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# The Crystal Structure of $Cr_2F_5$

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The crystal structure of $Cr_2F_5$ was determined by a single-crystal X-ray diffraction study and was refined by the method of least-squares with use of anisotropic temperature factors. The chromium ions exist in two valence states (II, III) in an ordered arrangement and are distinguished by their fluoride-ion environments. The octahedra of fluoride ions about the $Cr^{3+}$ ions are almost regular, but the octahedra which coordinate the $Cr^{2+}$ ions are distorted by having two long Cr–F distances. These configurations are explained by ligand-field theory. The anisotropy of thermal motion is discussed.

## Introduction

The crystal structures of $CrF_2$ and $CrF_3$ were reported by Jack & Maitland (1957), confirming the symmetry of the fluoride-ion octahedra predicted by ligand-field theory (Orgel & Dunitz, 1957). The structure of $CrF_3$ was also studied by Knox (1960). In $CrF_3$ the chromium(III) ions are coordinated by regular octahedra of fluoride ions at a distance of 1·90 Å, but in $CrF_2$ the chromium(II) ions are coordinated by octahedra with four nearly equal Cr–F bonds of 1·98 and 2·01 Å and two long Cr–F bonds of 2·43 Å. The distortion of the octahedra in $CrF_2$ was attributed to the repulsive force exerted on the ligands along the $z$ axis by an electron in the $3d_{z^2}$ orbital of the spinfree $Cr^{2+}$ ion. This orbital is unoccupied in trivalent chromium and all six bonds are equivalent. All of the chromium(II) halides exhibit distorted halide octahedra; a comparison of these structures was made by Tracey, Gregory & Lingafelter (1962). The magnetic structures of $CrF_3$ and $CrF_2$ were investigated by Wollan, Child, Koehler & Wilkinson (1958) and by Cable, Wilkinson & Wollan (1960) respectively.

The binary system $CrF_2$–$CrF_3$ (Sturm, 1962) has a single intermediate compound whose composition varies from $CrF_{2.40}$ to $CrF_{2.45}$. Single crystals with compositions in this range were examined by X-ray diffraction methods. From a determination of the unit-cell dimensions and the probable space group, it seemed likely that the structure is based on an ideal stoichiometry of $CrF_{2.50}$, *i.e.* $Cr_2F_5$. There is an analogous phenomenon, for example, in the compound FeO which has the NaCl structure with ideal 1:1 composition, but which actually exists only in the range $FeO_{1.06}$ to $FeO_{1.12}$ (Jette & Foote, 1933).

A complete structure determination was therefore undertaken to ascertain this ideal structure for $Cr_2F_5$ and to examine the possibility that the chromium ions in two valence states in the same crystal could be distinguished by their fluoride-ion environments.

## Experimental

The crystals of $Cr_2F_5$ were complexly twinned, but small single-crystal fragments were selected and three-dimensional X-ray diffraction data were collected by means of a General Electric Single-Crystal Orienter, a scintillation counter, and Mo $K\alpha$ radiation. The stationary crystal, stationary counter method was used. The crystal system is monoclinic,

$$a=7{\cdot}773\pm0{\cdot}005,\ b=7{\cdot}540\pm0{\cdot}005,\ c=7{\cdot}440\pm0{\cdot}005\ \text{Å}\ ,\quad \beta=124{\cdot}25\pm0{\cdot}1^\circ,\ Z=4;$$

and the most probable space group is $C2/c$. The structure was solved from h0$l$ and $hk$0 Patterson projections, and initial parameters for refinement were obtained from subsequent electron-density projections. The atoms are located in the following equipoints listed by *International Tables for X-Ray Crystallography* (1952): chromium in 4($a$) and 4($b$); fluorine in 4($e$) and two sets of 8($f$). The variable parameters associated with these atomic positions and individual isotropic temperature factors were adjusted by least-squares refinement employing three-dimensional data and unit weights. The refined values are given in Table 1. The discrepancy factor, $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$, for 285 observed reflections is 0·051.

An analysis of the structure at this stage of the determination gave evidence that the different values of the isotropic temperature factors for the fluoride ions were physically meaningful; therefore a refinement of the structure with anisotropic temperature factors was carried out. A temperature factor of the form

$$\exp\left[(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)\right]$$

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* Operated for the U.S. Atomic Energy Commission by Union Carbide Corporation.

