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# Electron Density Distribution in Crystals of Potassium Trifluorocobaltate(II)

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## Abstract

The electron density distribution in crystals of $KCoF_3$ was investigated on the basis of X-ray intensity data collected by diffractometry at 293 K. The characteristic residual electron density around the $Co^{2+}$ ion in the octahedral crystal field was observed on the difference Fourier maps when spherical scattering factors were used for the $Co^{2+}$ ion. With aspherical scattering factors for the 3*d* electrons of the $Co^{2+}$ ion, structure amplitudes were calculated for two electron configurations, *i.e.* high spin $^4T_g(t_{2g})^5(e_g)^2$ and low spin $^2E_g(t_{2g})^6(e_g)$. Refinement on the assumption of high spin decreased the $R$ value significantly (0·0077) from that (0·0088) obtained with the spherical refinement, while assumption of low spin increased the value (0·0120). The difference density maps obtained after these refinements also showed that the high-spin $(t_{2g})^5(e_g)^2$ electron configuration is a good approximation of the electronic state for the $Co^{2+}$ ion in cubic $KCoF_3$ crystals at room temperature. [Crystal data: cubic, $Pm3m$, $a$ = 4·0688 (7) Å, $V$ = 67·36 (3) Å$^3$, $Z$ = 1, $D_x$ = 3·821 Mg m$^{-3}$, $\lambda$(Mo $K\alpha$) = 0·7107 Å, $\mu$(Mo $K\alpha$) = 7·943 mm$^{-1}$, $T$ = 293 K; 743 reflections with $|F| > 3\sigma|F|$.]

## Introduction

In recent years investigations on the distribution of 3*d* electrons have been intensively performed on crystals of transition-metal compounds by X-ray diffraction methods. Aspherical electron density distributions around divalent cobalt ions in trigonal and tetrahedral crystal fields were observed in crystals of $\gamma$-$Co_2SiO_4$ (Marumo, Isobe & Akimoto, 1977) and $CoAl_2O_4$ (Toriumi, Ozima, Akaogi & Saito, 1978) respectively. On the deformation density maps of $\gamma$-$Co_2SiO_4$ eight positive peaks were observed around the $Co^{2+}$ ion on the lines along the $\langle 111\rangle$ directions of the cubic lattice, and six negative peaks on the Co—O bonds. These peaks indicate that the electron density of the $t_{2g}$ orbitals is higher than that of the $e_g$ orbitals as a result of splitting of the *d* orbitals in a quasi-octahedral field. The deformation density around the $Co^{2+}$ ion in $CoAl_2O_4$ clearly shows that the density on the $t_{2g}$ orbitals is lower than that on the $e_g$, giving an arrangement of negative and positive peaks reversed to that in an octahedral field.

The present study was undertaken to increase knowledge on electron density distributions around the transition-metal ions in an octahedral field. In the octahedral crystal field, the ground state of a $Co^{2+}$ ion can be either high spin $(t_{2g})^5(e_g)^2$ or low spin $(t_{2g})^6(e_g)$ depending upon the strength of the crystal field. The refinements were performed for both configurations with aspherical scattering factors and the residual densities after these refinements were compared.

## Experimental

Single crystals of $KCoF_3$ synthesized by the flux method were shaped into spheres 0·13 mm in diameter by Bond's (1951) method in order to ensure a constant illumination of X-rays on the specimen and to make the intensity corrections easy. After the crystal was

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Table 1. *Experimental conditions*

| | | | |
|---|---|---|---|
| Diameter of specimen | 0·13 mm | Maximum number of repetitions | 10 |
| Radiation | Mo $K\alpha$ | Number of measured reflections | 746 |
| Monochromator | Graphite | Number of reflections used | 743 |
| $2\theta_{\max}$ | 130° | Independent reflections | 156 |
| Scan technique | $\omega$–$2\theta$ | | |
| Scan speed | 4° min$^{-1}$ in $2\theta$ | | |
| Scan width | $(1\cdot4 + 0\cdot35 \tan\theta)°$ for $0° \leq 2\theta \leq 90°$<br>$(1\cdot4 + 0\cdot3 \tan\theta)°$ for $90° < 2\theta < 130°$ | | |

confirmed to be a single crystal from Weissenberg photographs, it was mounted on a Philips automated four-circle diffractometer. The lattice constants were determined from 31 $2\theta$ values obtained with Mo $K\alpha_1$ radiation in the range higher than 88°; they are given in the *Abstract* together with other crystal data. Intensities of reflections were collected in an octant of reciprocal space within 130° in $2\theta$. As for reflections with very strong intensities, equivalent reflections in other octants of reciprocal space were measured in order to correct for an anisotropic extinction effect. Each reflection was repeatedly measured up to ten times to reduce the statistical counting error. Experimental conditions are summarized in Table 1. The corrections for the Lp factors were carried out with the usual procedure. Absorption corrections were performed with the values of the absorption-correction factors $A^*$ listed in *International Tables for X-ray Crystallography* (1967). The mean path length $\bar{T} = (\mathrm{d}A^*/\mathrm{d}\mu)/A^*$ was calculated for each reflection for the subsequent extinction correction. Here, $\mu$ is the linear absorption coefficient, and $\mathrm{d}A^*/\mathrm{d}\mu$ was obtained by numerical differentiation.

