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Wavelength Dependence of Moderate Extinction Effects in an Extended-face Crystal of Cadmium Selenide*

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Abstract

X-ray intensity measurements have been carried out with an extended-face single crystal of hexagonal CdSe using four different wavelengths. The wavelength dependence of moderate extinction effects ($y > 0{\cdot}7$, where y is the secondary extinction factor) was investigated by analysing the Bragg intensities using Zachariasen's (1967) theory, with and without the $\sin 2\theta$ factor (θ being the Bragg angle), which was claimed to have been omitted from the original expression for the diffraction cross section in a perfect crystallite (Becker and Coppens 1974*a*, 1974*b*). The resulting Hamilton (1965) R factors for the different extinction models tested do not enable one to make conclusive statements in regard to the 'best' model, but the refined values of the domain radius r and the mosaic-spread parameter g suggest that the crystal is neither of type I (i.e. $r \gg \lambda g$, where λ is the wavelength) nor of type II (i.e. $r \ll \lambda g$). The wavelength dependence of the extinction effects is adequately accounted for in terms of the models tested.

1. Introduction

The long-standing inconsistency between observed and calculated Bragg intensities of real (partly imperfect) crystals as a result of extinction is a vexing and central problem which limits the reliability and accuracy of the interpretation of the vast and accumulating store of diffraction data. Over the years the problem has received much attention from theoreticians. Experimental studies have been directed into two channels: on the one hand, attempts have been made to confirm theoretical predictions and, on the other, efforts have been made to find methods for the experimental determination of extinction-free data. [One of the many interests of A. McL. Mathieson, for example, has led to significant contributions to the second category (see e.g. Mathieson 1976*a*, 1976*b*, 1977*a*, 1977*b*, 1979).] The present paper belongs to the first category.

The need to use multi-wavelength studies to characterize the extinction effects of a given crystal specimen has been discussed by a number of authors (see e.g. Cooper *et al.* 1973; Dawson 1975). Recently, several studies of extinction effects as a function of wavelength have been carried out (e.g. Niimura *et al.* 1975; Cooper and Rouse 1976; Howard and Jones 1977; Cooper 1979). In most of these investigations the crystal specimens have been spherical, making use of an imperfect extended-face crystal of particular interest. The advantages of the extended-face crystal technique (Mair *et*

* Dedicated to Dr A. McL. Mathieson on the occasion of his 65th birthday.

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al. 1971*a*, 1971*b*) for accurate measurement of integrated intensities also make such a study highly desirable.

In this paper we report on X-ray intensity measurements from an extended-face single crystal of CdSe using the four different wavelengths 0·561, 0·711, 1·542 and 2·085 Å, denoted by λ_1, λ_2, λ_3 and λ_4, and corresponding to the characteristic X-ray lines of Ag Kα, Mo Kα, Cu Kα and Cr Kβ respectively.

The formula for the secondary extinction factor y, as defined by Zachariasen (1967), requires the refinement of the effective domain radius

$$r^* = r/\{1+(r/\lambda g)^2\}^{\frac{1}{2}}, \tag{1}$$

where r is the mean radius of the (spherical) perfect-crystal domains, λ is the wavelength of the incident radiation and g is the quantity in the isotropic gaussian distribution law describing the misalignment of the domains. In order to include a $\sin 2\theta$ factor (θ being the Bragg angle), which was claimed to have been omitted from the expression for the diffraction cross section in a perfect crystallite (Becker and Coppens 1974*a*, 1974*b*), r in equation (1) is replaced by $r \sin 2\theta$.* The main consequence of this additional angle dependence is that the differentiation between type I ($r \gg \lambda g$) and type II ($r \ll \lambda g$) crystals becomes less distinct for severe extinction.

In the present case the extinction effects are moderate ($y > 0{\cdot}7$) and the inclusion of the $\sin 2\theta$ factor will be seen to result in little or no improvement in the agreement between observed and calculated structure factors.

