functions of $(t/\Lambda \cos\theta_B)$ are given and can be compared with those in Kato II (Figs. 2 and 3).

In the Kato and in the Al Haddad & Becker treatments, the mixed integrated intensities are obtained *via* the intensity distributions $I_0^m(s_0, s_g)$ and $I_g^m(s_0, s_g)$. This is not the case in our approach based on the simple transfer equations and which only requires very simple mathematics.

The statistical diffraction theory will probably be developed much further. There are many open questions, for instance the relation between the correlation lengths τ and τ_e. Efforts will be made to overcome the limitation $\tau \ll \Lambda$. Such questions have not been considered in the present paper which is strictly devoted to Kato's equations in the form defined in Kato (1980*a*).

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A Time-of-Flight Neutron Diffraction Study of Anharmonic Thermal Vibrations in SrF_2, at the Spallation Neutron Source ISIS

BY J. B. FORSYTH, C. C. WILSON AND T. M. SABINE*

Neutron Science Division, Rutherford Appleton Laboratory, Chilton, Didcot, Oxon OX11 0QX, England

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Abstract

Measurements have been made, at wavelengths in the range 0·3-6·2 Å, of *hhl* reflections of SrF_2 on the single-crystal diffractometer (SXD) at the ISIS Spallation Neutron Source. After application of a variable-wavelength extinction correction to the derived $|F_{hkl}|$ values, a refinement of the anharmonicity parameter β_F of the fluorine atoms was carried out, yielding a value of $-4{\cdot}19\,(30)\times10^{-19}$ J Å^{-3}.

Introduction

The anharmonic thermal vibrations of the tetrahedrally bound atoms in fluorite structures have been widely studied using monochromatic neutron beams from reactor sources (Cooper, Rouse & Willis, 1968; Cooper & Rouse, 1971; Mair & Barnea, 1971; Mair, Barnea, Cooper & Rouse, 1974). The purpose of this study was to investigate, as part of the commissioning of the single-crystal diffractometer (SXD) at ISIS, a well characterized sample of SrF_2 using the white-beam neutrons from a pulsed source and to demonstrate the advantages of a pulsed source for high-resolution studies exploiting the high flux of shorter-wavelength neutrons. The measurements were carried out using a single (20 × 20 mm) scintillator detector while SXD awaits the completion of a 300 × 300 mm Anger camera position-sensitive detector (Forsyth, Lawrence & Wilson, 1988).

The simplest potential describing the anharmonic thermal vibrations in the strontium fluoride structure is (Cooper, Rouse & Willis, 1968)

$$V_j(\mathbf{r}) = V_{0j} + \tfrac{1}{2}\alpha_j(x_j^2 + y_j^2 + z_j^2) + \beta_j(x_j y_j z_j) \qquad (1)$$

where j = Sr, F and x_j, y_j and z_j are the coordinates of the thermal displacement of the jth atom. The $(x_j^2 + y_j^2 + z_j^2)$ term is the normal harmonic potential with α_j related to the mean square displacement of atom j and the term in β_j reflects the contribution of anharmonicity to the third-order term in the potential.

Owing to the centrosymmetry at the Sr site, $\beta_{Sr} = 0$. However β_F for the tetrahedrally bonded fluorine atoms has an appreciable effect on the observed intensities for reflections where the sum of indices $|h|+|k|+|l| = 4n \pm 1$. After Mair & Barnea (1971) we can write for the ratio of two structure factors

$$|F_+|/|F_-| = 1 - (2b_F/b_{Sr}) \times \exp\left[(B_{Sr} - B_F)\left(\frac{h^2+k^2+l^2}{4a^2}\right)\right] \times (B_F/4\pi a)^3(\beta_F/kT)(|h_1k_1l_1| + |h_2k_2l_2|) \qquad (2)$$

where $|F_\pm|$ are the structure factors for reflections *hkl* with $|h|+|k|+|l| = 4n \pm 1$, b_{Sr} and b_F are the scattering

* Attached from Department of Physics, New South Wales Institute of Technology, Sydney, Australia.

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lengths, B_{Sr} and B_F are the isotropic temperature factors, a is the cubic cell parameter, k is the Boltzmann constant, T is the absolute temperature and β_F is the anharmonicity parameter for fluorine.