Table 1. *Final coordinates, standard deviations, and temperature factors from isotropic least-squares refinement*

| Ion | $x$ | $\sigma(x)$ | $y$ | $\sigma(y)$ | $z$ | $\sigma(z)$ | $B$ | $\sigma(B)$ |
|---|---|---|---|---|---|---|---|---|
| $Cr^{3+}$ | 0 | — | 0 | — | 0 | — | 0·49 | 0·04 |
| $Cr^{2+}$ | 0 | — | 0·5000 | — | 0 | — | 0·77 | 0·05 |
| $F^-(1)$ | 0 | — | 0·0474 | 0·0012 | 0·2500 | — | 1·41 | 0·15 |
| $F^-(2)$ | 0·2959 | 0·0009 | −0·0190 | 0·0009 | 0·1774 | 0·0009 | 1·19 | 0·10 |
| $F^-(3)$ | 0·0212 | 0·0010 | 0·2462 | 0·0011 | −0·0307 | 0·0010 | 1·64 | 0·10 |

Table 2. *Final positional parameters and standard deviations from anisotropic least-squares refinement*

| Ion | $x$ | $\sigma(x)$ | $y$ | $\sigma(y)$ | $z$ | $\sigma(z)$ |
|---|---|---|---|---|---|---|
| $Cr^{3+}$ | 0 | — | 0 | — | 0 | — |
| $Cr^{2+}$ | 0 | — | 0·5000 | — | 0 | — |
| $F^-(1)$ | 0 | — | 0·0475 | 0·0007 | 0·2500 | — |
| $F^-(2)$ | 0·2955 | 0·0005 | −0·0192 | 0·0005 | 0·1762 | 0·0006 |
| $F^-(3)$ | 0·0207 | 0·0006 | 0·2448 | 0·0004 | −0·0304 | 0·0006 |

Table 3. *Final anisotropic temperature coefficients* ($Å^2 \times 10^3$)

| Ion | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|
| $Cr^{3+}$ | 3·5 ± 0·3 | 2·9 ± 0·3 | 3·3 ± 0·3 | −0·1 ± 0·5 | 2·9 ± 0·5 | 0·5 ± 0·5 |
| $Cr^{2+}$ | 5·4 ± 0·3 | 2·4 ± 0·3 | 4·8 ± 0·4 | −0·2 ± 0·5 | 3·6 ± 0·5 | −0·4 ± 0·5 |
| $F^-(1)$ | 12·5 ± 1·3 | 8·5 ± 0·9 | 7·1 ± 1·3 | 0 | 13·4 ± 2·2 | 0 |
| $F^-(2)$ | 4·0 ± 0·6 | 7·5 ± 0·7 | 7·5 ± 0·8 | 1·6 ± 1·1 | 3·1 ± 1·2 | 3·3 ± 1·2 |
| $F^-(3)$ | 13·6 ± 1·0 | 2·7 ± 0·5 | 12·0 ± 0·9 | −1·2 ± 1·1 | 14·6 ± 1·5 | 0·8 ± 1·2 |