2. Experimental

Cadmium selenide possesses the hexagonal wurtzite structure (Zachariasen 1926). The preparation and characteristics of the crystal, labelled specimen no. 2, used in this study were described by Freeman *et al.* (1977). The crystal was mounted on a Philips PW1100/20 computer-controlled four-circle X-ray diffractometer powered by a stabilized Philips PW1130/90 generator. Integrated intensities were measured by the extended-face crystal technique (Mair *et al.* 1971*a*, 1971*b*; Freeman *et al.* 1977), using a NaI(Tl) scintillation detector in conjunction with pulse-height analysis. The measurements were obtained using $\omega/2\theta$ scans of width $3°\theta$ starting $1{\cdot}5°\theta$ below the peak maximum. The background was measured from stationary counts at both limits of the scan. The measurements were carried out at 293(2) K and the rectangular detector aperture was 1·5° by 2°.

Significant multiple diffraction peaks, most numerous for λ_1, were avoided by rotating the crystal about the scattering vector of a given reflection to a position within a region where 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 *et al.* 1971*a*). The intensities were measured in positions no more than 2° in azimuth from the symmetric aspects.

The X-ray source in this experiment was supplied from Ag, Mo, Cu and Cr tubes used in conjunction with a graphite (002) flat-crystal monochromator and an incident-

* It should be pointed out that the secondary extinction models of Becker and Coppens (1974*a*, 1974*b*, 1975) are, themselves, not applicable to the special geometric conditions of extended-face crystals and are not, as such, tested here.

beam collimator 0·5 mm in diameter. The selection of the four wavelengths was guided by the demands of the experiment (for example, to have a reasonably large range of wavelengths and to avoid close proximity to the Cd and Se K-absorption edges) and certain practical limitations (for example, those of intensity and the range of adjustment of the PW1100/20 tower angle). In order to avoid anomalies in the measured intensities due to surface effects, the appropriate diffractometer angles were kept within limits which ensured that the glancing angle between the incident beam and the crystal face was not too low.

The internal consistency of the measured integrated Bragg intensities was judged by the agreement between symmetrically equivalent reflections, each having been measured several times. The average deviations of an intensity from the mean value of the set of measurements to which it belonged were 0·59%, 0·56%, 0·50% and 0·68% for λ_1, λ_2, λ_3 and λ_4 respectively. The intensities of equivalent reflections were averaged, after thermal diffuse scattering (TDS) corrections had been applied, and isotropic extinction models were used (there was no evidence of significant anisotropy).

Reference reflections were measured at regular intervals throughout the data collection to monitor fluctuations in the system; these proved to be insignificant.

3. Analysis

The four data sets were analysed by a least-squares refinement program, which uses the IMSL (1975) library subroutine ZXSSQ to minimize the difference between observed and calculated structure factors. The quantity minimized was

$$M = \sum_i w_i(|F_{oi}|-|F_{ci}|)^2, \tag{2}$$

where w_i is the weight given to $|F_{oi}|-|F_{ci}|$, with $|F_{oi}|$ and $|F_{ci}|$ being the observed and calculated absolute values of the structure factor for the ith observation respectively. The only parameters which are refined at each wavelength are the scale factor and the extinction parameter(s). The subroutine ZXSSQ uses a modification of the Levenberg–Marquardt algorithm for solving nonlinear least-squares problems, which eliminates the need for explicit derivatives.

The observed intensities were corrected for one-phonon TDS effects (Harada and Sakata 1974; Sakata and Harada 1976; Sakata *et al.* 1983). The elastic constants of Berlincourt *et al.* (1963) were used, and the lattice parameters were $a = 4{\cdot}299$ Å and $c = 7{\cdot}010$ Å (NBS 1957). The Bragg intensities were then corrected for the Lorentz and polarization factors, the latter including the effect of the monochromator (Azaroff 1955). The square roots of the remaining quantities were divided by the refined scale factor to yield the $|F_{oi}|$ values.

