A Synchrotron Radiation Study of Potassium Zinc Fluoride Perovskite

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Abstract

Vibration amplitudes and electron-deformation densities, $\Delta\rho$, have been determined for $KZnF_3$ from diffraction data measured using focused synchrotron radiation with $\lambda = 0.7000$ (2) Å at the Photon Factory, KEK, Japan. The lack of systematic variation of intensity with path length indicates that secondary extinction is not significant, a result confirmed when the strong intensities measured using a weaker parallel beam with $\lambda = 0.5000$ (2) Å showed no dependence on λ. The 0.7 Å study is generally concordant with, but more precise ($R = 0.008$, $wR = 0.006$) than earlier analyses with Mo $K\alpha$ radiation. The charge of $+0.47$ (4) e determined for the Zn atom is larger than that calculated with extinction corrections which minimize differences between observed and calculated structure factors. Near the Zn nucleus $\Delta\rho$ is mildly anisotropic, with a topography similar to that found for closed-shell atoms in related perovskite structures.

Introduction

At room temperature the compounds KMF_3, with M = Mn, Co, Fe, Ni and Zn, have the cubic $Pm\bar{3}m$ structure that characterizes the perovskite series. There is strong scientific interest in this series, partly because of the ferroelectricity, superconductivity and other technologically important properties of particular members. Some of these properties are related to deviations from the ideal structure. A full understanding of the effect of structural distortions is more likely to be achieved if the ideal case is thoroughly understood.

The simplicity of the closed-shell electronic configuration for Zn^{2+} encourages the use of $KZnF_3$ as an archetypal ideal structure. $KZnF_3$ was studied with Mo $K\alpha$ radiation by Buttner & Maslen (1988), referred to below as B&M, who reported vibration parameters and atomic charges consistent with trends identified by Maslen & Spadaccini (1989) for the KMF_3 series as a whole. Subsequent experiments (Maslen & Spadaccini, 1993) indicate that these trends require correction for bias originating in unreliable extinction corrections determined by minimizing differences between observed and calculated structure factors. Improved secondary-extinction corrections may be evaluated from the variation of reflection intensity with path length. These corrections can be verified, and the significance of primary extinction assessed, from the variation of intensity with wavelength.

Synchrotron radiation, being readily tuned to different wavelengths, is a valuable tool for studying extinction. The high intensity of that radiation permits the study of crystals that are sufficiently small for diffraction to be nearly kinematic (Bachman, Kohler, Schulz & Weber, 1985), while providing adequate precision in the measurements of the weaker structure factors. The reduced extinction improves the accuracy of strong low-order structure factors which are particularly important when measuring interatom movements of electrons that determine the polarity of structures.

Experimental

Vertically polarized X-radiation with $\lambda = 0.7000$ (2) Å diffracted from an Si(111) double-

crystal monochromator was focused with a curved mirror (Satow & Iitaka, 1989). By positioning the specimen slightly off-focus, changes to the synchrotron radiation intensity which occur as a result of instabilities in the particle beam are minimized. For $\lambda = 0.5000$ (2) Å, radiation with similar polarization was diffracted from an Si(422) double-crystal monochromator. The focusing mirror was not used because it is not effective at short wavelengths, and the beam is almost parallel. The beam intensity at the sample was about one twentieth of that for the 0.7 Å focused beam.

KZnF$_3$ crystals were grown from aqueous solution as described by B&M. The specimen selected for study had sharp edges and well faceted {111}, (100) and (010) reflective faces, with a (110) growth face and dimensions indicated in Fig. 1. Reflection intensities were measured systematically for the complete sphere of reciprocal space with $\sin\theta/\lambda < 1.087$ Å^{-1}. Averaging over a full sphere reduces systematic error by the partial cancellation of some high-order multipole components from the error function. This is particularly powerful for cubic structures with large numbers of equivalent reflections, as verified by test calculations which omit absorption corrections. Six standard reflections were monitored every 100 reflections to check the stability of the incident beam. The measured intensities were modified for fluc-
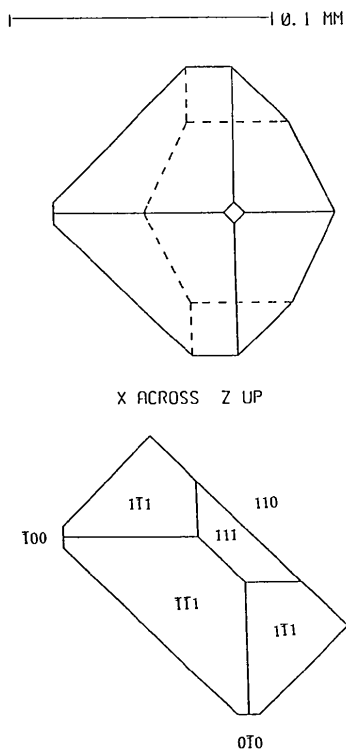
Table 1. Experimental and refinement data for KZnF$_3$