Table 4. *Observed and calculated structure factors*

| h | k | ℓ | $\lvert F_o \rvert$ | $F_c$ |
|---|---|---|---|---|
| 0 | 0 | 2 | 140.4 | 140.0 |
| 0 | 0 | 4 | 139.6 | 139.4 |
| 0 | 0 | 6 | 91.9 | 88.6 |
| 0 | 0 | 8 | 50.8 | 49.7 |
| 0 | 0 | 10 | 36.1 | 34.9 |
| 0 | 2 | 0 | 184.7 | 182.6 |
| 0 | 2 | 2 | 46.0 | 39.2 |
| 0 | 2 | 3 | 11.2 | 12.0 |
| 0 | 2 | 4 | 87.7 | 86.1 |
| 0 | 2 | 5 | 11.0 | 9.5- |
| 0 | 2 | 6 | 74.9 | 73.6 |
| 0 | 2 | 8 | 48.6 | 47.1 |
| 0 | 4 | 0 | 212.8 | 213.0 |
| 0 | 4 | 2 | 116.6 | 121.3 |
| 0 | 4 | 3 | 8.2 | 9.3 |
| 0 | 4 | 4 | 103.4 | 102.7 |
| 0 | 4 | 6 | 81.8 | 78.4 |
| 0 | 4 | 8 | 43.6 | 42.9 |
| 0 | 6 | 0 | 83.5 | 79.6 |
| 0 | 6 | 2 | 52.2 | 55.8 |
| 0 | 6 | 4 | 52.3 | 54.2 |
| 0 | 6 | 6 | 61.3 | 59.0 |
| 0 | 8 | 0 | 92.1 | 88.5 |
| 0 | 8 | 2 | 76.3 | 78.9 |
| 0 | 10 | 0 | 39.0 | 38.9 |
| 0 | 10 | 2 | 39.1 | 40.8 |
| 1 | 1 | 0 | 16.0 | 13.2 |
| 1 | 1 | 2 | 50.1 | 52.3- |
| 1 | 1 | 3 | 16.2 | 15.9 |
| 1 | 1 | 4 | 42.2 | 42.5 |
| 1 | 3 | 1 | 16.1. | 17.0- |
| 1 | 3 | 2 | 34.3 | 36.3- |
| 1 | 3 | 3 | 10.3 | 11.4- |
| 1 | 3 | 4 | 27.9 | 28.2 |
| 1 | 5 | 0 | 5.3 | 1.3- |
| 1 | 5 | 2 | 8.2 | 8.4- |
| 1 | 5 | 3 | 6.8 | 7.2 |
| 1 | 5 | 4 | 16.1 | 17.3 |
| 1 | 7 | 0 | 13.4 | 13.0- |
| 2 | 0 | 0 | 191.7 | 189.2 |
| 2 | 0 | 2 | 166.5 | 177.6 |
| 2 | 0 | 4 | 108.4 | 106.3 |
| 2 | 0 | 6 | 52.1 | 52.2 |
| 2 | 2 | 0 | 80.0 | 67.4 |
| 2 | 2 | 1 | 23.2 | 23.4- |
| 2 | 2 | 2 | 108.6 | 98.6 |
| 2 | 2 | 3 | 12.2 | 11.9 |
| 2 | 2 | 4 | 64.9 | 67.5 |
| 2 | 2 | 6 | 40.9 | 40.3 |
| 2 | 4 | 0 | 132.1 | 128.3 |
| 2 | 4 | 1 | 26.6 | 27.7- |
| 2 | 4 | 2 | 133.6 | 137.4 |
| 2 | 4 | 3 | 14.8 | 14.5 |
| 2 | 4 | 4 | 81.4 | 82.6 |
| 2 | 4 | 6 | 52.6 | 52.0 |
| 2 | 6 | 0 | 47.6 | 47.2 |
| 2 | 6 | 1 | 20.1 | 22.2- |
| 2 | 6 | 2 | 68.5 | 70.7 |
| 2 | 6 | 3 | 13.6 | 13.5 |
| 2 | 6 | 4 | 43.3 | 45.3 |
| 2 | 6 | 6 | 40.8 | 40.5 |
| 2 | 8 | 0 | 72.2 | 69.9 |
| 2 | 8 | 1 | 13.1 | 12.8- |
| 2 | 8 | 2 | 78.5 | 80.5 |
| 2 | 8 | 4 | 51.1 | 52.9 |
| 2 | 10 | 0 | 34.2 | 33.6 |
| 3 | 1 | 0 | 61.7 | 58.5 |
| 3 | 1 | 1 | 11.7 | 10.8- |
| 3 | 1 | 2 | 9.4 | 8.9- |
| 3 | 3 | 0 | 36.3 | 33.8 |
| 3 | 3 | 2 | 6.5 | 6.7- |
| 3 | 5 | 0 | 20.2 | 19.8 |
| 3 | 5 | 1 | 8.5 | 9.8- |
| 3 | 5 | 3 | 13.3 | 13.8 |
| 4 | 0 | 0 | 178.8 | 171.2 |
| 4 | 0 | 2 | 70.9 | 70.4 |
| 4 | 0 | 4 | 89.4 | 92.0 |
| 4 | 2 | 0 | 110.4 | 104.4 |
| 4 | 2 | 1 | 1.0 | 1.6- |
| 4 | 2 | 2 | 35.0 | 34.3 |
| 4 | 2 | 4 | 66.5 | 67.3 |
| 4 | 4 | 0 | 128.6 | 120.7 |
| 4 | 4 | 2 | 67.3 | 68.3 |
| 4 | 4 | 4 | 75.4 | 75.3 |
| 4 | 6 | 0 | 62.6 | 59.5 |
| 4 | 6 | 2 | 38.0 | 40.5 |
| 4 | 6 | 4 | 46.4 | 47.3 |
| 4 | 8 | 0 | 69.2 | 65.2 |
| 4 | 8 | 2 | 55.4 | 56.4 |
| 4 | 8 | 4 | 48.6 | 50.2 |
| 4 | 10 | 4 | 28.9 | 31.3 |
| 5 | 1 | 0 | 15.6 | 13.9- |
| 5 | 1 | 1 | 11.6 | 12.7- |
| 5 | 3 | 0 | 16.7 | 15.2- |