The calculated structure factor is related to the kinematically calculated structure factor F_{kj} by

$$|F_{cj}| = |F_{kj}|y_j^{\frac{1}{2}},$$

where y_j is the secondary extinction factor for the jth observation. The factor $|F_{kj}|$ was calculated using model III of Fakineos *et al.* (1982), which contains realistic constraints between the cubic anharmonic parameters in the temperature factors. The values of the four conventional hexagonal temperature parameters, the cubic anhar-

monic temperature parameter and the wurtzite position parameter needed for this model were taken from the results of an extensive single-wavelength (Mo Kα) room-temperature study of CdSe (same crystal) (Stevenson and Barnea 1984); they are listed in Table 1 for convenience. The relativistic Hartree–Fock spherical atomic scattering factors of Doyle and Turner (1968) and the anomalous dispersion corrections of Cromer and Liberman (1970) for λ_1, λ_2 and λ_3, and Hazell (1967) for λ_4, were also used.

Table 1. Parameters for the structure-factor calculation

The four B parameters are the conventional hexagonal temperature parameters, $|\beta_{332}|$ is the cubic anharmonic temperature parameter (see model III of Fakineos *et al.* 1982) and u is the wurtzite position parameter

Parameter	Value	Parameter	Value
B_{11}(Cd)	1·595(4) Å^2	B_{33}(Se)	1·284(10) Å^2
B_{33}(Cd)	1·627(8) Å^2	$\lvert\beta_{332}\rvert$	0·81(5)$\times 10^{-13}$ erg Å^{-3}
B_{11}(Se)	1·273(5) Å^2	u	0·37596(4)

The secondary extinction factor y_j was calculated using one of three models: I, equation (1), which involves refining r^*; II, equation (1), with r replaced by $r \sin 2\theta$ (Becker and Coppens 1974*a*, 1974*b*), which involves refining r and g; III, $r^* = r \sin 2\theta$, which involves refining r. The assumption that this crystal is of type I reduces equation (1) to $r^* = \lambda g$, and the assumption that the crystal is of type II reduces equation (1) to $r^* = r$. If the $\sin 2\theta$ factor is included and the type I assumption is made then $r^* = \lambda g$ still holds, provided that $\sin 2\theta$ is not too small. The two limiting forms of r^* mentioned above only affect the interpretation of the refined parameter. If the $\sin 2\theta$ factor is included and the type II assumption is made then $r^* = r \sin 2\theta$, which is model III (see Stevenson and Barnea 1983*a*, 1983*b*). The expressions used to define the secondary extinction factor are

$$y = (1 + 2p_2\, x/p_1)^{-\frac{1}{2}}, \quad p_n = \tfrac{1}{2}(1 + \cos^{2n} 2\theta), \quad x = r^* \lambda^{-1} Q \bar{T}, \qquad (3a, b, c)$$

where Q is the conventional crystallographic quantity, defined for example by Zachariasen (1967), and $\bar{T}$ is the mean pathlength through the crystal which, for an extended-face crystal, is given by the reciprocal of the linear absorption coefficient μ. For each of the four wavelengths $\bar{T}$ was calculated using tabulated mass absorption coefficients (see 'International Tables for X-ray Crystallography' 1962).

Correlation matrices were calculated in order to assess the interactions of the refined parameters, as were estimated standard deviations for the refined parameter values (Geller 1961; Rollett 1965). The Hamilton (1965) R factors and goodness-of-fit parameters were also calculated.

The weights w_i, appearing in equation (2), were found from

$$w_i = 1/\{\sigma^2(|F_{oi}|) + \sigma^2(|F_{ci}|)\},$$

where $\sigma^2(X)$ is the variance for quantity X. The calculation of $\sigma^2(|F_{oi}|)$ involved the summation of a variety of error sources including counting statistics, population statistics and the TDS correction, while $\sigma^2(|F_{ci}|)$ is due to the uncertainty in the extinction correction (the error associated with $1-y$ is taken to be 10%).

