structure and exhibits a composition-dependent ionic conductivity which increases, at 600 K, from 3·4 × 10^{-3} S m^{-1} for $x = 2{\cdot}0$, Na_2BeSiO_4, to 2·3 × 10^{-1} S m^{-1} for $x = 1{\cdot}8$, $Na_{1\cdot8}Be_{0\cdot9}Si_{1\cdot1}O_4$. The increase in conductivity with decreasing x is paralleled by a decreasing occupancy of Na-atom sites. The compound $Na_2BeSi_2O_6$ is found to be isostructural with the beryllium mineral chkalovite (Simonov, Egorov-Tismenko & Belov, 1976), with a filled cristobalite-type structure, and shows a conductivity value of 2·8 × 10^{-3} S m^{-1} at 600 K.

The conductivity of $Na_{10}Be_4Si_4O_{17}$ at 600 K is thus considerably lower than that of the best conductor, $Na_{1\cdot8}Be_{0\cdot9}Si_{1\cdot1}O_4$, but is of the same magnitude as those found for Na_2BeSiO_4 and $Na_2BeSi_2O_6$. The rather limited conductivity in $Na_{10}Be_4Si_4O_{17}$ may be understood as caused by the full occupancy of Na-atom sites and the denseness of the Na-atom arrangement. The migration of an Na atom can be expected to require a high activation energy, since it probably involves severe displacements of neighbouring Na atoms from their equilibrium positions and possibly displacements of the rigid $Be_4Si_4O_{17}$ units.

The conductivity may possibly be increased by introducing vacancies on the Na-atom sites by substituting *e.g.* Mg^{2+} for Na^+. Preparative work is in progress to investigate this possibility.

The authors wish to thank Professors M. Nygren and R. Norrestam for valuable discussions and great interest in this work. This investigation has received financial support from the Swedish Natural Science Research Council.

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Acta Cryst. (1990). **B46**, 739–742

Single-Crystal Neutron Diffraction Studies of MnF_2 as a Function of Temperature: the Effect of Magnetostriction

By W. Jauch

Hahn-Meitner-Institut, Glienicker Str. 100, D-1000 Berlin 39, Federal Republic of Germany

G. J. McIntyre

Institut Laue–Langevin, 156X, 38042 Grenoble CEDEX, France

and A. J. Schultz

Chemistry and Materials Science Divisions, Argonne National Laboratory, Argonne, Illinois 60439, USA

(*Received 13 March 1990; accepted 13 July 1990*)

Abstract

MnF_2 has been investigated at 295, 60 and 15 K by monochromatic neutron diffraction in order to determine the effect of antiferromagnetic order on the fluorine nuclear positional parameter. An internal displacement of 2·0 (3) × 10^{-3} Å is found between 295 and 15 K which is in excellent agreement with the result obtained from single-crystal time-of-flight neutron diffraction. At 15 K there is a significant difference between the neutron and γ-ray refined positional parameters.

Introduction

The influence of antiferromagnetic order on the fluorine position in MnF_2 has been the subject of

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previous studies by both γ-ray and time-of-flight (TOF) neutron diffraction (Jauch, Schultz & Schneider, 1988; hereafter referred to as I). The low temperature of the neutron experiment was reported as 15 K. A subsequent comparison of calculated and observed magnetic reflections, however, revealed that the sample temperature must have been around 60 K, *i.e.* just below the Néel temperature of 67 K. The reason for this experimental error has been identified as an almost missing contact between goniometer head and cold finger of the closed-cycle refrigerator.

Because the influence of magnetic order would be reduced near the Néel temperature a further TOF neutron experiment was therefore performed at 15 K where the temperature was controlled by monitoring the temperature dependence of the magnetic reflections (100) and (300). In order to confirm the TOF results and to give a definitive description of the mean thermal nuclear position of fluorine, monochromatic neutron diffraction experiments at 295, 60 and 15 K were also undertaken. Both these experiments are described in this paper and the results of all the neutron diffraction experiments presented.

Comparison of the results obtained with the different techniques allows an assessment of the accuracy that can be achieved with present single-crystal neutron diffraction analysis.