| 6 | 0 | 0 | 103.7 | 98.6 |
| 6 | 0 | 2 | 75.0 | 75.8 |
| 6 | 0 | 4 | 44.4 | 45.3 |
| 6 | 2 | 0 | 76.4 | 71.5 |
| 6 | 2 | 1 | 5.6 | 5.6- |
| 6 | 2 | 2 | 56.3 | 56.4 |
| 6 | 2 | 6 | 35.2 | 36.1 |
| 6 | 4 | 0 | 83.4 | 78.6 |
| 6 | 4 | 6 | 40.1 | 40.3 |
| 6 | 6 | 0 | 52.8 | 49.0 |
| 6 | 6 | 2 | 45.3 | 46.4 |
| 6 | 6 | 6 | 31.8 | 32.6 |
| 7 | 1 | 0 | 23.9 | 24.0 |
| 7 | 1 | 2 | 11.5 | 11.7- |
| 8 | 0 | 0 | 54.3 | 51.9 |
| 8 | 2 | 0 | 43.3 | 42.8 |
| 8 | 4 | 0 | 48.7 | 45.7 |
| 10 | 0 | 0 | 52.4 | 51.1 |
| 12 | 0 | 0 | 23.5 | 22.9 |
| -1 | 1 | 2 | 28.3 | 28.0 |
| -1 | 1 | 3 | 43.8 | 45.3 |
| -1 | 1 | 4 | 11.5 | 11.2- |
| -1 | 1 | 5 | 17.3 | 17.0 |
| -1 | 1 | 7 | 15.1 | 14.2 |
| -1 | 1 | 8 | 18.0 | 17.2 |
| -1 | 3 | 1 | 48.0 | 49.0- |
| -1 | 3 | 2 | 20.0 | 20.9 |
| -1 | 3 | 4 | 15.2 | 14.6- |
| -1 | 3 | 5 | 33.3 | 32.6- |
| -1 | 3 | 8 | 14.7 | 13.5 |
| -1 | 5 | 1 | 17.4 | 16.2- |
| -1 | 5 | 2 | 22.8 | 24.1 |
| -1 | 5 | 3 | 39.2 | 42.1 |
| -1 | 5 | 4 | 11.7 | 11.2- |
| -1 | 5 | 7 | 13.1 | 11.5 |
| -1 | 7 | 1 | 23.8 | 22.9- |
| -1 | 7 | 2 | 10.8 | 9.6 |
| -1 | 7 | 5 | 19.5 | 20.4- |
| -1 | 9 | 3 | 16.8 | 17.2 |
| -2 | 0 | 2 | 172.8 | 176.7 |
| -2 | 0 | 4 | 181.9 | 195.5 |
| -2 | 0 | 6 | 53.3 | 54.8 |
| -2 | 0 | 8 | 72.7 | 70.2 |
| -2 | 2 | 1 | 20.8 | 20.8- |
| -2 | 2 | 2 | 85.7 | 79.8 |
| -2 | 2 | 3 | 11.6 | 10.9 |
| -2 | 2 | 4 | 132.7 | 136.9 |
| -2 | 2 | 6 | 48.9 | 49.5 |
| -2 | 2 | 8 | 71.2 | 70.8 |
| -2 | 4 | 1 | 27.9 | 28.2- |
| -2 | 4 | 2 | 139.9 | 139.4 |
| -2 | 4 | 4 | 123.4 | 130.9 |
| -2 | 4 | 6 | 56.0 | 56.9 |
| -2 | 4 | 8 | 56.8 | 57.6 |
| -2 | 6 | 1 | 15.9 | 15.0- |
| -2 | 6 | 2 | 72.4 | 70.0 |
| -2 | 6 | 4 | 68.5 | 72.0 |
| -2 | 6 | 6 | 49.7 | 50.6 |
| -2 | 6 | 8 | 53.0 | 50.6 |
| -2 | 8 | 2 | 88.5 | 82.7 |
| -2 | 8 | 4 | 61.0 | 65.6 |
| -2 | 8 | 6 | 47.5 | 49.6 |
| -2 | 10 | 2 | 45.8 | 44.4 |
| -3 | 1 | 1 | 25.6 | 26.3 |
| -3 | 1 | 2 | 74.4 | 75.3- |
| -3 | 1 | 3 | 40.7 | 40.9 |
| -3 | 1 | 4 | 33.4 | 37.4 |
| -3 | 1 | 5 | 22.9 | 23.3 |
| -3 | 1 | 7 | 21.3 | 20.6 |
| -3 | 3 | 1 | 22.2 | 22.6- |
| -3 | 3 | 2 | 48.9 | 50.6- |
| -3 | 3 | 3 | 26.0 | 25.8- |
| -3 | 3 | 4 | 21.2 | 22.8 |
| -3 | 3 | 5 | 35.5 | 36.1- |
| -3 | 3 | 9 | 16.4 | 14.8- |
| -3 | 5 | 1 | 16.0 | 16.5 |
| -3 | 5 | 2 | 16.9 | 18.1- |
| -3 | 5 | 3 | 22.3 | 21.8 |
| -3 | 5 | 4 | 11.7 | 10.2 |
| -3 | 5 | 7 | 23.4 | 23.4 |
| -3 | 7 | 3 | 16.9 | 16.7- |
| -3 | 7 | 5 | 19.4 | 20.3- |
| -4 | 0 | 2 | 145.5 | 149.8 |
| -4 | 0 | 4 | 104.4 | 105.2 |
| -4 | 0 | 6 | 84.8 | 88.0 |
| -4 | 0 | 8 | 69.3 | 67.9 |
| -4 | 0 | 10 | 27.3 | 28.6 |
| -4 | 2 | 2 | 95.8 | 95.8 |
| -4 | 2 | 3 | 19.8 | 19.8 |
| -4 | 2 | 4 | 77.1 | 79.2 |
| -4 | 2 | 5 | 12.8 | 12.4- |
| -4 | 2 | 6 | 86.6 | 89.7 |
| -4 | 2 | 8 | 74.6 | 75.0 |
| -4 | 4 | 1 | 14.0 | 14.2- |
| -4 | 4 | 2 | 119.2 | 120.0 |
| -4 | 4 | 3 | 20.4 | 18.5 |