Table 2. Results of the refinements for model I

Values of r^*_{calc} are calculated from the values of r and g obtained from a least-squares refinement of the results in the second column. The correlation coefficient is between r^* and the scale factor. The values of g are calculated by assuming that $r^* = \lambda g$ (type I)

Wavelength	r^* (μm)	r^*_{calc} (μm)	Correlation coefficient	R (%)	Goodness of fit	g (mrad^{-1})
λ_1	0·136(11)	0·134	0·71	0·966	1·42	2·42(20)
λ_2	0·162(18)	0·166	0·72	1·186	1·82	2·27(25)
λ_3	0·298(30)	0·300	0·75	1·176	1·80	1·93(19)
λ_4	0·392(129)	0·354	0·91	2·164	2·67	1·88(62)

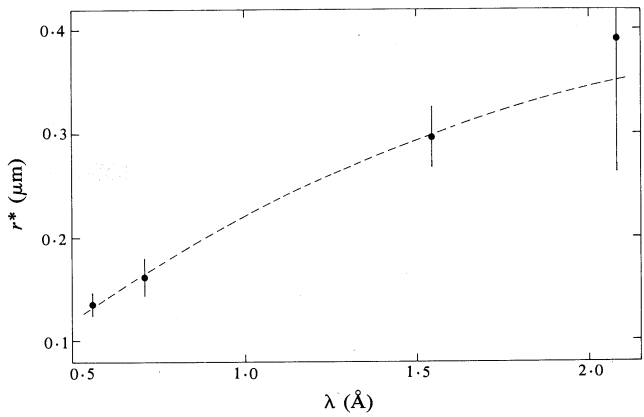

Fig. 1. Plot of r^* as a function of λ for CdSe. The dashed curve represents the least-squares fit of equation (1) to the four observed values.

4. Results

Model I. The results of these four refinements are shown in Table 2. The refined values of r^* increase monotonically with λ as predicted theoretically [unless $r^* = 0$ or $r^* = r$ (type II); see equation (1)]. Fig. 1 shows the four r^* values plotted as a function of λ. A least-squares refinement of the four values of r^*, in accordance with equation (1) and weighting each result by $1/\sigma^2(r^*)$, yielded $r = 0{\cdot}48(5)$ μm and $g = 2{\cdot}48(7)$ mrad^{-1} (with a correlation coefficient of 0·68 and $R = 2{\cdot}331\%$), which are physically reasonable values. These parameter values were used to calculate the r^*_{calc} in Table 2 and to produce the dashed curve in Fig. 1. The values of r^*_{calc} are in good agreement with the observations. The fourth r^* value plays a very small role in this determination of r and g, due to the size of $\sigma^2(r^*)$. These values of r and g satisfy neither the requirements of a type I crystal nor those of a type II: this is reflected in Table 2; if $r^* = r$ (type II) the values of r^* would be constant with λ, and if $r^* = \lambda g$ (type I) the values of g (calculated under this assumption and listed in the final column of Table 2) would not show a downward trend. (The values of g in the final column of Table 2 can, however, be considered constant within the error, making the type I assumption the more plausible of the two alternatives.)

Table 3. Experimental results for CdSe(λ_1)

Here $\Delta = |F_{oi}| - |F_{ci}|$, with $|F_{ci}|$ corresponding to model I

$h\,k\,l$	$\lvert F_{oi}\rvert$	$\lvert F_{ci}\rvert$	$\sigma(\Delta)$	y	α	$h\,k\,l$	$\lvert F_{oi}\rvert$	$\lvert F_{ci}\rvert$	$\sigma(\Delta)$	y	α
1 0 3	70·91	72·46	1·51	0·717	0·012	3 0 $\bar{2}$	46·96	46·93	0·31	0·923	0·042
1 0 $\bar{3}$	73·79	73·29	1·56	0·712	0·012	2 0 5	51·10	51·29	0·36	0·913	0·045
2 0 0	49·16	48·55	0·44	0·867	0·015	2 0 $\bar{5}$	49·89	50·45	0·35	0·915	0·045
1 1 2	68·42	66·22	1·08	0·772	0·015	2 2 0	59·38	59·36	0·57	0·890	0·052
2 0 1	33·03	32·88	0·24	0·939	0·016	3 1 1	18·49	18·54	0·10	0·989	0·059
2 0 $\bar{1}$	35·65	35·44	0·27	0·929	0·016	3 1 $\bar{1}$	20·63	20·70	0·14	0·987	0·059
2 0 2	33·87	33·94	0·25	0·941	0·019	2 1 5	44·21	44·52	0·28	0·941	0·060
2 0 $\bar{2}$	32·63	32·78	0·23	0·945	0·019	2 1 $\bar{5}$	43·17	43·71	0·27	0·943	0·060
2 0 3	63·34	62·68	0·76	0·834	0·025	3 1 2	20·55	20·56	0·14	0·987	0·063
2 0 $\bar{3}$	64·32	63·57	0·78	0·830	0·025	3 1 $\bar{2}$	19·55	19·61	0·13	0·988	0·063
2 1 0	40·52	40·57	0·26	0·929	0·028	4 0 1	15·94	15·90	0·09	0·993	0·074
1 1 4	9·90	9·71	0·05	0·996	0·029	4 0 $\bar{1}$	17·90	17·94	0·10	0·991	0·074
1 1 $\bar{4}$	9·56	9·37	0·05	0·996	0·029	4 0 $\bar{2}$	16·85	16·74	0·09	0·992	0·078
3 0 0	69·06	68·09	0·82	0·835	0·037	2 1 6	16·06	16·29	0·09	0·993	0·075
2 1 3	53·84	53·95	0·48	0·896	0·039	2 1 $\bar{6}$	17·00	17·20	0·09	0·992	0·075
2 1 $\bar{3}$	54·70	54·85	0·50	0·893	0·039	4 0 3	35·01	35·26	0·25	0·968	0·085
3 0 2	49·12	48·83	0·34	0·917	0·042	3 2 0	21·90	22·05	0·15	0·988	0·088

