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Severe extinction in calcium fluoride: a test of the Becker & Coppens extinction formalism.

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The extinction formalism of Becker & Coppens [*Acta Cryst.* (1974). A30, 129–147, 148–153] is applied to the analysis of room-temperature neutron diffraction data from a large calcium fluoride sphere. Despite severe (predominantly secondary) extinction, excellent agreement is obtained between observed and calculated structure factors. The values obtained for the harmonic vibrational parameters [$\alpha_{Ca}=5{\cdot}71\ (0{\cdot}42)\times10^{-12}$ erg Å^{-2}, $\alpha_F=4{\cdot}28\ (0{\cdot}22)\times10^{-12}$ erg Å^{-2}] and for the third-order anharmonic vibrational parameter [$\beta_F=-5{\cdot}7\ (2{\cdot}4)\times10^{-12}$ erg Å^{-3}] are in satisfactory agreement with previously published values.

As part of a project to investigate the structure of CaF_2 near its melting point, neutron diffraction data were collected over a range of temperatures from room temperature to 1200 C. The rapid decrease of diffracted intensity with increasing temperature dictated the choice of a large single crystal – a sphere 6·5 mm in diameter. As might be expected, the use of a large sample led to severe extinction problems at low temperatures with consequent unreliability of the thermal parameters.

Details of the experiment and a full analysis of the results will be published later. Measurements were made with neutrons of wavelength 0·981 Å. Sets of data were obtained at room temperature both with and without the high-temperature furnace described by Harvey & Merten (1975), the latter set being the more extensive and reliable. The initial refinement on this set using the usual Zachariasen (1967) extinction correction was particularly poor in that the anharmonic model (Willis, 1965; Dawson, Hurley & Maslen, 1967), refined to an R index of 3·1%, systematic differences were noted between observed and calculated structure factors, and the thermal parameters were significantly different from those in the literature (*e.g.* Strock & Batterman, 1972).

A non-linear least-squares regression program using numerical differentiation was developed so that higher-order anharmonic terms could be included easily in the refinement. This made it simple to test the extinction formalism recently advanced by Becker & Coppens (1974*a*,*b*), which provides for both primary and secondary extinction. They derive expressions for the extinction correction appropriate to Gaussian, Lorentzian or Fresnellian distributions of crystallites in a mosaic crystal. We assumed the Lorentzian form which is believed by Becker & Coppens (1974*a*) to resemble actual distributions most closely, and on this basis re-analyzed our data. Results of refinements using the Zachariasen and the Becker & Coppens extinction corrections are shown in Table 1. F_{obs} are the experimental structure factors averaged over equivalent reflexions and corrected for absorption and for thermal diffuse scattering (TDS) using the single-phonon correction of Cooper & Rouse (1968). F_{corr} are the calculated values given by

$$F_{corr}=s\,.\,y^{1/2}\,.\,F_c$$

where s is the scale factor; $y^{1/2}$ the extinction factor; and F_c the structure factor calculated on a model that includes, in addition to the harmonic vibrational parameters α_{Ca} and α_F, a third-order anharmonic vibrational parameter β_F (Dawson, Hurley & Maslen, 1967). The primary and secondary extinction factors $y_p^{1/2}$ and $y_s^{1/2}$ (where $y^{1/2}=y_p^{1/2}y_s^{1/2}$) are also listed for the Becker & Coppens refinement. Secondary extinction is seen to be predominant. The final values obtained for the two extinction parameters in this refinement were $r=1{\cdot}35\ (0{\cdot}16)\times10^{-3}$ cm and $g=7{\cdot}5\ (1{\cdot}6)\times10^{3}$. Scattering lengths were fixed at $b_{Ca}=0{\cdot}488\times10^{-12}$ cm (Atoji, 1961) and $b_F=0{\cdot}56\times10^{-12}$ cm (Neutron Diffraction Commission, 1972).