## Refinement

After weak reflections with $|F| < 3\sigma|F|$ had been omitted from the data set, least-squares refinements were tried with three kinds of electron-configuration models for the $Co^{2+}$ ion. At the beginning, spherical scattering factors of free ions were used for all the constituent atoms in the calculation. Next, aspherical scattering factors were employed for the $Co^{2+}$ ion by assuming the high-spin electron configuration $(t_{2g})^5(e_g)^2$. In the third refinement, the low-spin state $(t_{2g})^6(e_g)$ was assumed. The atomic and extinction parameters in these three refinements are given in Table 2.[†]

### (*a*) *Refinement with spherical scattering factors*

Since the structure is of the ideal perovskite type, there is no positional parameter to be refined in this structure. Atomic scattering factors and dispersion correction factors were taken from *International Tables for X-ray Crystallography* (1974) for $Co^{2+}$, $K^+$ and $F^-$ ions. The refinement was carried out with a modified version of the full-matrix least-squares program *LINEX* including the extinction correction after Becker & Coppens (1974*a*,*b*, 1975). The refinement with an extinction correction of anisotropic type I based on the assumption of the Gaussian mosaic-spread distribution gave a much improved $R$ value compared to that obtained with an extinction correction of type II. After this refinement, six equivalent reflections in the same octant of reciprocal space were averaged and all reflections in the other octant were discarded to synthesize the difference Fourier maps. The $R$ value was 0·0088 after this procedure.

Table 2. *Anisotropic temperature factors* ($\times 10^5$ Å$^{-2}$) *and anisotropic extinction parameters* ($\times 10^4$)

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

| Type of refinement | | (*a*) | (*b*) | (*c*) |
|---|---|---|---|---|
| Co | $U_{11}$<br>$U_{11} = U_{22} = U_{33}$ | 555 (2) | 550 (2) | 550 (3) |
| K | $U_{11}$<br>$U_{11} = U_{22} = U_{33}$ | 1411 (5) | 1416 (4) | 1418 (5) |
| F | $U_{11}$ | 649 (12) | 657 (12) | 664 (14) |
| | $U_{22}$<br>$U_{22} = U_{33}$ | 1898 (14) | 1890 (14) | 1877 (16) |
| | $G_{11}$ | 347 (22) | 390 (23) | 429 (28) |
| | $G_{22}$ | 329 (7) | 338 (7) | 342 (8) |
| | $G_{33}$ | 330 (7) | 338 (7) | 341 (9) |
| | $G_{12}$ | −235 (12) | −246 (13) | −254 (15) |
| | $G_{13}$ | 101 (16) | 106 (17) | 110 (21) |
| | $G_{23}$ | −132 (8) | −136 (8) | −139 (9) |

### (*b*) *Refinement with the high-spin state* $(t_{2g})^5(e_g)^2$ *assumed for* $Co^{2+}$

In $KCoF_3$ each $Co^{2+}$ ion is surrounded octahedrally by six $F^-$ ions and the point symmetry of the $Co^{2+}$ site is $m3m$. In the high-spin state five $3d$ electrons exist on the $t_{2g}$ level and two on the $e_g$ level. In this refinement, an aspherical scattering factor was employed for the $Co^{2+}$ ion and spherical ones for $F^-$ and $K^+$ ions. The scattering factor of the $Co^{2+}$ ion is the sum of the scattering factors of the Ar core and seven $3d$ electrons. The scattering factor of the former is in *International Tables for X-ray Crystallography* (1974) and an explicit form of scattering factor for each of the five $3d$ orbitals has been given previously (Tanaka, Konishi & Marumo, 1979, 1980). Since the triply-degenerate $t_{2g}$ and doubly-degenerate $e_g$ levels are occupied by five and two electrons in this model, respectively, each orbital of $t_{2g}$ is populated by $\frac{5}{3}$ electrons and that of $e_g$

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[†] A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35756 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

by one electron on average. The least-squares calculations were performed with the program *LINKT* written by one of the authors (KT). The $R$ value was reduced from 0·0088 to 0·0077 with this refinement.

