conventional extinction corrections for the two Bijvoet-pair reflections having approximately the correct relative magnitudes but not, for the low-angle data, the correct absolute magnitudes, at such a wavelength. This can occur at this wavelength because the Bijvoet ratios for the most extinguished reflections are small, *i.e.* the structure factors and the extinction factors for the Bijvoet-pair reflections are not very different. In the case of the 311/31$\bar{1}$ Bijvoet ratios between the absorption edges in Fig. 2, the Borrmann effect is believed to be having a considerably larger impact on the 311 reflection than on the 31$\bar{1}$ reflection, *i.e.* the relative, as well as the absolute, magnitudes of the conventional extinction corrections for the two Bijvoet-pair reflections are in error.

MMB showed that the removal of the most extinguished reflections did not alter the refined values of the temperature parameters, a point of some importance to us, since we use these parameters in our analysis.

It is apparent that no theory of extinction is capable of completely accounting for the observations between the absorption edges in Fig. 2, since the agreement between the observed and kinematically calculated Bijvoet ratios near the Se absorption edge requires that the two extinction factors, y_{311} and $y_{31\bar{1}}$, be nearly equal. It is improper, however, to omit extinction corrections on the grounds that kinematic calculations are in good accord with observation in a limited range of wavelengths. Such a course of action would also be inconsistent with the other experimental observations. Thus we now seek to improve, quantitatively, the agreement between theory and experiment by acknowledging the presence of a significant contribution from the Borrmann effect.

The data were analysed with the aid of two least-squares-refinement programs, written especially for this study. Both programs use the IMSL (1975) library subroutine *ZXSSQ* to minimize the difference between observed and calculated Bijvoet ratios when calculated kinematic structure factors have been determined. The parameters refined were r and g (no scale factor being necessary). *ZXSSQ* uses a modification of the Levenberg–Marquardt algorithm, for solving non-linear least-squares problems, which eliminates the need for explicit derivatives. A correlation matrix and estimated standard deviations for the refined parameter values are calculated (Geller, 1961; Rollett, 1965), together with Hamilton's R factor.

The first program varies r and g within the framework of the various extinction models discussed earlier. Using the observations in Table 2 we obtained, for the best fit, extinction parameters corresponding to type I crystal [$r \gg 1$ μm and g = 19 (2) mrad^{-1}, *cf.* 18 (6) mrad^{-1} in the previous section]. Using larger data sets for refinement resulted in no important changes, provided that those observations for which the Borrmann effect was believed to be important were omitted. However, comparison of Hamilton's R factors for the different extinction models (type I, type II and intermediate, primarily) showed little with which to recommend one model in preference to the others. Table 3 lists calculated Bijvoet ratios for different models of extinction (we ignore, for the moment, the last column) and corresponding to observations not already presented graphically. The calculated 311/31$\bar{1}$ and 551/55$\bar{1}$ Bijvoet ratios, using the extinction parameters from the least-squares refinement, were all within 3·5% of those in Figs. 2 and 3.

The systematic discrepancy observed within the region between the absorption edges for the low-angle (highly extinguished) reflections, which we attribute to the Borrmann effect, is reflected by the inclusion, in the data set for refinement, of Bijvoet ratios measured with 1·150 Å radiation. The observed 731/73$\bar{1}$ ($\theta \simeq 51°$) and 551/55$\bar{1}$ ($\theta \simeq 46°$) Bijvoet ratios are in good agreement with theory but the inclusion of the 531/53$\bar{1}$ ($\theta \simeq 37°$) Bijvoet ratio causes a significant increase in Hamilton's R factor and the inclusion of the 311/31$\bar{1}$ ($\theta \simeq 20°$) Bijvoet ratio results in the refinement failing to converge.

