$3d$ electron distributions and that $(t_{2g})^6(e_g)^2$ is a good approximation for the $3d$ electron configuration in the Ni^{2+} ion. However, the remaining peaks in Fig. 4 indicate also that the population of e_g orbitals, which extend toward ligands, may be a little larger than 2. By the population refinement with the model $(t_{2g})^{6-p}(e_g)^{2+p}$, we obtained 0·30 (8) for p. The deformation density map after this refinement shows that the positive peaks in Fig. 4 have disappeared and there remains no significant peak around the Ni^{2+} ion.

Conclusion

With the X-ray diffraction technique, the Mn^{2+} ion in $KMnF_3$ crystals was confirmed to be in the high-spin state in the same way as applied to the Co^{2+} ion in $KCoF_3$ crystals (Kijima, Tanaka & Marumo, 1981). The large difference between the residual densities in Figs. 1 and 2, and between those in Figs. 3 and 4 assure that a careful X-ray study is accurate enough to detect the difference of the electron configurations in transition metals. The X-ray diffraction method may be applied also to mixed-valence complexes and to many other compounds where the determination of the electron configuration of transition metals is important.

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Electron Density Distribution in Crystals of Iron(II) Potassium Trifluoride

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Abstract

The electron density distribution in a crystal of $KFeF_3$ was investigated on the basis of X-ray intensity data collected by diffractometry at 298 K. The deformation densities around the Fe^{2+} ion in an octahedral field were analysed by utilizing aspherical scattering factors. The refinement assuming the high-spin state for the Fe^{2+} ion decreased the R value to 0·0072 from the 0·0075 obtained with spherical scattering factors, while that assuming the low-spin state increased the value to 0·0142. Further, the refinement of electron populations for t_{2g} and e_g orbitals gave the electronic state as $(t_{2g})^{3·93}(e_g)^{2·07}$. The difference Fourier maps after these refinements also showed that the high-spin model is a good approximation to the electronic state of the Fe^{2+} ion in the cubic $KFeF_3$ crystal at room temperature. [Crystal data: $M_r = 151·95$, cubic, $Pm3m$, $a = 4·1198$ (1) Å, $V = 69·924$ Å^3, $Z = 1$, $D_x = 3·60$ g cm^{-3}, $\mu(Mo\,K\alpha_1) = 90·89$ cm^{-1}.]

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Introduction

For the last ten years studies on the density distribution of $3d$ electrons have been actively performed on crystals of transition-metal compounds by X-ray diffraction. In early years deformation densities of $3d$ electrons in crystal fields were qualitatively studied in crystals of $[Co(NH_3)_6][Co(CN)_6]$ (Iwata & Saito, 1973), γ-Ni_2SiO_4 (Marumo, Isobe, Saito, Yagi & Akimoto, 1974), γ-Co_2SiO_4 (Marumo, Isobe & Akimoto, 1977) and $CoAl_2O_4$ (Toriumi, Ozima, Akaogi & Saito, 1978). More recently, we have investigated the electron density distributions in a series of KMF_3 (M: Mn, Co and Ni) crystals and determined the $3d$ electron configurations by computing the numbers of electrons in t_{2g} and e_g orbitals (Kijima, Tanaka & Marumo, 1981, 1983). From the study on $KCoF_3$, it was found that the electron configuration of the Co^{2+} ion was close to $(t_{2g})^5(e_g)^2$. In the case of $KNiF_3$, the $(t_{2g})^6(e_g)^2$ configuration was revealed to be a proper model for the Ni^{2+} ion. As to the Mn^{2+} ion in $KMnF_3$, the electron configuration $(t_{2g})^3(e_g)^2$ of the high-spin state corresponding to the spherical-atom model was shown to be a good representation of the real electron configuration. Each of these works shows that X-ray diffractometry is a useful method for determining the electronic states of the transition-metal ions in crystals.

The present study was performed to investigate the electron density distribution in $KFeF_3$ as part of the study on electronic states of transition-metal atoms in KMF_3 crystals.