### (*b*) *Refinement with the low-spin state* $(t_{2g})^6(e_g)$ *assumed for* $Co^{2+}$

With the low-spin state $(t_{2g})^6(e_g)$, the least-squares calculations were performed with the program *LINKT*. After this refinement the $R$ value was 0·0120. In this model, the populations of respective $3d$ orbitals of $t_{2g}$ and $e_g$ levels are 2 and 0·5.

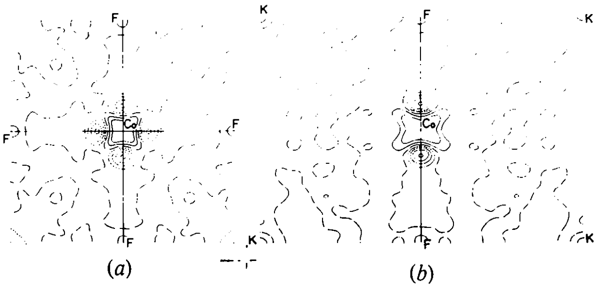

Fig. 1. Sections of the difference Fourier map after the refinement with spherical scattering factors through the planes (*a*) $x = 0$ and (*b*) $y = x$. Contours are at intervals of 0·2 e Å$^{-3}$. Negative and zero contours are in broken and dashed–dotted lines, respectively.

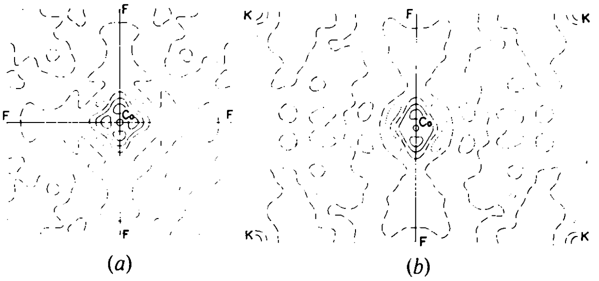

Fig. 2. Sections of the difference Fourier map after the refinement with the high-spin state assumed through the planes (*a*) $x = 0$ and (*b*) $y = x$. The electron density at the center of the $Co^{2+}$ ion is 0·16 e Å$^{-3}$ and this point is the lowest within the range of 0·5 Å from the Co nucleus. Contours are at intervals of 0·2 e Å$^{-3}$. Negative and zero contours are in broken and dashed–dotted lines, respectively.

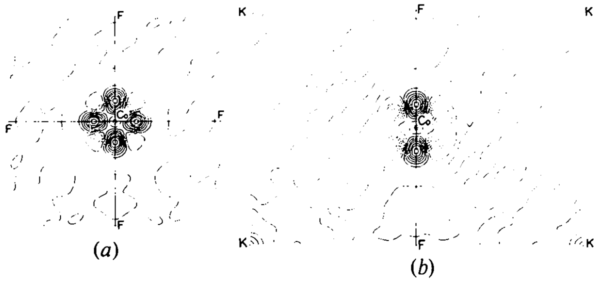

Fig. 3. Sections of the difference Fourier map after the refinement with the low-spin state assumed through the planes (*a*) $x = 0$ and (*b*) $y = x$. Contours are at intervals of 0·2 e Å$^{-3}$. Negative and zero contours are in broken and dashed–dotted lines, respectively.

## Results and discussion

Fig. 1 shows the deformation density around the $Co^{2+}$ ion obtained after the spherical-atom refinement. Six large negative peaks with a depth of $-0·83$ e Å$^{-3}$ are located on the Co—F bonds at 0·47 Å from the Co nucleus. Eight small positive peaks are also observed at about 0·5 Å from the Co nucleus in the $\langle 111 \rangle$ directions, avoiding ligands. This feature is also observed in $\gamma$-$Co_2SiO_4$ (Marumo *et al.*, 1977) though the point symmetries of the metals were different. The six negative peaks on the Co—F bonds in Fig. 1 indicate that the electron density of the $t_{2g}$ orbital is higher than that of the $e_g$ orbital. However, it is difficult to know from Fig. 1 alone whether the $3d$ electronic state of the $Co^{2+}$ ion in $KCoF_3$ is high spin or low spin. Even if the electronic state is low spin, qualitatively similar peaks would appear on the difference Fourier maps after the refinement with spherical scattering factors, because the electron population should also be higher in the $t_{2g}$ orbital than in the $e_g$ orbital in the low-spin state. Therefore, a quantitative analysis was carried out with aspherical scattering factors for the $3d$ electrons to distinguish the electronic state.