We chose to measure pairs of reflections with equal $h^2+k^2+l^2$ values. In the harmonic approximation such reflections would have equal intensities. When anharmonicity is present, however, some variation can be expected for pairs whose $|h|+|k|+|l|=4n\pm1$, according to (2). The value of β_F at room temperature has been determined previously as $-3{\cdot}95\,(46)\times 10^{-19}$ J Å^{-3} (Cooper & Rouse, 1971).

Experimental

The sample of SrF_2 used was cylindrical of height 8 mm, diameter 2·5 mm, aligned with ⟨110⟩ vertical. Intensities were measured at room temperature on the SXD at ISIS in the equatorial plane, accessing *hhl* reflections. Extraction of intensities was performed by fitting the time evolution of the peaks with a function

$$\varphi(t) = G(\sigma, t) * [R\exp(-t/\tau_f) + (1-R)\exp(-t/\tau_s)] \qquad (3)$$

where $G(\sigma, t)$ is a Gaussian ($\sigma\sim3$ μs), R is a switch function between the two decaying exponentials described by $\tau_s\sim32$ μs, $\tau_f\sim3$ μs and $*$ represents convolution. This peak shape reflects the performance of the ambient water moderator viewed by SXD (Taylor, 1984). Typical peak fits are shown in Fig. 1.

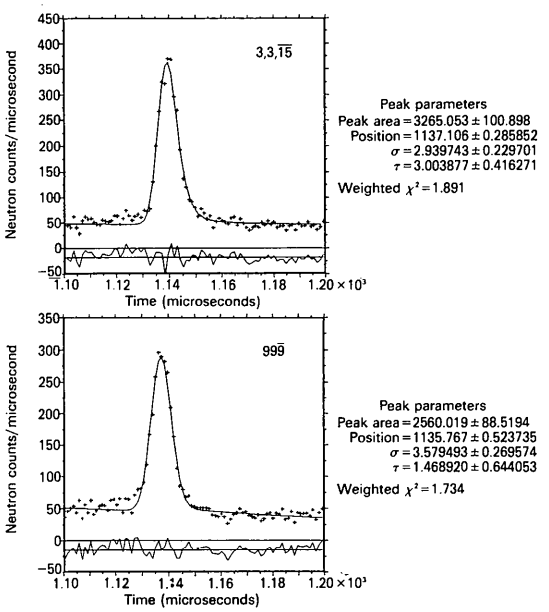

Fig. 1. The 3, 3, $\bar{1}5$ (top) and 9 9 $\bar{9}$ (bottom) reflections of SrF_2, fitted by the function in equation (3). In the harmonic approximation these two reflections would have equal intensities. The observed intensity difference is due to the anharmonic thermal vibrations exhibited by the fluorine atoms.

Table 1. *The final parameters from the refinements without (N) and with (A) fluorine anharmonicity included*

Only those parameters with e.s.d.'s quoted were refined.

Parameter	*N*	*A*
b_{Sr} ($\times10^{-12}$ cm)	0·690	
b_F ($\times10^{-12}$ cm)	0·560	
Number of reflections	16	
Scale factor	1·10 (4)	1·107 (9)
B_{Sr} (Å^2)	0·539 (30)	0·539
B_F (Å^2)	0·732	0·732
β_F ($\times10^{-19}$ J Å^{-3})		−4·02 (28)
R factor (unweighted)	0·0441	0·0219

Table 2. $|F(hkl)|$ *values used in anharmonicity refinement* ($|F_{obs}|$), *together with those calculated from the refinement without* ($|F^N_{calc}|$) *and with* ($|F^A_{calc}|$) *fluorine anharmonicity included*

All values put on the same scale for comparison.

h	*k*	*l*	$\lvert F_{obs}\rvert$	$\lvert F^N_{calc}\rvert$	$\lvert F^A_{calc}\rvert$
5	5	7	1·9123	1·8367	1·8996
3	3	9	1·8349	1·8367	1·8225
7	7	1	1·8342	1·8367	1·8347
1	1	11	1·5691	1·6682	1·6822
7	7	5	1·5757	1·6682	1·6172
5	5	11	1·4575	1·3761	1·4394
1	1	13	1·4112	1·3761	1·3831
3	3	13	1·3070	1·2906	1·2786
9	9	5	1·3293	1·2906	1·2270
7	7	11	1·2409	1·1353	1·2244
5	5	13	1·0705	1·1353	1·0943
3	3	15	1·0600	1·0310	1·0563
9	9	9	0·9582	1·0310	0·9421
11	11	1	1·0128	1·0310	1·0224
7	7	15	0·8247	0·7481	0·8165
11	11	9	0·6312	0·7481	0·6607

As stated above only reflections with $|h|+|k|+|l|$ odd ($=4n\pm1$) were measured. All four equivalents were measured for each reflection in the data set and averaged data were used throughout. Owing to the high flux of short-wavelength neutrons from the ISIS source, data were collected to very high $(\sin\theta)/\lambda = 1{\cdot}696$ Å^{-1}, even though the source was operating at an average intensity of less than 10% of its final performance.