| -4 | 4 | 4 | 79.7 | 79.5 |
| -4 | 4 | 5 | 22.3 | 21.9- |
| -4 | 4 | 6 | 77.2 | 78.1 |
| -4 | 4 | 8 | 53.9 | 53.8 |
| -4 | 6 | 2 | 73.4 | 71.7 |
| -4 | 6 | 3 | 22.5 | 20.9 |
| -4 | 6 | 4 | 53.8 | 52.4 |
| -4 | 6 | 5 | 13.8 | 12.7- |
| -4 | 6 | 6 | 70.8 | 69.6 |
| -4 | 6 | 8 | 51.4 | 51.6 |
| -4 | 8 | 2 | 75.9 | 73.4 |
| -4 | 8 | 4 | 52.0 | 50.4- |
| -4 | 8 | 5 | 13.6 | 13.6- |
| -4 | 8 | 6 | 54.8 | 55.4 |
| -5 | 1 | 1 | 12.2 | 11.9 |
| -5 | 1 | 2 | 11.5 | 11.7 |
| -5 | 1 | 3 | 34.0 | 34.0 |
| -5 | 1 | 4 | 20.8 | 21.4 |
| -5 | 1 | 5 | 21.8 | 22.4 |
| -5 | 1 | 6 | 25.7 | 27.0- |
| -5 | 1 | 7 | 14.8 | 15.5 |
| -5 | 1 | 8 | 23.9 | 23.6 |
| -5 | 3 | 1 | 33.3 | 33.7- |
| -5 | 3 | 2 | 15.8 | 11.6 |
| -5 | 3 | 3 | 10.8 | 11.0- |
| -5 | 3 | 4 | 13.5 | 13.6 |
| -5 | 3 | 5 | 26.3 | 25.7- |
| -5 | 3 | 6 | 16.7 | 17.0- |
| -5 | 3 | 7 | 12.8 | 12.2- |
| -5 | 3 | 8 | 19.6 | 19.2 |
| -5 | 5 | 2 | 13.3 | 13.0 |
| -5 | 5 | 3 | 31.4 | 29.4 |
| -5 | 5 | 5 | 13.3 | 13.1 |
| -5 | 7 | 1 | 21.8 | 22.4- |
| -5 | 9 | 3 | 13.9 | 12.6 |
| -6 | 0 | 2 | 62.3 | 61.9 |
| -6 | 0 | 4 | 123.3 | 124.8 |
| -6 | 0 | 6 | 54.0 | 55.5 |
| -6 | 0 | 8 | 51.4 | 52.0 |
| -6 | 0 | 10 | 42.5 | 42.1 |
| -6 | 2 | 2 | 47.4 | 46.7 |
| -6 | 2 | 4 | 111.9 | 113.6 |
| -6 | 2 | 6 | 66.2 | 67.3 |
| -6 | 2 | 8 | 63.7 | 64.8 |
| -6 | 2 | 10 | 54.3 | 54.6 |
| -6 | 4 | 2 | 62.0 | 61.9 |
| -6 | 4 | 4 | 92.2 | 91.9 |
| -6 | 4 | 6 | 54.0 | 54.2 |
| -6 | 4 | 8 | 42.7 | 43.0 |
| -6 | 6 | 2 | 43.8 | 47.9 |
| -6 | 6 | 4 | 69.7 | 67.8 |
| -6 | 6 | 6 | 60.9 | 57.6 |
| -6 | 6 | 8 | 49.7 | 47.6 |
| -6 | 8 | 2 | 50.7 | 51.5 |
| -6 | 8 | 4 | 52.7 | 51.7 |
| -6 | 8 | 6 | 46.8 | 44.0 |
| -7 | 1 | 2 | 7.5 | 8.4- |
| -7 | 1 | 3 | 19.1 | 19.3 |
| -7 | 1 | 5 | 9.8 | 10.5 |
| -7 | 1 | 6 | 12.4 | 12.4 |
| -7 | 1 | 7 | 13.6 | 13.6 |
| -7 | 3 | 5 | 26.0 | 25.4- |
| -7 | 3 | 6 | 14.7 | 14.1 |
| -7 | 5 | 3 | 19.4 | 18.8 |
| -7 | 5 | 7 | 15.8 | 17.0 |
| -7 | 7 | 5 | 19.4 | 19.3- |
| -8 | 0 | 2 | 72.0 | 73.6 |
| -8 | 0 | 4 | 58.9 | 59.3 |
| -8 | 0 | 6 | 41.6 | 42.0 |
| -8 | 0 | 8 | 62.9 | 61.4 |
| -8 | 0 | 10 | 24.7 | 25.1 |
| -8 | 2 | 2 | 65.0 | 68.3 |
| -8 | 2 | 4 | 61.4 | 61.9 |
| -8 | 2 | 6 | 55.7 | 55.4 |
| -8 | 2 | 8 | 74.0 | 73.0 |
| -8 | 2 | 10 | 38.4 | 38.2 |
| -8 | 4 | 2 | 61.9 | 64.8 |
| -8 | 4 | 4 | 49.3 | 49.5 |
| -8 | 4 | 6 | 41.9 | 42.3 |
| -8 | 4 | 8 | 50.3 | 49.6 |
| -8 | 6 | 2 | 53.2 | 54.0 |
| -8 | 6 | 4 | 44.6 | 45.7 |
| -8 | 6 | 6 | 52.1 | 50.1 |
| -9 | 1 | 4 | 20.4 | 22.0 |
| -9 | 3 | 4 | 17.7 | 18.4 |
| -9 | 5 | 4 | 9.8 | 10.7 |
| -10 | 0 | 2 | 30.1 | 31.4 |
| -10 | 0 | 4 | 46.2 | 47.6 |
| -10 | 0 | 6 | 45.6 | 45.5 |
| -10 | 0 | 8 | 33.7 | 32.8 |
| -10 | 2 | 4 | 50.1 | 51.0 |
| -10 | 2 | 6 | 54.5 | 55.1 |
| -10 | 2 | 8 | 44.3 | 43.2 |
| -10 | 4 | 4 | 39.3 | 40.7 |
| -10 | 4 | 6 | 42.4 | 42.2 |