Experimental

The crystal of $KFeF_3$ used in this study was synthesized by the flux method by Professor A. Ito of Ochanomizu University. A piece of the crystal was shaped into a sphere with a diameter of 0·13 mm by the Bond (1951) method. The lattice constant was determined from 51 2θ values larger than 80° measured with graphite-monochromated Mo $K\alpha_1$ radiation. The crystal data of $KFeF_3$ are given in the *Abstract*. Integrated intensities were collected on an automated Rigaku AFC-5 four-circle diffractometer using the ω–2θ scan technique to $2\theta_{max} = 130°$; scan speed 4° min⁻¹ (2θ). The scan width was set as $(A + B\tan\theta)°$, where θ is the Bragg angle and A and B are constants, to make the range of measurement as narrow as possible ($A = 1·8$, $B = 0·3$ for $0 \le 2\theta \le 40°$; $A = 1·4$, $B = 0·3$ for $40 < 2\theta \le 130°$). The measurement was repeated up to ten times per reflection (894 measured reflections, 151 unique) until the value of $\sigma F/F$ became below 0·01, where F is the structure factor and σF is its standard deviation. An absorption correction was performed with the absorption-correction factor A^*

given in *International Tables for X-ray Crystallography* (1967). The mean path length $\bar{T} = (dA^*/d\mu)/A^*$ was calculated with the program *DADMYU* for the subsequent extinction correction. Here, μ is the linear absorption coefficient.

Refinement

The Fe^{2+} ion has six electrons in the $3d$ orbitals. In an octahedral field it is either in the high-spin state $(t_{2g})^4(e_g)^2$ or the low-spin state $(t_{2g})^6$ according to the strength of the ligand field. We tried least-squares refinements by assuming four kinds of electron-configuration models for the Fe^{2+} ion as described below.

(1) *Refinement based on the spherical-atom model*

We assumed the free-ion model for Fe^{2+}, and spherical scattering factors were used for all the constituent atoms in the calculation. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974). The refinement was performed in four steps:

(a) with only isotropic temperature factors;

(b) with anisotropic temperature factors;

(c) with anisotropic temperature factors and an isotropic extinction parameter; and

(d) with anisotropic temperature factors and by assuming anisotropic extinction of type I.

The usual discrepancy factors R and R_w were (a) 0·0433 and 0·0485, (b) 0·0305 and 0·0424, (c) 0·0075 and 0·0101, (d) 0·0075 and 0·0092, respectively. The temperature factors and extinction parameters after the final step (d) of the refinement are in Table 1. The R and R_w values after the various refinements are also compared in Table 1.†

(2) *Refinement assuming the high-spin state*

The high-spin state was assumed for the Fe^{2+} ion and aspherical scattering factors were used for the structure factor calculation. Aspherical scattering factors were defined to be the sum of the scattering factors of the Ar core and $3d$ electrons. The former is in *International Tables for X-ray Crystallography* (1974) and the expressions for the latter are given by Tanaka, Konishi & Marumo (1979, 1980). The least-squares refinement was performed with the program *LINKT* written by one of the authors (KT). All of the thermal and extinction parameters were changed. The R and R_w

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† A list of structure factors and Fig. 4 have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38543 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *The anisotropic temperature factors* ($\text{Å}^2 \times 10^5$) *and anisotropic extinction parameters* ($\times 10^6$)

The atomic positions are (0,0,0) for Fe, $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ for K and $(\frac{1}{2},0,0)$ for F. The form of the anisotropic temperature factor is defined as $\exp\{-2\pi^2 a^{*2}(h^2 + k^2 + l^2)U_{11}\}$ for K and Fe and $\exp\{-2\pi^2 a^{*2} \times [h^2 U_{11} + (k^2 + l^2)U_{22}]\}$ for F.