Experimental

MnF_2 has a rutile-type structure (space group $P4_2/mnm$) with Mn at (000) and F at (xx0). The lattice constants are $a = 4{\cdot}8736$, $c = 3{\cdot}3102$ Å at 295 K, $a = 4{\cdot}8736$, $c = 3{\cdot}3020$ Å at 60 K, and $a = 4{\cdot}8736$, $c = 3{\cdot}3000$ Å at 15 K with standard deviations of less than 2×10^{-4} Å as reported by Haefner (1964). The single-crystal sample used in these experiments was the same 3·7 mm diameter sphere used in the earlier experiments (I).

TOF data

The TOF data were collected with the Laue technique on the single-crystal diffractometer (SCD) at the Argonne pulsed spallation neutron source IPNS. Details of data collection and reduction to structure factors have been described in I. Because of the increased flux at IPNS the counting time per histogram could be reduced to 3 h; each histogram contained about 60 reflections.

Monochromatic data sets

The experiments were performed on the four-circle diffractometer D9 located at the hot source of the High-Flux Reactor of the Institut Laue–Langevin. A Ge(220) monochromator was used to give a wavelength of 0·5506 (1) Å, based on a refinement of the centred angles assuming the 15 K cell parameters to be correct. In order to eliminate second-order contamination an Hf filter was used. The instrument is equipped with a small two-dimensional detector which is used in single reflection mode (Lehmann, Kuhs, McIntyre, Wilkinson & Allibon, 1989). The observed counts were reduced to integrated intensities employing a method that minimizes the relative standard deviation $\sigma(I)/I$ (Wilkinson, Khamis, Stansfield & McIntyre, 1988). Data sets were collected at 295, 60 and 15 K up to $\sin\theta/\lambda = 1{\cdot}4$ Å^{-1} with a counting time of 2–4 min per reflection. An absorption correction could be omitted since $\mu R = 0{\cdot}067$.

Refinement of data

The low-temperature data sets contain mixed nuclear and magnetic reflections ($h + k + l$ odd). Reflections of this type with $\sin\theta/\lambda \leq 0{\cdot}7$ Å^{-1} were excluded from the final refinements.

TOF data

Refinements based on $|F|^2$ were performed using a multiwavelength program based on *ORFLS* (Busing, Martin & Levy, 1962). The observations were weighted according to $w = (\sigma_{cs}^2 + P^2|F|^4 + K)^{-1}$ with σ_{cs}^2 = counting statistical variance, $P = 0{\cdot}04$ (instrumental instability constant), K = constant. Extinction was accounted for by the Becker & Coppens (1974) Lorentzian model. The results are presented in Table 1.

Monochromatic data sets

XTAL (Hall & Stewart, 1989) and *PROMETHEUS* (Zucker, Perenthaler, Kuhs, Bachmann & Schulz, 1983) were used for the refinements. The scattering lengths were taken as b(Mn) = −3·73, b(F) = 5·654 fm. The refinements were with respect to $|F|^2$, with weights based on the counting statistical variance. Symmetry-equivalent reflections were not averaged. The extinction formalisms BC: Becker & Coppens (1974) and Z: Zachariasen (1967) were applied. Surprisingly, the best fits were obtained with the Zachariasen correction. Analyses of the room-temperature data, for example, resulted in the following goodness-of-fit parameters: 1·135, 1·156 and 1·218 for Z type I, BC type I (Lorentzian) and BC type I (Gaussian), respectively. The corresponding smallest value for the extinction correction ($y = I_{obs}/I_{calc}$) was $y(200) = 0{\cdot}35$, 0·31 and 0·26. The refinement results are also summarized in Table 1.

To the data measured at 295 K we applied structure-factor equations for anharmonic thermal motion based on the Gram–Charlier expansion

Table 1. *Refined structural parameters obtained from monochromatic (MON) and TOF neutrons*

Upper, middle and lower lines refer to 15, 60 and 295 K respectively.