Fig. 2 is the difference Fourier map around the $Co^{2+}$ ion calculated after the refinement with the high-spin model. Six large negative peaks around the Co nucleus in Fig. 1 completely disappear in Fig. 2 and new small positive peaks with heights of 0·49 e Å$^{-3}$ appear on the Co—F bonds at 0·24 Å from the Co nucleus. On the other hand, eight negative peaks with a depth of $-0·32$ e Å$^{-3}$ appear at 0·49 Å from the Co site on the lines along $\langle 111 \rangle$ in place of the eight positive peaks in Fig. 1. The residual densities in the region far from the $Co^{2+}$ ion were not changed significantly. Since the high-spin model improved both the residual density maps and the $R$ value significantly, it was confirmed that the real electronic state of the $Co^{2+}$ ion is close to the high-spin state. However, since new peaks appeared in Fig. 2, as stated above, this model does not represent exactly the real electronic state of the $Co^{2+}$ ion. Namely, in the real electronic state there seems to be fewer $3d$ electrons in the $t_{2g}$ orbitals than in the ideal $(t_{2g})^5(e_g)^2$ state. The difference Fourier maps (Fig. 2) suggest that the electronic state is intermediate between $(t_{2g})^5(e_g)^2$ and $(t_{2g})^4(e_g)^3$. Therefore, a refinement in which $x$ of $(t_{2g})^{5-x}(e_g)^{2+x}$ was treated as an unknown parameter was performed to investigate the populations of the $t_{2g}$ and $e_g$ orbtials quantitatively. The $R$ value reduced slightly from 0·0077 to 0·0076 and the $x$ value converged to 0·25 with this refinement. This result corresponds to the electronic state $(t_{2g})^{4\cdot75}(e_g)^{2\cdot25}$, and the low-spin model is unequivocally excluded. In fact, the difference Fourier maps after the refinement with the low-spin model (Fig. 3) gave very high positive and very deep negative peaks. The distance of 0·24 Å from the Co nucleus to the new positive peaks in Fig. 2 is, however, much shorter than the distance to the negative peaks in Fig. 1. Therefore, there may be other possibilities to be considered. One is the anharmonic vibration of the Co$^{2+}$ ion, which seems to have an effect at the closer point to the nucleus (Tanaka & Marumo, 1981).

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# Crystal Structures of Thionitrosyl Hexafluoroantimonate(V) and Thionitrosyl Undecafluorodiantimonate(V) at 293 K and of Thionitrosyl Undecafluorodiantimonate(V) at 121·5 K: the Effect of Thermal Motion on the Apparent NS Bond Length

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## Abstract

NS$^+$.SbF$_6^-$, $M_r$ = 281·8, orthorhombic, *Pbca*, $a$ = 13·999 (6), $b$ = 8·363 (4), $c$ = 10·468 (4) Å, $U$ = 1225·5 Å$^3$, $Z$ = 8, $D_x$ = 3·055 Mg m$^{-3}$, $\mu$(Mo $K\alpha$) = 4·76 mm$^{-1}$ at 293 (2) K. The structure was refined to $R$ = 0·032 for 2025 independent reflexions. NS$^+$.Sb$_2$F$_{11}^-$, $M_r$ = 498·3, monoclinic, $P2_1/c$, $a$ = 8·374 (2), $b$ = 11·792 (3), $c$ = 10·108 (3) Å, $\beta$ = 91·89 (4)°, $U$ = 997·6 Å$^3$, $Z$ = 4, $D_x$ = 3·328 Mg m$^{-3}$, $\mu$(Mo $K\alpha$) = 5·79 mm$^{-1}$ at 293 (2) K; $a$ = 8·191 (8), $b$ = 11·760 (8), $c$ = 9·935 (7) Å, $\beta$ = 92·88 (2)°, $U$ = 955·8 Å$^3$, $Z$ = 4, $D_x$ = 3·474 Mg m$^{-3}$, $\mu$(Mo $K\alpha$) = 6·04 mm$^{-1}$ at 121·5 (2·0) K. The structure was refined to $R$ = 0·036 for 2873 independent reflexions at room temperature and 0·037 for 1691 independent reflexions at low temperature. The structures may be described as ionic, with each S atom surrounded by five F atoms at distances of 2·6–2·8 Å. The apparent NS bond length shows a pronounced temperature dependence; a librational analysis of the three structures led to the corrected value $r$(NS) = 1·42 (1) Å.

## Introduction

Glemser & Koch (1971) showed that NSF reacts with SbF$_5$ to give a crystalline product which they formulated on the basis of the IR and Raman spectra as NS$^+$.SbF$_6^-$. The transient existence of NS$^+$ in the gas

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