	Refinements			
	(1) Spherical $(t_{2g})^{3\cdot6}(e_g)^{2\cdot4}$	(2) High spin $(t_{2g})^4(e_g)^2$	(3) Low spin $(t_{2g})^6$	(4) $(t_{2g})^{3\cdot93}(e_g)^{2\cdot07}$
K U_{11}	1793 (4)	1796 (4)	1797 (6)	1796 (4)
Fe U_{11}	715 (2)	710 (2)	705 (3)	709 (2)
F U_{11}	934 (12)	944 (12)	978 (18)	944 (13)
U_{22}	2600 (13)	2592 (13)	2499 (20)	2592 (13)
G_{11}	823 (19)	836 (19)	823 (29)	837 (19)
G_{22}	828 (67)	908 (67)	1113 (107)	901 (67)
G_{33}	519 (21)	522 (20)	482 (31)	523 (20)
G_{12}	−83 (27)	−84 (27)	−94 (42)	−84 (27)
G_{13}	168 (16)	165 (16)	147 (24)	165 (16)
G_{23}	−124 (25)	−126 (25)	−135 (38)	−125 (25)
R	0·0075	0·0072	0·0142	0·0071
R_w	0·0092	0·0089	0·0136	0·0089

values were reduced to 0·0072 and 0·0089, respectively. Parameters after this refinement are listed in Table 1.

(3) Refinement assuming the low-spin state

The low-spin state was assumed in this refinement. The high-spin state showed a good fit to the observation as described in the foregoing section and it is also supported by a magnetic study (Machin, Martin & Nyholm, 1963). Therefore, this refinement was performed to demonstrate that the X-ray diffraction method can clearly discriminate the spin state of the Fe^{2+} ion. All the thermal and extinction parameters were changed, and the R and R_w values were markedly increased to 0·0142 and 0·0136, respectively. The parameters obtained are in Table 1.

(4) Numbers of electrons in t_{2g} and e_g orbitals

The populations of electrons in t_{2g} and e_g orbitals were determined by assuming the electron configuration $(t_{2g})^p(e_g)^{6-p}$. The parameter p is the number of electrons in the t_{2g} orbital. We changed p, and the thermal and extinction parameters. The value of p was determined to be 3·93 (7), and R and R_w values were 0·0071 and 0·0089, respectively. Parameters after this refinement are given in Table 1.

Results and discussion

Figs. 1(a) and 1(b) are the difference Fourier maps after the refinement with the spherical-atom model. Six large negative peaks with depths $-0\cdot77$ e Å^{-3} are observed at 0·37 Å from the Fe^{2+} nucleus on the Fe—F bonds, and eight positive peaks with heights 0·32 e Å^{-3}

are located at 0·55 Å in the $\langle 111 \rangle$ directions. These negative and positive peaks are supposed to be due to the deformation of $3d$ electron distributions.

Figs. 2(a) and 2(b) are the difference Fourier maps after the refinement with the assumption of high-spin electron configuration for the Fe^{2+} ion. Large negative peaks on the Fe—F bonds in Fig. 1(a) disappeared after this refinement, and new negative peaks with depths of $-0\cdot34$ e Å^{-3} appeared at 0·35 Å from the Fe^{2+} ion along $\langle 111 \rangle$ in place of the positive peaks in Fig. 1(b). It is evident that the residual peaks in these two maps are significantly reduced compared to those in the former ones.

On the other hand, the difference Fourier maps assuming the low-spin state (Fig. 3a, b) clearly show
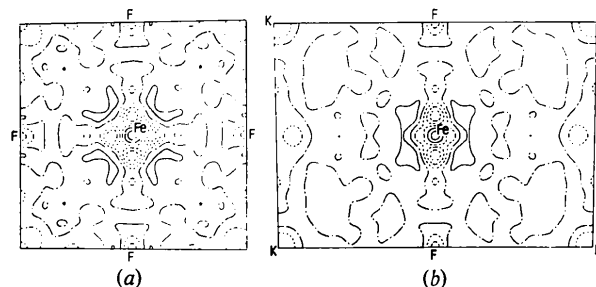