Table 1. *Structure factors and extinction factors*

h k l	$\lvert F_{obs}\rvert$	$\lvert F_{corr}\rvert$ Becker & Coppens	$\lvert F_{corr}\rvert$ Zachariasen	$10^3\,.\,y_p^{1/2}$ Becker & Coppens	$10^3\,.\,y_s^{1/2}$ Becker & Coppens
2 2 0	182	185	200	859	423
4 0 0	198	201	212	869	476
4 2 2	212	208	216	879	511
4 4 0	219	214	218	888	543
6 2 0	215	215	217	897	567
4 4 4	215	215	215	905	590
6 4 2	216	214	211	912	609
8 0 0	213	213	208	919	629
6 6 0	206	209	202	925	642
8 2 2	206	209	203	925	644
1 1 1	105	108	98	982	691
3 1 1	114	118	110	983	781
3 3 1	117	118	113	985	821
3 3 3	118	118	115	986	841
5 1 1	117	117	114	986	845
5 3 1	166	116	114	987	860
5 3 3	112	111	111	988	877
5 5 1	110	109	110	989	886
7 1 1	110	110	111	989	885
5 5 3	109	109	111	989	888
7 3 1	107	105	108	990	894
7 3 3	107	105	109	990	896
5 5 5	95	95	99	992	911
7 5 1	99	100	105	991	902
2 0 0	124	126	116	971	637
2 2 2	138	135	127	974	721
4 2 0	138	137	130	977	768
4 4 2	132	131	129	981	822
6 0 0	133	132	130	981	825
6 2 2	128	127	127	983	840
6 4 0	123	123	125	985	856
6 4 4	113	113	119	988	880
8 2 0	112	113	119	988	880

The thermal parameters and R indices for the two refinements are listed in Table 2 together with harmonic thermal parameters calculated from the frequency spectrum by Elcombe & Pryor (1970). Also included in the table are results from a further refinement on our own data with the fluorine scattering length allowed to vary, and from a neutron diffraction study by Cooper & Rouse (1970, 1971). The Cooper & Rouse study is comparable to ours in that the data were equally severely affected by extinction, an

Table 2. *Thermal parameters and R indices*

	Present experiment				
	Zachariasen extinction (1)	Becker & Coppens extinction (1)	Becker & Coppens extinction (2)	Elcombe & Pryor	Cooper & Rouse
α_{Ca} (10^{-12} erg Å^{-2})	6·4 (1·1)	5·36 (0·36)	5·71 (0·42)	6·30	6·30
α_F (10^{-12} erg Å^{-2})	5·6 (0·8)	4·41 (0·22)	4·28 (0·22)	4·56	4·56
$-\beta_F$ (10^{-12} erg Å^{-3})	16 (18)	6·1 (2·7)	5·7 (2·4)	–	5·7 (1·2)
R	0·031	0·011	0·0099	–	0·04

(1) b_F held at $0{\cdot}56\times10^{-12}$ cm
(2) b_F refined to $0{\cdot}576\ (0{\cdot}009)\times10^{-12}$ cm

anharmonic model was assumed for the fluorite structure and a TDS correction was applied. These authors proposed a modified version of the Zachariasen extinction correction (Cooper & Rouse, 1970); nevertheless, the values they obtained initially for the harmonic vibrational parameters α_{Ca} and α_F appear to be unacceptably high and subsequently (Cooper & Rouse, 1971) they fixed both parameters at the calculated values of Elcombe & Pryor (1970).

As can be seen from Tables 1 and 2 the Becker & Coppens extinction theory gives a significantly improved fit to the model. The agreement between F_{obs} and F_{corr} is most satisfactory even for highly extinguished low-angle reflexions such as the 220 reflexion whose intensity is 87 % extinguished. Reasonable agreement is obtained between the experimentally determined harmonic vibrational parameters and those calculated by Elcombe & Pryor. The agreement between the values of the anharmonic vibrational parameter β_F is also most satisfactory, particularly since we measured only low-index reflexions.

Finally, although one should not overemphasize the physical significance of the two extinction parameters r and g of the Becker & Coppens formalism, they at least behaved sensibly as a function of temperature over the range of our experiments. Both remained constant (within error) to between 750 and 1000 C when they began to fall rapidly with increasing temperature. This suggests that the crystal softened and began to deform under pressure from the mounting. By contrast the extinction parameter r^* from the Zachariasen refinement showed a general but somewhat erratic decline with temperature.

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