was assumed for each atom. The observations were weighted as the reciprocal of their variances, which were estimated from the following expression:

$$\sigma^2(F) = \frac{F^2}{4(T-B)^2}\,[T+B+0{\cdot}0004(T-B)^2]$$

in which $T$ = total count, $B$ = background count, and the additive term involving $T-B$ is to allow for errors proportional to the net count, such as variation in the beam intensity and absorption errors. A discussion of this scheme of weighting counter data is given by Busing & Levy (1957). With this refinement the discrepancy coefficient decreased to 0·032. The positional parameters, standard diviations, and anisotropic temperature factors are listed in Tables 2 and 3. The new positional parameters are within one standard

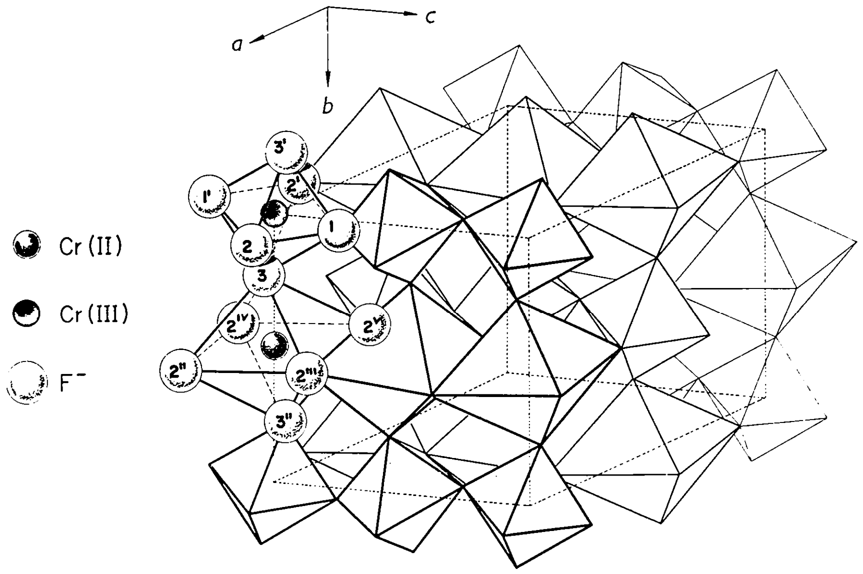

Fig. 1. Structure of $\mathrm{Cr_2F_5}$. Each octahedron contains a chromium ion at its center. One of each of the two types of octahedral coordination is shown in detail. Primed numbers indicate symmetry-related ions.

deviation of the previous values, but the new standard deviations are smaller. The observed and calculated structure factors are shown in Table 4.