Molecular weight, M_r	161.47	
Space group	$Pm\bar{3}m$	
Specimen	Truncated octahedron	
Wavelength (Å)	0.7	0.5
Cell dimension (Å)	4.0611 (9)	4.0581 (5)
Maximum variation of standards based on I (%)	6.0	2.1
Instability factor c from standards $[\sigma^2(I) = \sigma^2_{counts} + cI^2]$	9.79×10^{-5}	4.88×10^{-5}
Reflections measured	3105	2944
Linear absorption coefficient (mm^{-1})	10.33	4.06
Absorption correction min./max.	1.61; 2.06	1.21; 1.34
R_{int} (before; after absorption)	0.063; 0.030	0.084; 0.079
Independent reflections	104	104
R factor	0.008	0.019
wR factor	0.006	0.015
χ	1.496	1.344

tuations in the standards and the variances adjusted as suggested by Rees (1977). The stronger intensities were reduced by an absorber with an attenuation factor of 4.56. Lorentz–polarization and absorption corrections (Alcock, 1974) were evaluated analytically. The 0.5 Å data was measured in a similar manner, but nine standard reflections were measured after every 150 reflections to monitor beam stability, and the attenuation factor for the stronger reflections was 1.841.

The 0.7 Å data is more accurate as indicated by the lower R_{int} value in Table 1.* The improvement is partly due to the improved counting statistics resulting from higher beam intensity, but there was closer agreement between equivalents even for the stronger reflections, for which accuracy is limited more by beam stability than by counting statistics. This confirms that the 0.7 Å beam was more stable than the 0.5 Å beam, as expected from their focused and parallel geometries.

Structure factors were evaluated using the spherical atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV), with dispersion corrections $\Delta f'$, $\Delta f''$ of 0.115, 0.125 at 0.5 Å, 0.196, 0.243 at 0.7 Å for K; 0.307, 0.764 at 0.5 Å, 0.317, 1.413 at 0.7 Å for Zn; and 0.007, 0.005 at 0.5 Å, 0.017, 0.010 at 0.7 Å for F, evaluated by Creagh (1990). Least-squares refinement was performed with the residual based on F and $w = 1/\sigma^2(F_o)$. Further details of the data measurement and analysis are given in Table 1. Computer programs *STARTX, DIFDAT, ABSORB, ADDATM, ADDREF, FC, CRYLSQ, BONDLA, FOURR, CHARGE, CONTRS, SLANT* and *PLOT* from the *XTAL* 3.0 system (Hall & Stewart, 1990) installed on a Sun 3/280 computer, were used in the analysis.

F_o and F_c values for several structure factors are listed in Table 2. It is tempting to interpret the

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Fig. 1. Shape of the KZnF$_3$ crystal used for data collection.

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* A full list of structure factors for the 0.7 Å data has been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71011 (3 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

difference between F_o and F_c for the strong 011 and 002 reflections in terms of extinction. The need for caution is indicated by the difference coefficient with the opposite sign for the 111 reflection, which is so large that its contribution to the least-squares residual exceeds by far that from any other reflection. The Gauss–Markov condition for validity of the least-squares process requires that the weighted residuals be randomly distributed, preferably with a normal distribution. It is unlikely that the most probable set of parameters coincides with the least-squares minimum if that requirement is not satisfied. Ideally this difficulty should be eliminated by calculating structure factors with more accurate models. In practice it is difficult to construct such models in an unbiassed way. The weighting of the 111 structure factor in the refinement was, therefore, reduced until its contribution to $\Sigma \omega \Delta^2$ was comparable with that of other reflections with large residuals, at which stage the refinement parameters were not excessively sensitive to that weighting.