Table 4. Experimental results for CdSe(λ_2)

$h\,k\,l$	$\lvert F_{oi}\rvert$	$\lvert F_{ci}\rvert$	$\sigma(\Delta)$	y	α	$h\,k\,l$	$\lvert F_{oi}\rvert$	$\lvert F_{ci}\rvert$	$\sigma(\Delta)$	y	α
1 0 3	76·24	74·69	1·25	0·758	0·010	2 0 5	51·92	52·41	0·33	0·929	0·038
1 0 $\bar{3}$	77·35	76·03	1·32	0·751	0·010	2 0 $\bar{5}$	50·42	51·09	0·31	0·932	0·038
2 0 0	49·57	49·51	0·38	0·891	0·012	2 2 0	60·22	60·52	0·45	0·910	0·044
1 1 2	70·58	68·76	0·91	0·805	0·013	3 1 1	18·35	18·37	0·11	0·992	0·050
2 0 1	33·05	33·02	0·28	0·952	0·013	3 1 $\bar{1}$	21·59	21·71	0·15	0·989	0·050
2 0 $\bar{1}$	37·22	36·96	0·32	0·940	0·013	2 1 5	45·16	45·40	0·26	0·952	0·051
2 0 2	34·53	34·75	0·29	0·952	0·016	2 1 $\bar{5}$	43·77	44·13	0·25	0·955	0·051
2 0 $\bar{2}$	32·50	32·95	0·27	0·956	0·016	3 1 2	21·00	21·06	0·12	0·990	0·053
2 0 3	64·40	63·96	0·60	0·864	0·021	3 1 $\bar{2}$	19·48	19·58	0·11	0·991	0·053
2 0 $\bar{3}$	65·81	65·40	0·64	0·858	0·021	4 0 1	15·66	15·72	0·09	0·995	0·063
2 1 0	41·04	41·16	0·24	0·943	0·024	4 0 $\bar{1}$	18·72	18·87	0·11	0·992	0·063
1 1 4	11·65	11·39	0·05	0·996	0·025	4 0 2	18·02	18·07	0·11	0·993	0·066
1 1 $\bar{4}$	11·31	10·94	0·05	0·996	0·025	4 0 $\bar{2}$	16·65	16·69	0·10	0·994	0·066
3 0 0	70·72	69·77	0·66	0·864	0·032	2 1 6	16·07	16·24	0·09	0·994	0·063
2 1 3	54·80	54·72	0·37	0·916	0·033	2 1 $\bar{6}$	17·46	17·66	0·10	0·993	0·063
2 1 $\bar{3}$	56·14	56·16	0·39	0·912	0·033	4 0 3	35·18	35·48	0·30	0·974	0·072
3 0 2	50·50	50·25	0·31	0·931	0·036	3 2 0	22·08	22·28	0·16	0·990	0·075
3 0 $\bar{2}$	47·21	47·24	0·28	0·939	0·036						

The experimental results are given in Tables 3–6, which list the Miller indices (h, k, l), the factors $|F_{oi}|$ and $|F_{ci}|$ using model I, and the values of $\sigma(|F_{oi}|-|F_{ci}|)$, y and the TDS correction factor α.