Thermal diffuse scattering

It is well known (Willis & Pryor, 1975) that one-photon inelastic scattering has a maximum at the Bragg position and that the simple procedure of assuming a flat background beneath the peak (as in this work) is in general insufficient for the determination of accurate integrated intensities.

In the present experiment, advantage is taken of the fact that, as the incident neutron energy increases, higher-order phonon processes become increasingly important, and the probability of lower-order processes eventually tends to zero. As more phonons are excited the momentum conservation condition, which

Table 3. *Pairs of reflections measured for* SrF_2, *showing agreement between expected and measured* F_+/F_- *ratios*

The 'expected' values were calculated using $\beta_F = -3{\cdot}95 \times 10^{-19}$ J Å^{-3}, the 'calculated' values using $\beta_F = -4{\cdot}19 \times 10^{-19}$ J Å^{-3}.

			Ratio (F_+/F_-)		
$\sum(h^2+k^2+l^2)$	Pair		Expected	Measured	Calculated
99	5 5 7	$(4n+1)$	1·045	1·042 (4)	1·047
	3 3 9	$(4n-1)$			
	5 5 7	$(4n+1)$	1·039	1·043 (5)	1·041
	7 7 1	$(4n-1)$			
123	1, 1, 11	$(4n+1)$	1·042	0·996 (5)	1·045
	7 7 5	$(4n-1)$			
171	5, 5, 11	$(4n+1)$	1·043	1·032 (6)	1·046
	1, 1, 13	$(4n-1)$			
187	3, 3, 13	$(4n-1)$	1·000	0·983 (8)	1·000
	9 9 5	$(4n-1)$			
219	7, 7, 11	$(4n+1)$	1·119	1·160 (19)	1·126
	5, 5, 13	$(4n-1)$			
243	3, 3, 15	$(4n+1)$	1·113	1·107 (11)	1·120
	9 9 9	$(4n-1)$			
	3, 3, 15	$(4n+1)$	1·034	1·044 (9)	1·036
	11, 11, 1	$(4n-1)$			
323	7, 7, 15	$(4n+1)$	1·205	1·308 (31)	1·217
	11, 11, 9	$(4n-1)$			
363	11, 11, 11	$(4n+1)$	1·226	1·207 (45)	1·240
	13, 13, 5	$(4n-1)$			
	1, 1, 19	$(4n+1)$	1·090	1·110 (40)	1·095
	13, 13, 5	$(4n-1)$			

Maximum $(\sin\theta)/\lambda = 1{\cdot}696$ Å^{-1} ($Q = 21{\cdot}2$ Å^{-1}).

is responsible for the one-phonon peak, is weakened and the incoherent approximation, corresponding to a flat background, becomes increasingly accurate. The anharmonic features are most evident in reflections obtained with short-wavelength neutrons and for these reflections it is reasonable to make the incoherent approximation. A detailed discussion of the relative magnitudes of the n-phonon cross sections as a function of specimen temperature and incident neutron energy is given by Gurevich & Tarasov (1968).

Results

Refinement of the $|F_{hkl}|$ values measured for these reflections was carried out in the program *XFLS3* which is the least-squares program *ORFLS* (Busing, Martin & Levy, 1962) modified to include anharmonic effects (Mair & Barnea, 1971). Extinction, which is severe in this crystal, was corrected for in a variable-wavelength adaptation of the extinction correction in the Cambridge Crystallographic Subroutine Library (CCSL) (Matthewman, Thompson & Brown, 1982), using one angular mosaic parameter in a Becker-Coppens Gaussian model (Forsyth & Wilson, 1988).

The results of the refinements quite clearly show the effect of the anharmonicity. The refined parameters are shown in Table 1. For the small number of 'anharmonicity-affected' reflections used the fluorine isotropic thermal parameter B_F tended to be unstable, and so its value was fixed at that obtained from the refinement of a full equatorial SrF_2 data set collected on SXD (Forsyth & Wilson, 1988), $B_F = 0{\cdot}732$ Å^2. The refinement of the $4n \pm 1$ reflections without anharmonicity converged to an R factor of 0·0441 (unit weights). However, when the anharmonicity parameter was included in the refinement, R was reduced to 0·0219, a marked improvement. Observed and calculated structure factors for these refinements are shown in Table 2.