Intensities for each strong symmetry-independent reflection were plotted as a function of path length which, because of the crystal's shape as shown in Fig. 1, changes for symmetry-related reflections. The intensities for the 011 or 002 reflections did not vary systematically with path length, i.e. the intensity versus path-length curve did not have a significant slope. That result was confirmed by calculating extinction corrections with the full data set, following the formalism of Maslen & Spadaccini (1993). Neither was there any relative increase in the mean intensities for the strong reflections in the $\lambda = 0.5$ Å data, confirming that extinction was not significant. Thus the model-independent evidence indicates that extinction does not affect the data appreciably. Consequently no corrections for extinction were applied.

Structural parameters

The structural parameters are compared with those of B&M in Table 3. The standard deviations in the mean-square vibration amplitudes for the 0.7 Å data are roughly half those from the B&M analysis. The amplitudes are systematically about 5% smaller. A possible relationship between these discrepancies and scan truncation was considered. An increased temperature factor would be expected if the Mo $K\alpha$ reflections were increasingly truncated at high angles because of α_1/α_2 splitting. The use of a θ-dependent scan range ensured that any errors of this type were small, but as the mosaic distribution did not generate an ideal Gaussian profile, minor discrepancies in determining the background correction are possible. Truncation of background with the two synchrotron radiation types is not identical because the profiles

Table 2. *Observed and calculated structure factors for selected reflections*

h	k	l	$\sin\theta/\lambda$	F_o	F_c	φ	Δ	$\omega^{1/2}\Delta$	σ
0	0	1	0.1231	18.58	18.80	0	−0.22	−1.32	0.17
0	0	2	0.2462	48.60	49.93	0	−1.34	−3.49	0.38
0	0	3	0.3694	11.89	11.84	0	0.05	0.49	0.10
0	0	4	0.4925	25.65	25.58	0	0.07	0.24	0.29
0	0	5	0.6156	5.94	5.92	0	0.02	0.57	0.03
0	0	6	0.7387	13.91	13.74	0	0.17	0.98	0.17
0	0	7	0.8618	3.34	3.31	0	0.03	0.81	0.04
0	0	8	0.9850	7.75	7.67	0	0.09	2.33	0.04
0	1	1	0.1741	31.08	31.79	0	−0.70	−7.23	0.10
0	2	2	0.3482	37.55	37.89	0	−0.34	−2.58	0.13
0	3	3	0.5224	15.43	15.41	0	0.02	0.25	0.09
0	4	4	0.6965	15.24	15.17	0	0.07	0.79	0.09
0	5	5	0.8706	7.02	6.96	0	0.06	1.24	0.05
0	6	6	1.0447	6.49	6.54	0	−0.05	−2.07	0.03
1	1	1	0.2132	8.97	7.81	180	1.15	22.09	0.05
2	2	2	0.4265	30.27	30.53	0	−0.25	−1.44	0.18
3	3	3	0.6397	1.03	0.96	0	0.05	1.31	0.04
4	4	4	0.8530	10.34	10.33	0	0.01	0.45	0.03
5	5	5	1.0662	1.57	1.54	0	0.03	0.73	0.04

Table 3. *Refined structural parameters* (Å^2)

	0.7 Å		0.5 Å		B&M	
	U_{11}	U_{22}	U_{11}	U_{22}	U_{11}	U_{22}
Zn	659 (2)	—	584 (9)	—	691 (5)	—
K	1450 (3)	—	1404 (19)	—	1507 (7)	—
F	715 (10)	1904 (10)	604 (60)	1860 (65)	760 (23)	1976 (23)

for focused and parallel beams differ, but the background intensities for the synchrotron experiments are low, and errors as a result of truncation in those experiments must be small.

Part of the discrepancy can be attributed to the extinction corrections, which interact with the vibration amplitudes via the scale factor. By over-correcting the values measured for the strong low-order reflections the temperature factor would be increased, but test calculations indicated that the effect is not large enough to explain the whole of the discrepancy. Neither scan truncation nor extinction explains why the disagreement is larger for the $\lambda = 0.5$ Å analysis. Although e.s.d.'s are larger for the short-wavelength data, the discrepancies are too systematic to be explained by increased standard deviations alone.

Atomic charges

Atomic charges, calculated by projecting $\Delta\rho$ onto atomic density basis functions (Hirshfeld, 1977), are listed in Table 4. Those charges are less than the final values in all three analyses. The accuracy of the $\lambda = 0.5$ Å results is limited by the relatively inaccurate low-order structure factors, indicated by the large standard deviations for that analysis. The positive charge on Zn, which has a high atomic number compared with F or K, is low for the B&M data with extinction corrections determined from F_o versus F_c agreement. Because the extinction corrections were determined from F_o versus F_c agreement it is probable that extinction is over-estimated for all the structures

Table 4. *Atomic charges from the Hirshfeld partitioning of $\Delta\rho$ (e)*

	0.7 Å	0.5 Å	B&M
Zn	0.47	0.29	0.18
K	0.24	0.66	0.47
F	-0.23	-0.31	-0.21

reviewed by Maslen & Spadaccini (1989). The positive charge on the transition metals would be correspondingly under-estimated in that review, changing slightly the trends originally reported by those authors.