Model II. The results of these four refinements are shown in Table 7. The refinements for λ_3 and λ_4 would not converge properly when both r and g were refined, and so r was held fixed at the average value from the λ_1 and λ_2 refinements, namely 0·46(8) μm. The average of the four values of g is 3·7(1·6) mrad^{-1}, and these values of r and g are very similar to those from model I. Thus the same conclusions are reached regarding the 'type' of this crystal. The values of R in Table 7 show no significant improvement over those in Table 2.

Table 5. Experimental results for CdSe(λ_3)

$h\,k\,l$	$\lvert F_{oi}\rvert$	$\lvert F_{ci}\rvert$	$\sigma(\Delta)$	y	a	$h\,k\,l$	$\lvert F_{oi}\rvert$	$\lvert F_{ci}\rvert$	$\sigma(\Delta)$	y	a
1 0 3	77·33	76·61	1·37	0·743	0·006	2 0 5	50·20	50·16	0·37	0·895	0·021
1 0 $\bar{3}$	74·01	74·64	1·26	0·754	0·006	2 0 $\bar{5}$	52·03	52·12	0·41	0·887	0·021
2 0 0	48·97	49·72	0·38	0·887	0·007	2 2 0	60·07	59·26	0·56	0·857	0·024
1 1 2	64·05	65·54	0·79	0·815	0·007	3 1 1	23·78	23·35	0·15	0·976	0·026
2 0 1	38·42	38·98	0·26	0·931	0·008	3 1 $\bar{1}$	18·45	18·40	0·10	0·985	0·026
2 0 $\bar{1}$	32·52	33·32	0·32	0·949	0·008	2 1 5	43·93	43·45	0·27	0·921	0·027
2 0 2	31·86	32·85	0·31	0·953	0·009	2 1 $\bar{5}$	45·69	45·33	0·30	0·915	0·027
2 0 $\bar{2}$	34·63	35·53	0·22	0·945	0·009	3 1 2	19·56	19·44	0·13	0·984	0·028
2 0 3	65·96	65·44	0·71	0·833	0·012	3 1 $\bar{2}$	21·92	21·69	0·14	0·980	0·028
2 0 $\bar{3}$	63·06	63·30	0·65	0·843	0·012	4 0 1	20·53	20·38	0·13	0·982	0·031
2 1 0	41·48	41·20	0·28	0·930	0·014	4 0 $\bar{1}$	15·77	15·82	0·08	0·989	0·031
1 1 4	14·57	14·45	0·08	0·991	0·014	4 0 2	16·52	16·60	0·09	0·988	0·033
1 1 $\bar{4}$	15·01	14·98	0·08	0·990	0·014	4 0 $\bar{2}$	18·55	18·64	0·10	0·985	0·033
3 0 0	70·97	68·43	0·82	0·817	0·018	2 1 6	18·17	18·24	0·09	0·986	0·031
2 1 3	56·50	55·90	0·48	0·873	0·018	2 1 $\bar{6}$	15·95	16·15	0·08	0·989	0·031
2 1 $\bar{3}$	53·99	53·77	0·43	0·882	0·018	4 0 3	36·69	36·88	0·24	0·940	0·034
3 0 2	46·93	46·34	0·31	0·910	0·020	3 2 0	22·18	22·37	0·14	0·977	0·035
3 0 $\bar{2}$	51·90	50·79	0·38	0·893	0·020						

Table 6. Experimental results for CdSe(λ_4)