Since Zachariasen's inclusion of the Borrmann effect in the extinction formalism and its experimental test for CaF_2 (Zachariasen, 1968*b*,*c*) little work has been devoted to this topic (Prager, 1971; Dawson, 1975; Bonnet, Delapalme, Fuess & Thomas, 1975). Zachariasen (1968*b*) states that the Borrmann effect will be mainly confined to strong reflections in type II ($r \ll \lambda g$) mosaic crystals for which $r \geq 1$ μm and normal absorption is high ($\mu_0 \bar{T} \geq 1$). Zachariasen's theory, with the inclusion of the Borrmann effect, does not allow for primary extinction explicitly. However, for a type II crystal this can be justified, even if primary extinction is significant (Pryor & Sanger, 1970; Cooper

Table 3. *The observed Bijvoet ratios not already presented graphically and calculated values using different models of extinction*

h k l	λ (Å)	B_{obs} (%)	B_{kin} (%)	B_{calc} (%) I	B_{calc} (%) II	B_{calc} (%) III
3 3 1	0·711	6·6 (1)	6·4	4·5	4·5	5·7
3 3 3	0·711	−5·1 (1)	−6·5	−5·0	−5·0	−6·0
5 1 1	0·711	6·6 (3)	6·5	5·0	5·0	6·0
5 3 1	0·561	−3·0 (4)	−5·0	−3·9	−4·0	−4·7
5 3 1	1·150	40·9 (1·8)	43·2	33·7	33·9	40·1
5 3 1	1·392	−2·0 (6)	−1·9	−1·2	−1·2	−1·6
7 3 1	0·561	5·5 (4)	5·8	5·1	5·2	5·6
7 3 1	0·850	10·8 (3)	13·3	12·1	12·2	13·0

I: r = 3·3 μm, g = 29 mrad^{-1}–secondary extinction alone
II: $r \gg 1$ μm, g = 19 mrad^{-1}–secondary extinction alone
III: r = 0·46 μm, $g \gg 10$ mrad^{-1}–Borrmann effect included

& Rouse, 1976). This arises because, in Zachariasen's notation, the primary-extinction term is given by

$$x_p = rQ_0\,\bar{t}/\lambda,$$

where $\bar{t}$ is the mean path length through a single domain. The quantity neglected in (5) is

$$x'_p = rQ_0\,\bar{t}\{1 - [1 + (r/\{\lambda g\})^2]^{-1/2}\}/\lambda$$

which can be written as

$$x'_p = x_p(1 - r^*/r).$$

In order to include x'_p in (3)–(6), x_s is replaced by $x_s + x'_p$. For type II crystals $r^* \simeq r$ and so, even though x_p may be significant, x'_p is not.

The question of whether this ZnSe specimen can be classified as type II is unresolved at this stage. It should, however, be pointed out that Barnea (1973) successfully interpreted a set of intensity data assuming that the same specimen was, indeed, of type II. Moreover, Becker & Coppens (1974*a*,*b*) predict that the crystal 'type' may vary with Bragg angle and that, for very small Bragg angles, any crystal will behave as a type II crystal (the extinction formulae being then largely dependent on *r*).

Zachariasen (1968*b*) assumes that the crystal is centrosymmetric; this is not the case for ZnSe. Consequently, changes to the theory were made (see the Appendix) to allow for the noncentrosymmetric nature of ZnSe.

Our second least-squares-refinement program varies *r* and *g* within this modified theory, with the inclusion of the sin 2θ factor (Becker & Coppens, 1974*a*,*b*). This additional factor does not affect the argument concerning the neglect of x'_p. Refinement of the data showed that *g* was extremely large and so *r* alone was varied with *g* constrained to be very large, consistent with type II behaviour. A refinement of all data in Figs. 2 and 3, with the exception of Bijvoet ratios measured with 0·950 and 1·300 Å radiation, yielded $r = 0{\cdot}46\,(13)$ μm. This is in excellent agreement with MMB's value of $r^* = 0{\cdot}51\,(7)$ μm for Mo $K\alpha$ radiation, since $r^* \simeq r$ if the crystal is indeed type II. However, given the inadequacy of the extinction correction used by MMB, this agreement must be treated as being somewhat fortuitous at this stage. In fact, the authors, in analysing the data of MMB with other models of extinction (including one allowing for the presence of the Borrmann effect), have subsequently found the value of *r* to be approximately 1 μm. The analysis of the data of MMB will be published elsewhere.