The pairs of reflections measured are shown in Table 3, together with the ratio F_+/F_- predicted by (2) with $\beta_F = -3{\cdot}95 \times 10^{-19}$ J Å^{-3} and the observed F_+/F_- ratio. It can be seen that there is good agreement between the calculated and observed values of this ratio. In only one pair does the ratio disagree with the sense of the intensity change, namely for the pair 1,1,11 and 775 where the $4n+1$ reflection 1,1,11 is measured to have lower intensity than the $4n-1$, 775.

The β_F parameter determined from the refinement was $-4{\cdot}02\,(28) \times 10^{-19}$ J Å^{-3}. A least-squares fit of the observed F_+/F_- ratios yielded $\beta_F = -4{\cdot}19\,(30) \times 10^{-19}$ J Å^{-3}, in good agreement with that from the refinement. It can be seen that the value of β_F obtained in this experiment agrees well with previous work but is more precisely determined, in spite of the fact that the experimental data can be collected in substantially less time. The ability of SXD to exploit the high neutron flux at the short wavelengths (down to $\lambda = 0{\cdot}25$ Å and below) available on a pulsed source is shown by the high $(\sin\theta)/\lambda$ reached in this work. It is hoped to investigate the temperature dependence of the anharmonicity effect at these high $(\sin\theta)/\lambda$ values in the near future when a furnace will be available on SXD.

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On the Probabilistic Theory of Isomorphous Data Sets: General Joint Distributions for the SIR, SAS and Partial/Complete Structure Cases

BY SUZANNE FORTIER* AND GUR DAYAL NIGAM†

Department of Chemistry, Queen's University, Kingston, Canada K7L 3N6

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Abstract

By characterizing isomorphism in reciprocal space [*i.e.* diffraction data sets are isomorphous if they have the same geometry (the same reciprocal-lattice unit cell) and the same symmetry] it is shown that the diffraction data of a native protein and of its heavy-atom derivatives, the calculated data of a partial structure and the observed data of its associated complete structure, and the Friedel-pair data of an anomalously scattering crystal structure all belong to the more general class of isomorphous data sets. Their joint probability distributions for two- and three-phase structure invariants are shown to be isomorphous: they have the same functional form and differ only in individual atomic scattering factors. General joint probability distributions, which can be used for any isomorphous data pairs, are presented.

1. Introduction

Isomorphism is usually defined in direct space as, for example, the 'similarity of crystal shape, unit-cell dimensions, and structure between substances of similar chemical composition' (Glusker & Trueblood, 1985). For the present work, it is convenient to characterize isomorphism in reciprocal space; *i.e.* diffraction data sets are isomorphous if they have the same geometry (the same reciprocal-lattice unit cell) and the same symmetry. Differences between isomorphous data are thus to be found in the intensities of individual reflections, and therefore in the scattering power of a subset of atoms. This allows us to consider a variety of diffraction data sets as representing cases of isomorphous data sets: for example, the diffraction data of a native protein and of its heavy-atom derivatives, the calculated data of a partial structure and the observed data of its associated complete structure, X-ray and neutron data measured on the same substance, and, finally, the Friedel-pair data of an anomalously scattering crystal structure.

Through the use of the method of joint probability distributions, formulae have been obtained to estimate the value of two- and three-phase structure invariants for the cases of isomorphous replacement (Hauptman, 1982*a*; Giacovazzo, Cascarano & Zheng Chao-de, 1988; Srinivasan & Parthasarathy, 1976), anomalous dispersion (Hauptman, 1982*b*; Giacovazzo, 1983*a*) and partial/complete structure (Beurskens, Prick, Doesburg & Gould, 1979; Srinivasan & Parthasarathy, 1976; Giacovazzo, 1983*b*; Sim, 1959). In the present paper, it is shown that the joint probability distributions are isomorphous: that is, they have the same functional form and differ only in individual atomic scattering factors. General joint probability distributions, which can be used for any isomorphous data pairs, are presented.

* Author to whom all correspondence should be addressed.
† Present address: Department of Physics, Indian Institute of Technology, Kharagpur 721 302, India.

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