Deformation density

The $\Delta\rho$ maps for the 0.7 Å data shown in Figs. 2 and 3 are the (001) and (110) planes corresponding to Figs. 1(*a*) and 2 of B&M. Although the maps for the different radiation types are similar in general, there are differences in detail. In the synchrotron-radiation map local maxima at the atomic sites replace minima in the Mo $K\alpha$ map. This modification of the $\Delta\rho$ topography is no doubt related to the θ-dependence of the measurements responsible for the temperature-factor differences between the experiments.

The region of depleted density surrounding the Zn cation is clearly defined in Figs. 2 and 3, as is the depletion at the structural cavity centred on the point $\frac{1}{2},\frac{1}{2},0$ midway between adjacent K atoms. The electron density is transferred from the vicinity of the atoms and the structural cavity to the broad sea of positive density in the internuclear region.

To within a scale factor, $\Delta\rho$ near the Zn position closely resembles that near Ti in the isostructural $SrTiO_3$ compound as reported using similar data measured at the Photon Factory (Maslen, 1990). In both maps there is a local maximum in $\Delta\rho$ at the atomic sites, flanked by minima directed towards the K or Sr cations. There are local maxima 0.8 and 1.0 Å along Zn—F and Sr—Ti, respectively. These features near Zn are more compact than those near Ti, as would be expected since the effective nuclear charge for Zn is higher than that for Ti. Zn^{2+} and Ti^{4+} are closed-shell cations with outer-shell configurations $3d^{10}$ and $3d^0$, respectively. The lower degree of polarization around Zn is consistent with a filled $3d^{10}$ subshell being less polarizable than a $3d^0$ configuration.

Concluding remarks

This analysis shows that diffraction experiments with the accuracy needed for charge-density studies of perovskite materials can be achieved with focused synchrotron radiation. The deformation densities show that closed-shell cations in solids are polarized significantly, but the electronic states of the atoms differ substantially from the corresponding free ions used in simple descriptions of ionic bonding. When the valence shell of the neighbouring atom overlaps with the closed-subshell density, electrons are removed from that region by exchange, which depletes the density where parallel spins overlap. This depleting effect is stronger for the cations which have core radii larger than those for anions with similar atomic number, and thus acquire positive charges.

The contribution of computer programs by their authors R. Alden, G. Davenport, R. Doherty, W. Dreissig, H. D. Flack, S. R. Hall, J. R. Holden, A.
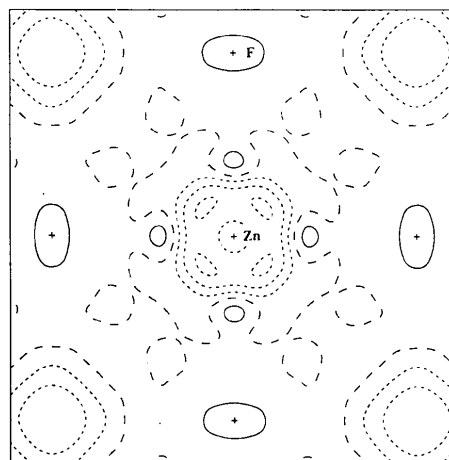

Fig. 2. $\Delta\rho$ for the $KZnF_3$ (001) plane containing Zn and F atoms related by a fourfold axis, map borders 5.0 × 5.0 Å. The contour intervals are at 0.15 e Å^{-3}, large dashes — zero, small dashes – negative contours.
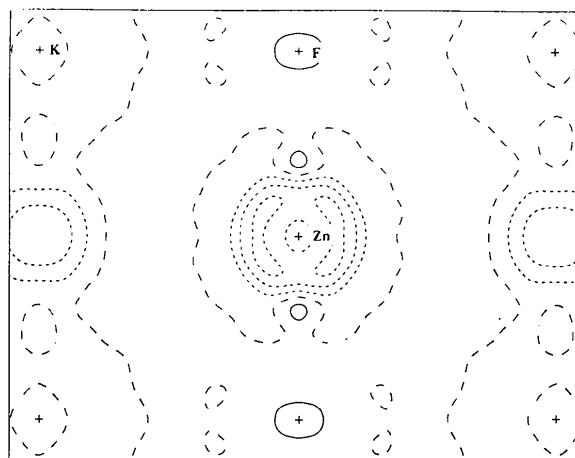

Fig. 3. $\Delta\rho$ for the $KZnF_3$ (110) plane containing K, Zn and F atoms, map borders 6.5 × 5.0 Å. The contour intervals are at 0.15 e Å^{-3}, large dashes — zero, small dashes – negative contours.