	MON	TOF
Manganese		
U_{11} (Å^2)	0·00221 (3)	0·00253 (16)
	0·00271 (4)	0·00258 (7)
	0·00894 (5)	0·00796 (8)
U_{33}	0·00170 (4)	0·00184 (25)
	0·00197 (6)	0·00180 (14)
	0·00597 (5)	0·00558 (16)
U_{12}	−0·00014 (4)	−0·00012 (8)
	−0·00034 (6)	−0·00037 (5)
	−0·00157 (5)	−0·00155 (6)
Fluorine		
x	0·30464 (2)	0·30464 (3)
	0·30477 (2)	0·30480 (2)
	0·30498 (2)	0·30491 (3)
U_{11} (Å^2)	0·00485 (3)	0·00525 (14)
	0·00548 (3)	0·00566 (6)
	0·01532 (4)	0·01433 (8)
U_{33}	0·00379 (3)	0·00416 (23)
	0·00417 (4)	0·00399 (13)
	0·00975 (4)	0·00931 (14)
U_{12}	−0·00177 (2)	−0·00171 (4)
	−0·00203 (3)	−0·00253 (2)
	−0·00758 (4)	−0·00755 (5)
No. of observations	791	494
	351	1018
	578	1120
No. of unique reflections	477	420
	296	309
	505	340
$R(F^2)$	0·024	0·046
	0·029	0·045
	0·029	0·051
$R_{\rm stat}(F^2)$	0·015	0·020
	0·012	0·021
	0·027	0·034
$wR(F^2)$	0·036	0·063
	0·032	0·059
	0·028	0·067

Notes: $R(F^2) = \sum|F^2_{\rm obs} - F^2_{\rm calc}|/\sum F^2_{\rm obs}$; $R_{\rm stat}(F^2) = \sum\sigma_{\rm cs}(F^2_{\rm obs})/\sum F^2_{\rm obs}$; $wR(F^2) = [\sum w(F^2_{\rm obs} - F^2_{\rm calc})^2/\sum wF^4_{\rm obs}]^{1/2}$.

(Zucker & Schulz, 1982). It turned out that the thermal motion of Mn is well approximated by the harmonic second-order terms (the six fourth-order terms are all less than 2σ) whereas some of the third- and fourth-order terms for F are significantly non-zero. The anharmonic refinement, carried out based on $|F|$, gives a significantly better result ($\chi^2 = \sum w\Delta^2 = 740{\cdot}9$) than the harmonic one ($\chi^2 = 820{\cdot}5$). The positivity of the resulting probability density function (p.d.f.) for F has been checked. The p.d.f. has its largest extension perpendicular to the plane of the Mn—F bonds. The sense of the skewness of the p.d.f. along [110] is such that the p.d.f. of F is up to 10% higher towards its neighbour F than towards Mn. Hence, the p.d.f. is in accordance with the expectation that the F atom should vibrate preferentially into the interstices in the crystal environment. The structural parameters are listed in Table 2.

Table 2. *Refinement with anharmonic temperature factors*

$T(H) = [1 - \tfrac{4}{3}\pi^3 ic_{jkl}h_jh_kh_l + \tfrac{2}{3}\pi^4 d_{jklm}h_jh_kh_lh_m]T_{\rm harm}(H)$ for the 295 K monochromatic neutron data.

Manganese	
U_{11} (Å^2)	0·00907 (5)
U_{33}	0·00612 (6)
U_{12}	−0·00156 (5)
Fluorine	
x	0·30493 (4)
U_{11} (Å^2)	0·01579 (11)
U_{33}	0·01006 (11)
U_{12}	−0·00744 (10)
$c_{111} \times 10^3$	0·00005 (14)
$c_{133} \times 10^3$	−0·00039 (11)
$c_{112} \times 10^3$	−0·00001 (6)
$d_{1111} \times 10^4$	0·00057 (15)
$d_{3333} \times 10^4$	0·00098 (50)
$d_{1122} \times 10^4$	0·00004 (7)
$d_{1133} \times 10^4$	0·00029 (9)
$d_{1112} \times 10^4$	0·00008 (7)
$d_{1233} \times 10^4$	0·00010 (9)
No. of observations	578
$wR(F)$	0·0140

Discussion

The positional parameters at low temperature obtained from the two neutron experiments are virtually identical. At room temperature the bond length in the (001) plane resulting from a harmonic refinement of the monochromatic data is slightly larger [2·10202 (14) Å] than the corresponding value obtained from the TOF data [2·10154 (21) Å]. This difference is removed when anharmonic terms are included [2·10167 (28) Å]. We consider the positional parameter derived from the anharmonic refinement to be the more reliable estimate (*e.g.* Scheringer, 1986). The reason why an anharmonic refinement of the TOF data is not needed is the less extensive range in $\sin\theta/\lambda$: 6% of the TOF data have $\sin\theta/\lambda > 1{\cdot}2$ Å^{-1} as compared to 35% of the monochromatic data at room temperature.