Figs. 4 and 5 show the new results, together with a repetition of the calculated ratios based on extinction alone, for the 311/31$\bar{1}$ and 551/55$\bar{1}$ Bijvoet ratios, respectively. The main improvement lies between the absorption edges in Fig. 4, with only small changes elsewhere. The residual discrepancies between theory and experiment in this region are most likely due to limitations of Zachariasen's theory (Werner, 1969; Prager, 1971; Dawson, 1975; Cooper & Rouse, 1976) and possible systematic inaccuracies in the quantities needed for Bijvoet-ratio calculation (*e.g.* anomalous dispersion corrections). Hamilton's R factors were calculated for the entire set of 311/31$\bar{1}$ and 551/55$\bar{1}$ data, with the exception of the measurements at 1·300 Å, and the results obtained were: 0·158 (kinematic); 0·172 (extinction); 0·127 (extinction including the Borrmann effect). The appropriate R-factor ratios correspond to a rejection of the hypothesis that the Borrmann effect does not make significant contributions to the data at the 0·5% significance level (Hamilton, 1965).

The last column of Table 3 lists calculated Bijvoet ratios, allowing for the Borrmann effect, for those observations not presented graphically. Table 4 displays values of *r* and *g* for a number of crystals, obtained by more conventional methods. The values obtained in the present study are typical of those listed. In addition, Sakata, Cooper, Rouse & Willis (1978) have investigated the wavelength dependence of extinction in UO_2 by using neutrons of four wavelengths.

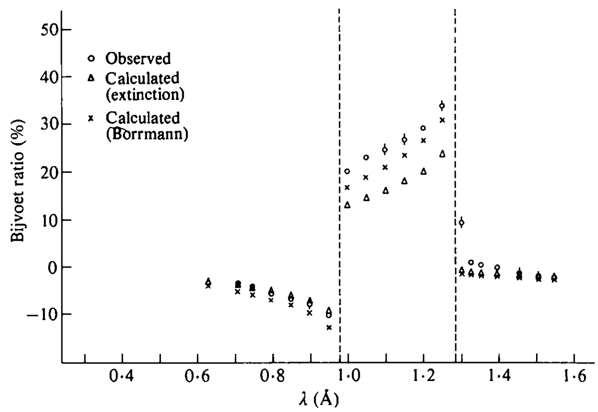

Fig. 4. The variation of the 311/31$\bar{1}$ Bijvoet ratio with wavelength.

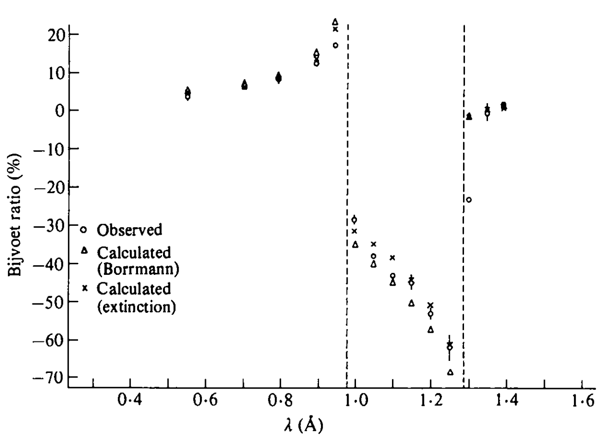

Fig. 5. The variation of the 551/55$\bar{1}$ Bijvoet ratio with wavelength.

Table 4. *Extinction parameters for various crystals*

In all but the last three cases, these parameters were determined from two or three values of the effective domain radius $r^*(\lambda)$. Prager & Harvey (1975) and Harvey & Prager (1975) used the Becker & Coppens theory for neutron data collected at a single wavelength.

	r (μm)	g (mrad^{-1})	Source
LiF	0·11	0·3	Zachariasen (1969)
α-SiO_2	0·46	>7	Zachariasen (1969)
Be_2SiO_4	1·2	12	Zachariasen (1969)
Be_2BO_4H	2·0	16	Zachariasen (1969)
CaF_2	3·2	57	Zachariasen (1969)
Si	0·65	9·2	Prager (1971)
ZnS	⩾0·1	1·4	Cooper, Rouse & Fuess (1973)
ZnTe	0·41	1·3	Cooper, Rouse & Fuess (1973)
KCl	0·13	0·8	Cooper & Rouse (1973)
$AuGa_2$	0·5	10	Prager & Harvey (1975)
CaF_2	13·5	7·5	Harvey & Prager (1975)
ZnSe	0·46	⩾10	Present study

Discussion and conclusions

It has been shown that in accurate analyses of Bijvoet ratios the use of kinematically calculated intensities or structure factors requires justification and, in some cases, may lead to serious discrepancies between theory and experiment. Least-squares refinements employing kinematic models to calculate Bijvoet ratios may yield inaccurate parameter values artificially adjusted to compensate for inadequacies in the model.