## Discussion of the structure

In the structure of $\mathrm{Cr_2F_5}$, shown in Fig. 1, each chromium ion is coordinated by an octahedron of fluoride ions. The shape of each octahedron is determined by the valence state of its central cation; the two different configurations are represented by the octahedra about $\mathrm{Cr^{3+}}$ at 0, 0, 0 (which we call a 'trivalent octahedron') and about $\mathrm{Cr^{2+}}$ at 0, $\frac{1}{2}$, 0 (a 'divalent octahedron'). Table 5 gives the pertinent interionic distances and angles in the crystal and their standard deviations.

The trivalent octahedra are nearly regular, with an average Cr–F bond length of 1·89 Å, close to the value of 1·90 Å in $\mathrm{CrF_3}$. The divalent octahedron consists of a $\mathrm{Cr^{2+}}$ ion at the center of a planar group of four fluoride ions (F(2‴), F(3). F $2^{\mathrm{iv}}$), F(3″), Fig. 1) which is approximately square. The $\mathrm{Cr^{2+}}$ ion also has two longer bonds to fluoride ions at 2·57 Å (F(2″), F($2^{\mathrm{v}}$), Fig. 1). The long bonds are tilted away from the normal to the planar square by 18·5° in the direction of two corners of the square. This results in F(2″) and F($2^{\mathrm{v}}$) each being at distances of 3·73, 3·51, 3·04, and 2·71 Å from the ions in the square (Table 5).

Table 5. *Interionic distances, angles, and standard deviations from anisotropic refinement*

| Distance | | σ |
|---|---|---|
| $\mathrm{Cr^{3+}}$–F(1) | 1·894 Å | 0·002 Å |
| $\mathrm{Cr^{3+}}$–F(2) | 1·904 | 0·004 |
| $\mathrm{Cr^{3+}}$–F(3) | 1·877 | 0·003 |
| $\mathrm{Cr^{2+}}$–F(2″)* | 2·572 | 0·004 |
| $\mathrm{Cr^{2+}}$–F(3) | 1·955 | 0·004 |
| $\mathrm{Cr^{2+}}$–F(2‴) | 2·010 | 0·005 |
| Trivalent octahedron | | |
| F(1)–F(2) | 2·692 | 0·004 |
| F(1)–F(3) | 2·640 | 0·005 |
| F(1)–F(3′) | 2·694 | 0·006 |
| F(1)–F(2′) | 2·679 | 0·006 |
| F(2)–F(3) | 2·682 | 0·005 |
| F(2)–F(3′) | 2·666 | 0·005 |
| Divalent octahedron | | |
| F(2″)–F($2^{\mathrm{iv}}$) | 2·718 | 0·007 |
| F(2″)–F(2‴) | 3·731 | 0·003 |
| F(2″)–F(3) | 3·041 | 0·005 |
| F(2″)–F(3″) | 3·410 | 0·005 |
| F($2^{\mathrm{iv}}$)–F(3) | 2·795 | 0·005 |
| F(2‴)–F(3) | 2·813 | 0·006 |
| Angle | | σ |
| F(2) –$\mathrm{Cr^{3+}}$–F(1) | 90·28° | 0·14° |
| F(2) –$\mathrm{Cr^{3+}}$–F(3) | 90·34 | 0·15 |
| F(3) –$\mathrm{Cr^{3+}}$–F(1) | 88·84 | 0·18 |
| F(2‴)–$\mathrm{Cr^{2+}}$–F(3) | 90·38 | 0·14 |
| F(2‴)–$\mathrm{Cr^{2+}}$–F($2^{\mathrm{v}}$) | 71·58 | 0·15 |
| F(2″)–$\mathrm{Cr^{2+}}$–F(3) | 83·21 | 0·13 |

* See Fig. 1 for identification of ions with primed notation

Jack & Maitland (1957) did not describe the configuration of the octahedron in the structure of $\mathrm{CrF_2}$ except for cation–anion distances, but a detailed examination shows that it is also distorted. In this structure there is also a nearly square arrangement of four fluoride ions and two more distant ones. If the fluoride ion at 2·43 Å is designated the apex of the octahedron, then the distances from the apex to the corners of the square are 3·51, 3·13, 2·81, and 2·76 Å. The angles between the apical fluoride, the chromium ion, and each of two adjacent corners of the square