$h\,k\,l$	$\lvert F_{oi}\rvert$	$\lvert F_{ci}\rvert$	$\sigma(\Delta)$	y	a	$h\,k\,l$	$\lvert F_{oi}\rvert$	$\lvert F_{ci}\rvert$	$\sigma(\Delta)$	y	a
1 0 3	75·73	77·02	1·29	0·758	0·005	2 0 $\bar{3}$	62·27	61·45	0·75	0·832	0·009
2 0 0	48·68	49·26	0·43	0·892	0·006	2 1 0	41·65	40·54	0·24	0·923	0·010
2 0 1	39·97	39·54	0·36	0·929	0·006	3 0 0	70·00	67·23	0·87	0·809	0·013
2 0 $\bar{1}$	30·04	30·99	0·23	0·956	0·006	2 1 3	56·44	55·48	0·58	0·863	0·013
2 0 2	31·02	31·64	0·24	0·953	0·007	2 1 $\bar{3}$	52·34	52·33	0·50	0·877	0·013
2 0 $\bar{2}$	35·19	35·63	0·31	0·941	0·007	3 0 2	43·36	44·27	0·29	0·906	0·014
2 0 3	66·89	64·58	0·80	0·817	0·009	3 0 $\bar{2}$	51·25	50·87	0·48	0·878	0·014

Table 7. Results of the refinements for model II

The correlation coefficient is between r and g, while y_{min} is the minimum extinction factor. For the λ_3 and λ_4 refinements, r was held fixed at the average value from the λ_1 and λ_2 refinements

Wavelength	r (μm)	g (mrad^{-1})	Correlation coefficient	R (%)	Goodness of fit	y_{min}
λ_1	0·530(137)	3·50(92)	0·83	0·935	1·38	0·735
λ_2	0·393(85)	5·45(4·66)	0·83	1·139	1·74	0·784
λ_3	*0·462*	2·45(49)	—	1·276	1·98	0·772
λ_4	*0·462*	3·21(4·14)	—	2·185	2·81	0·775

Table 8. Results of the refinements for model III

The correlation coefficient is between r and the scale factor

Wavelength	r (μm)	Correlation coefficient	R (%)	Goodness of fit	y_{min}
λ_1	0·379(29)	0·72	1·002	1·43	0·753
λ_2	0·356(34)	0·73	1·150	1·72	0·790
λ_3	0·336(41)	0·74	1·430	2·17	0·777
λ_4	0·499(194)	0·93	2·437	2·83	0·736

Model III. The results of these four refienements are shown in Table 8. The values of R here are generally higher than those in Tables 2 and 7.

5. Discussion and Conclusions

The analysis of the extensive Mo Kα data set from which the parameter values in Table 1 were taken (Stevenson and Barnea 1984) yielded a value of r^* (model I) of 0·27(3) μm and a value of r (model III) of 0·41(4) μm which, considering that the associated values of $y_{\min}$ are 0·925 and 0·922 respectively, are in reasonable accord with the corresponding values in Tables 2 and 8 respectively, i.e. with so little extinction in the data set r^* and r are difficult to determine reliably. Of the 35 independent reflections in Table 4, 16 appear in the more extensive data set (Stevenson and Barnea 1984) and the average difference between the values of $|F_{oi}|$ is 0·43%, indicating good reproducibility.

It is interesting to note that in this crystal extinction does not, in general, increase with increasing λ, in spite of r^* being a monotonically increasing function of λ. This is attributed to the trend in the relatively large values of μ for CdSe (143·2, 272·9, 1007·0 and 2197·8 cm^{-1} for λ_1, λ_2, λ_3 and λ_4 respectively), which makes the decrease of $\bar{T}$ with λ very important (see equations 3).

In the present study the data for each λ have been refined separately to ensure that the wavelength-dependent effects are evident. In this case of moderate extinction for an extended-face crystal, the extinction models have adequately accounted for the wavelength-dependent trends. However, further studies on crystals exhibiting larger extinction effects are required. These will present a more stringent test for the existing extinction models.

The values of the extinction parameters r and g for this crystal do not satisfy the criteria of a type I or a type II crystal, and so this specimen is best described as 'intermediate'. These parameter values are typical of those determined by other authors for a variety of materials (see e.g. Zachariasen 1969; Cooper *et al.* 1973; Cooper and Rouse 1973; Prager and Harvey 1975; Stevenson and Barnea 1983*a*, 1983*b*).

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