References

ALCOCK, N. W. (1974). *Acta Cryst.* A30, 332–335.

BACHMAN, R., KOHLER, H., SCHULZ, H. & WEBER, H.-P. (1985). *Acta Cryst.* A41, 35–40.
BUTTNER, R. H. & MALSEN, E. N. (1988). *Acta Cryst.* C44, 1707–1709.
CREAGH, D. C. (1990). Private communication.
HALL, S. R. & STEWART, J. M. (1990). Editors. *XTAL*3.0 *User's Manual.* Univs. of Western Australia, Australia, and Maryland, USA.
HIRSHFELD, F. L. (1977). *Isr. J. Chem.* 16, 198–201.
MASLEN, E. N. (1990). Private communication.
MASLEN, E. N. & SPADACCINI, N. (1989). *Acta Cryst.* B45, 45–52.
MASLEN, E. N. & SPADACCINI, N. (1993). *Acta Cryst.* A49. In the press.
REES, B. (1977). *Isr. J. Chem.* 16, 180–186.
SATOW, Y. & IITAKA, Y. (1989). *Rev. Sci. Instrum.* 60, 2390–2393.

X-ray Study of the Electron Density in Calcite, CaCO₃

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Abstract

The electron density in synthetic calcite, $CaCO_3$, has been determined using diffraction data for a naturally faced single crystal measured with X-ray Mo $K\alpha$ ($\lambda = 0.71073$ Å) radiation. Extinction corrections that minimize differences between equivalent reflection intensities are closely approximated by the values which optimize the extinction parameter as part of the least-squares structure refinement. Deformation electron densities evaluated with the two techniques are closely similar. There are 0.26 e Å^{-3} high-density maxima in the C—O bonds and 0.28 e Å^{-3} maxima at the O-atom lone pairs. There is no evidence in the least-squares parameters and deformation maps for deviation from CO_3-group planarity or disorder. Space group $R\bar{3}c$, hexagonal, $M_r = 100.09$, $a = 4.991$ (2), $c = 17.062$ (2) Å, $V = 368.1$ (3) Å^3, $Z = 6$, $D_x = 2.709$ Mg m^{-3}, μ(Mo $K\alpha$) $= 2.134$ mm^{-1}, $F(000) = 300$, $T = 293$ K, $R = 0.017$, $wR = 0.023$, $S = 4.52$ for 328 unique reflections.

Introduction

Calcite, $CaCO_3$, is an abundant carbonate mineral. Its structure is isomorphous with that of several carbonate constituents of sedimentary rocks, including magnesium- and iron-bearing carbonates. These calcite-type minerals are often used as model compounds for investigating structural sources of optical anisotropy.

The calcite structure has the same space group, $R\bar{3}c$, as another widely distributed mineral, corundum (α-Al_2O_3), for which the electron density has been measured several times over the past decade. Deformation-density maps in a recent synchrotron radiation study of a small corundum specimen by Maslen, Streltsov, Streltsova, Ishizawa & Satow (1993) differ significantly from those reported previously. The discrepancies were attributed to the extinction corrections which in the earlier studies were determined by refining the corrections along with the structure by least-squares minimizing of differences between observed and calculated structure factors (Streltsov & Maslen, 1992).

In an alternative approach to extinction corrections for small crystals, Maslen & Spadaccini (1993) determine extinction parameters by least-squares minimizing of differences between intensities for equivalent reflections with different path lengths. This eliminates any dependence of the extinction estimates on structure-factor models which may occur if corrections are determined as part of the structure refinement. The number of equivalent reflection intensities for high-symmetry structures is larger than the number of observations relevant to extinction in structure refinements with symmetry-unique observations. This increase in numbers improves the statistical significance of the results which are derived. For corundum the influence of extinction on the diffraction data indicated by the equivalent-reflection technique was much smaller