This wavelength-dependent study of ZnSe has revealed an inadequacy of conventional extinction theory in attempting to account for all systematic discrepancies between observed and kinematically calculated Bijvoet ratios. Improvement in the quantitative agreement between theory and experiment has been attained by including the Borrmann effect in the conventional extinction theory, in accordance with Zachariasen (1968*b*,*c*). Some discrepancy between observed and calculated values still remains. These discrepancies can be attributed to the limitations of Zachariasen's theory. By invoking the Borrmann effect we may be attributing a degree of crystal perfection to our specimen which limits the validity of Zachariasen's formulation. Considerations of the Borrmann effect necessarily involve specimens with significant crystal perfection which exhibit appreciable primary extinction (remembering that x_p' may be neglected even when x_p is significant, for a type II crystal).

Use of Bijvoet ratios at various wavelengths has obviated the need to refine simultaneously a scale factor and extinction parameters. The procedure is limited by the sensitivity of the ratio to extinction effects, but can yield meaningful parameters for cases of moderate to high extinction in crystals with sizable Bijvoet differences [the most severe extinction effects witnessed in the present case represent a reduction in intensity in excess of 40% and the largest observed Bijvoet ratio was −61·5 (3·7)% for the $551/55\bar{1}$ pair of reflections with 1·250 Å radiation]. This type of approach may be particularly suited to neutron studies, especially with longer wavelengths, for which extinction effects are more pronounced. In the absence of anomalous scattering effects, a ratio of two diverse intensities (one significantly affected by extinction and the other not) may prove to be a suitable experimental quantity. With neutrons extinction effects are not restricted to small Bragg angles because the scattering lengths are largely angle-independent and furthermore experiments are not complicated by uncertain polarization factors. New, tunable, high-intensity X-ray sources, such as the synchrotron, also offer the possibility of very accurate and extensive multiwavelength data. A similar intensity ratio to that suggested above may also be used for centrosymmetric crystals.

Realistic estimates of the standard deviations for the values of r and g are generally quite high. This is in accord with the experiences of other authors and is not characteristic of the method used here in particular (Cooper, Rouse & Fuess, 1973; Cooper & Rouse, 1976).

The use of more extensive data sets may make it possible to carry out separate analyses in different wavelength regions. This technique could not only test the wavelength dependence of the models being used, but also suggest other models. Clearly, the ultimate aim would be to interpret successfully all the data with a single model.

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APPENDIX

Extension of Zachariasen's formalism to noncentrosymmetric crystals

In order to include the Borrmann effect in the extinction formalism for ZnSe we merely extend the existing theory (Zachariasen, 1968*b*,*c*) to the noncentrosymmetric case, where in general $|F_{hkl}| \neq |F_{\bar{h}\bar{k}\bar{l}}|$.

The expression for the modified absorption coefficient μ has the same form as before (Zachariasen, 1968*b*):

$$\mu = \mu_0 \pm K\mu_{hkl}\,\bar{\kappa}_k,$$

where $K = 1$ ($|\cos 2\theta|$) for the normal (parallel) component of polarization. μ_{hkl}, a term related to diffraction, is now given, with the use of Abramowitz & Stegun (1965), by

$$\mu_{hkl} = 2^{1/2}\, r_c\, \lambda[(X'^2 + X''^2)^{1/2} - X']^{1/2}/V,$$

where

$$F_{hkl}\, F_{\bar{h}\bar{k}\bar{l}} \equiv X' + iX''.$$

$\bar{\kappa}_k$ is given by

$$\bar{\kappa}_k = z \log_e \{(1 + z')/(1 - z')\}/[\pi z'] \quad \text{for } z \le 1$$

and

$$\bar{\kappa}_k = 2/\pi \quad \text{for } z \ge 1$$

(by the requirements of dynamical theory), where

$$z = 2r^* K |F_{hkl} F_{\bar{h}\bar{k}\bar{l}}|^{1/2}\, r_c\, \lambda/(V \sin 2\theta)$$

and

$$z' = (1 - z^2)^{1/2}$$

now. The form of the extinction factor is then the same as that of Zachariasen (1968*b*).

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