The thermal parameters at low temperature are in remarkably good agreement. The values derived from the monochromatic data are the more reliable ones. The good agreement, however, indicates that the many wavelength-dependent factors necessary to reduce integrated intensities to structure factors for the Laue TOF method have been adequately determined. The thermal parameters at 295 K are too small in the Laue TOF case, with the exception of the U_{12} values which agree well. In view of the low-temperature results, the discrepancy in U_{11} and U_{33} probably should be attributed to thermal diffuse scattering.

The TOF data are much more affected by extinction than the monochromatic data. In the TOF case the refined values of the mosaic spread are in good agreement with the width of rocking curves of about 11″ as determined by double-crystal γ-ray diffraction (see I for more details). The corresponding values deduced from the monochromatic data are too small by a factor of about three (Table 3). A similar situation occurs in γ-ray diffraction when

Table 3. *Refined values of the mosaic spread (full width at half height in seconds of arc) as obtained from monochromatic and TOF neutrons for model Z*

	MON	TOF
15 K	3·8 (1)	8·1 (3)
60 K	3·2 (1)	10·2 (3)
295 K	4·0 (1)	12·4 (4)

extinction is pronounced only for few reflections which leads to refined mosaic spreads that are considerably smaller than the experimental estimates. It thus appears that the extinction corrections will be overestimated in least-squares refinements that are based on data sets where only a small part of the reflections are affected by extinction.

The overall counting statistical precision of a data set may be summarized by the statistical R factor, $R_{\rm stat}(F^2) = \sum\sigma_{\rm cs}(F^2)/\sum F^2$, which imposes a lower limit to the conventional crystallographic R factor, $R(F^2) = \sum|F^2_{\rm obs} - F^2_{\rm calc}|/\sum F^2_{\rm obs}$. It is apparent from Table 1 that the TOF data are subject to additional uncertainties besides counting statistics to a higher degree than the monochromatic data. The agreement of the derived results, however, indicates these additional uncertainties to be of a random rather than of a systematic nature.

The purpose behind the measurement of data sets with two methods was to check whether the mean thermal nuclear positions of fluorine differ in the paramagnetic and antiferromagnetically ordered state. Actually, the low temperature of the neutron investigation reported in I as 15 K was about 60 K. We now find that at 15 K, the magnetostrictive shifts $\Delta x = x(15\ {\rm K}) - x(295\ {\rm K})$ are $-2{\cdot}9\ (4) \times 10^{-4}$ and $-2{\cdot}7\ (4) \times 10^{-4}$ using monochromatic and TOF neutrons, respectively. This corresponds to an average shift of $1{\cdot}95\ (20) \times 10^{-3}$ Å in the Mn—F distance within the plane normal to the c axis. This shift is different from the result deduced from γ-ray diffraction: $\Delta x = -4{\cdot}8\ (7) \times 10^{-4}$. The implications of this subtle difference will be discussed in a forthcoming paper, dealing with the charge density distribution in MnF_2.

The work at Argonne was supported by the Office of Basic Energy Sciences, Division of Materials Sciences, US Department of Energy, under contract W-31-109-Eng-38.

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Acta Cryst. (1990). **B46**, 742–747

Structures of Na(In,Sc)Si_2O_6 Clinopyroxenes Formed at 6 GPa Pressure

BY HARUO OHASHI, TOSHIKAZU OSAWA AND AKIRA SATO

National Institute for Research in Inorganic Materials, Namiki 1-1, *Tsukuba, Ibaraki* 305, *Japan*

(*Received* 4 *January* 1990; *accepted* 12 *July* 1990)

Abstract

Crystal structures have been refined from single-crystal X-ray data for nine synthetic clinopyroxenes in the system $NaInSi_2O_6$–$NaScSi_2O_6$, crystallized at 1770 K and 6 GPa pressure. The structures are isomorphous with other sodium pyroxenes. The space group is $C2/c$, $Z = 4$. In and Sc occupy a distorted octahedral ($M1$) site. The $M1$—$M1$ distances and the $M1$—O1—$M1$ angles correlate with the mean $M1$—O1 distances in such a way as to follow two different trends, suggesting that there are two different electronic states for the octahedral In^{3+} ions. The Si—O distances constitute two populations which can be related to the mean electronegativity of the octahedral ($M1$) ions. From the Si—O distances, the electronegativites of the two In^{3+} ions are 1·2 and 1·7 on Pauling's scale.

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