Table 6. *The principal axis r.m.s. thermal displacements and orientations**

| Ion | $r$ | $\mu(r)$ | $\varphi(r, 1)$ | $\varphi(r, 2)$ | $\varphi(r, 3)$ |
|---|---|---|---|---|---|
| $Cr^{3+}$ | 1 | 0·077 ± 0·004 Å | 48 ± 8° | 44 ± 10° | 100 ± 14° |
| | 2 | 0·089 ± 0·004 | 74 ± 16 | 118 ± 17 | 147 ± 19 |
| | 3 | 0·096 ± 0·004 | 133 ± 10 | 59 ± 12 | 121 ± 19 |
| $Cr^{2+}$ | 1 | 0·083 ± 0·004 | 80 ± 11 | 79 ± 13 | 15 ± 17 |
| | 2 | 0·094 ± 0·004 | 127 ± 5 | 139 ± 6 | 76 ± 17 |
| | 3 | 0·125 ± 0·003 | 141 ± 4 | 51 ± 4 | 89 ± 4 |
| $F^-(1)$ | 1 | 0·100 ± 0·011 | 5 ± 7 | 85 ± 7 | 90 ± 0 |
| | 2 | 0·156 ± 0·009 | 90 ± 0 | 90 ± 0 | 180 ± 0 |
| | 3 | 0·162 ± 0·009 | 95 ± 7 | 5 ± 7 | 90 ± 0 |
| $F^-(2)$ | 1 | 0·087 ± 0·007 | 78 ± 6 | 16 ± 7 | 101 ± 6 |
| | 2 | 0·134 ± 0·007 | 141 ± 12 | 74 ± 7 | 56 ± 12 |
| | 3 | 0·156 ± 0·006 | 54 ± 12 | 88 ± 6 | 36 ± 12 |
| $F^-(3)$ | 1 | 0·087 ± 0·009 | 98 ± 6 | 87 ± 4 | 7 ± 5 |
| | 2 | 0·150 ± 0·006 | 162 ± 11 | 107 ± 12 | 97 ± 6 |
| | 3 | 0·171 ± 0·006 | 106 ± 11 | 17 ± 11 | 96 ± 4 |

* $\mu(r)$ is the r.m.s. displacement along axis $r$, and $\varphi(r, j)$ is the angle between axis $r$ and the $j$th cartesian axis.

are 76° and $78\frac{1}{2}$°. Thus, the long Cr–F bond is inclined towards the edge of the square rather than towards a corner.

The causes of distortion of the divalent octahedra in both structures are twofold. First, the tetragonal extension of two Cr–F bonds is due to the repulsion of the fluoride ions by electrons in the $d_{z^2}$ orbital of $Cr^{2+}$, and secondly, the deviation from tetragonal symmetry is needed to achieve close packing of fluoride ions. In $CrF_2$ the ions in the equatorial square of the octahedron are all in contact, and the tilt of the long Cr–F bond towards the edge of the square provides close packing of fluoride ions in two (equivalent) faces of the octahedron. The configuration is similar in $Cr_2F_5$, but the contraction of the edge shared by two octahedra results in further distortion. In $CrF_2$ the octahedra share corners only.

The octahedra in $Cr_2F_5$ are connected in an infinite network by sharing corners and edges. The trivalent octahedra share corners with each other and with the divalent octahedra, while the divalent octahedra share edges among themselves and share corners with two different adjacent trivalent octahedra. In the layers approximately parallel to the (010) plane, one type of fluoride ion, F(2), is shared by two divalent cations and one trivalent cation. The strength of each of the three bonds to this fluoride ion is $+\frac{1}{3}$, $+\frac{1}{3}$, and $+\frac{1}{2}$, respectively, so that a local electrical imbalance of $+\frac{1}{6}$ exists. The fluoride ion, F(1), which serves as a link between two trivalent octahedra receives two bonds of strength $+\frac{1}{2}$, exactly neutralizing its negative charge. The fluoride ion which connects a divalent with a trivalent octahedron along the **b** axis receives two bonds of strength $+\frac{1}{2}$ and $+\frac{1}{3}$, respectively, leaving an imbalance of $-\frac{1}{6}$.

For each ion the r.m.s. components along its principal axes of thermal motion were calculated from the anisotropic temperature factors (Table 3) with the Busing–Levy program (1959). In Table 6 these displacements, $\mu(r)$, are given in addition to the orientation of the principal axes relative to cartesian axes, defined as follows. Cartesian axis 1 is along **c**, axis 3 is along **b**, and axis 2 is in the direction of $-\mathbf{c}\times\mathbf{b}$. The thermal motion is in qualitative agreement with expectation from the arrangement of ions in the structure. The motion of the $Cr^{3+}$ ion is nearly isotropic because of its symmetrical environment, while the displacement of the $Cr^{2+}$ ion is appreciably greater in the direction of its long Cr–F bonds. Each of the crystallographically independent fluoride ions has its smallest thermal displacement nearly along its bond direction to a $Cr^{3+}$ ion. Perpendicular to these bonds, the motions of F(1) and F(3) are greater than that of F(2), since F(1) and F(3) are each approximately on a line joining two cations, while F(2) is shared by three cations in a triangular array.

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