Fig. 1. Sections of the difference Fourier map after the refinement with the spherical scattering factors through the planes (a) $x = 0$ and (b) $x = y$. Contours are at intervals of 0·2 e Å^{-3}. Negative and zero contours are in broken and dashed–dotted lines, respectively.
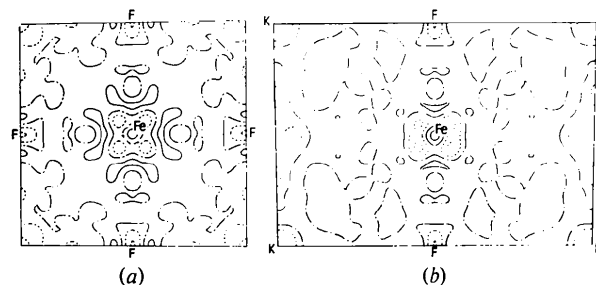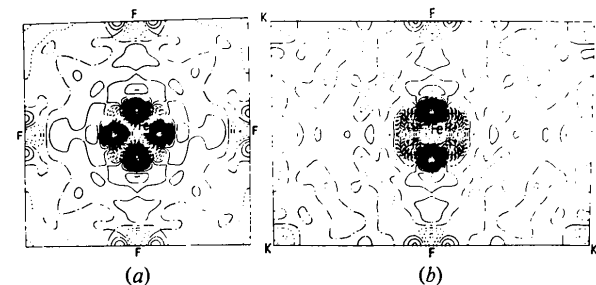

Fig. 2. Sections of the difference Fourier map after the refinement assuming the high-spin state through the planes (a) $x = 0$ and (b) $x = y$. Contours are at intervals of 0·2 e Å^{-3}. Negative and zero contours are in broken and dashed–dotted lines, respectively.

Fig. 3. Sections of the difference Fourier map after the refinement assuming the low-spin state through the planes (a) $x = 0$ and (b) $x = y$. Contours are at intervals of 0·2 e Å^{-3}. Negative and zero contours are in broken and dashed–dotted lines, respectively.

that this assumption is not valid as was already demonstrated by the much higher R and R_w values.

As there were still small residual peaks in residual density maps after the refinement assuming the high-spin state, the electron populations of t_{2g} and e_g orbitals were refined by the least-squares procedure. The difference Fourier maps after this refinement are shown in Figs. 4(a) and 4(b).* Compared wtih Figs. 2(a) and 2(b), however, no significant changes are found in these maps. The number of electrons in each orbital is also equal to that of the high-spin state within the experimental errors. Accordingly, the real electronic state of the Fe^{2+} ion in KFeF$_3$ is considered to have the high-spin electron configuration $(t_{2g})^4(e_g)^2$.

Around the F$^-$ ion four positive peaks with heights of 0·21 e Å^{-3} are observed at about 0·2 Å from the F$^-$ nucleus in the directions perpendicular to the Fe–F bond. It is likely that these peaks appeared due to the anharmonic thermal vibration of the F$^-$ ion, because similar but slightly larger peaks were observed around the F$^-$ ion in the deformation density map of KMnF$_3$ crystals, which show a phase transition related to vibration of the F$^-$ ion at 187 K. The thermal parameters of the F$^-$ ion in KFeF$_3$ also support this expectation.

We have investigated the electron density distributions in a series of KMF$_3$ compounds. We can conclude from these studies that the X-ray diffraction technique can distinguish at least the spin states of the first-series transition-metal elements when they are contained in crystals with simple structures.

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* See deposition footnote.

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Charge-Density Distribution in Crystals of CuAlO$_2$ with *d–s* Hybridization

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Abstract

The electron-density distribution in crystals of CuAlO$_2$ was investigated on the basis of X-ray intensity data collected by single-crystal diffractometry. The crystal has a delafossite CuFeO$_2$ structure, containing the Cu$^+$ ion with linear twofold coordination. Several peaks observed on the difference Fourier maps after the spherical-atom refinement were well explained by assuming aspherical scattering factors of electrons in

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