Tableau 2. *Principales caractéristiques géométriques des anions cycliques* P_3O_9 *dans* $BaKP_3O_9.H_2O$
(Å *et degrés*)

P(1)	O(E11)	O(E12)	O(L12)	O(L13)
O(E11)	1,48 (3)	119 (2)	106 (2)	108 (2)
O(E12)	2,57 (5)	1,50 (4)	109 (2)	112 (2)
O(L12)	2,47 (4)	2,55 (4)	1,62 (3)	101 (1)
O(L13)	2,52 (4)	2,60 (4)	2,51 (4)	1,64 (2)

P(2)	O(E21)	O(E22)	O(L12)	O(L23)
O(E21)	1,46 (3)	120 (2)	111 (2)	110 (2)
O(E22)	2,54 (4)	1,48 (3)	105 (2)	108 (2)
O(L12)	2,53 (4)	2,45 (4)	1,61 (3)	102 (2)
O(L23)	2,53 (4)	2,51 (4)	2,52 (4)	1,63 (3)

P(3)	O(E31)	O(E32)	O(L13)	O(L23)
O(E31)	1,46 (3)	121 (2)	101 (2)	108 (2)
O(E32)	2,56 (4)	1,48 (3)	112 (2)	112 (2)
O(L13)	2,39 (4)	2,57 (4)	1,62 (2)	100 (1)
O(L23)	2,50 (4)	2,57 (4)	2,49 (4)	1,62 (3)

P(1)–P(2)	2,95 (2)	P(1)–O(L12)–P(2)	131 (2)
P(1)–P(3)	2,91 (2)	P(1)–O(L13)–P(3)	126 (2)
P(2)–P(3)	2,90 (2)	P(2)–O(L23)–P(3)	126 (2)

Tableau 3. *Distances cations–oxygènes dans les polyèdres de coordination des cations associés dans* $BaKP_3O_9.H_2O$ (Å)

K–O(L23)	2,75 (3)	Ba–O(E11)	2,62 (3)
K–O(E21)	2,79 (3)	Ba–O(E22)	2,75 (3)
K–O(E32)	2,88 (3)	Ba–O(E31)	2,76 (3)
K–O(L12)	2,89 (3)	Ba–O(E32)	2,83 (3)
K–O(E21)	2,90 (3)	Ba–O(W)	2,84 (3)
K–O(E12)	2,93 (3)	Ba–O(E31)	2,87 (3)
K–O(E22)	2,94 (3)	Ba–O(E12)	2,89 (3)
K–O(E22)	3,04 (3)	Ba–O(W)	3,10 (3)
K–O(L12)	3,21 (3)	Ba–O(E12)	3,34 (3)

O(E21)–O(E22) commune. Les atomes de potassium enchaînés se répartissent également dans deux plans parallèles très proches. Le résultat est une famille de plans doubles parallèles. Pris en sandwich entre ces plans se trouvent les enchaînements unidimensionnels des polyèdres de baryum suivant la direction **a**, chaque

polyèdre étant lié à l'un de ses deux voisins par l'arête commune O(W)–O(W) et à l'autre par une face commune de forme losangique dont les diagonales sont O(E12)–O(E12) et O(E31)–O(E31). La mise en commun du sommet O(E12) entre un polyèdre de baryum et un polyèdre de potassium appartenant à un plan double situé d'un côté et des arêtes O(E12)–O(E22) et O(E22)–O(E32) entre le même polyèdre de baryum et deux polyèdres de potassium appartenant au plan double situé de l'autre côté assure la liaison entre les deux types d'enchaînement (Figs. 1 et 2).

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Electron-Density Distribution in Crystals of CoAl₂O₄

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The electron-density distribution in crystals of $CoAl_2O_4$ [cubic, $Fd3m$, $a = 8.095$ (1) Å, $Z = 8$] has been determined by single-crystal X-ray diffraction. The residual electron-density around the Co atom in the tetrahedral site was observed on the final difference maps. The asphericity can be interpreted by a crystal-field model and is attributable to an excess charge density in the e orbitals and a deficiency in the t_2 orbitals. The valence-electron populations of the atoms were refined and the net charges of the Co, Al and O atoms were estimated to be $+1.5$ (1), $+2.8$ (1) and -1.8 e respectively. Consequently, the compound is largely ionic. Residual electron density also appeared around the O atom, indicating a slightly covalent character for the Co–O bond.

Introduction

For compounds in which the transition-metal atoms are located in an octahedral environment, studies of the electron-density distribution of $3d$ electrons have been carried out by X-ray diffraction (Iwata & Saito, 1973; Marumo, Isobe, Saito, Yagi & Akimoto, 1974; Shintani, Sato & Saito, 1975; Marumo, Isobe & Akimoto,

1977; Iwata, 1977). In order to observe the deformation density of a transition-metal ion in a tetrahedral field, we have undertaken a study of the spinel $CoAl_2O_4$.

This compound was selected for the following reasons: The behaviour of the $3d$ electrons of the Co atom may be treated by a simple crystal-field model; thermal smearing of the difference Fourier map may be relatively small, owing to the small thermal vibrations of the atoms; crystals of $CoAl_2O_4$ were known to have an almost normal spinel structure; and positional disorder between Co and Al atoms does not seem to have much effect on the deformation density of Co^{2+}, since the electron density distribution around Al^{3+} is expected to be spherical.

Experimental

Single crystals of $CoAl_2O_4$ were grown by slow cooling of a molten mixture of PbO, PbF_2, Al_2O_3 and Co_3O_4 from 1280 to 800°C under atmospheric pressure. A cobalt-blue octahedral crystal was selected for X-ray work. The distances between four pairs of opposite {111} faces are: 0·122, 0·097, 0·097 and 0·086 mm. The unit-cell dimensions were determined from ten 2θ values (65° ≤ 2θ ≤ 77°) measured on a diffractometer with Mo $K\alpha$ radiation. The crystal data are: cubic, $Fd3m$, $Z = 8$, $a = 8·095$ (1) Å, $U = 530·5$ (1) Å³, $\mu(Mo\ K\alpha) = 69·19$ cm⁻¹, $D_x = 4·43$ g cm⁻³. Intensities were collected on a Rigaku automated four-circle diffractometer with Mo $K\alpha$ radiation monochromated by a graphite plate. The experimental conditions are given in Table 1. Background counts were made at both ends of the scan range and the counting time was varied from 15 to 411 s, according to the peak counts and the scanning time. When the peak intensity exceeded 5500 counts s⁻¹, Ni-foil attenuators were inserted to avoid a counting loss. Scanning was repeated until $\sigma(|F_o|)/|F_o|$

became less than 0·005, where $\sigma(|F_o|)$ is the estimated standard deviation of F_o based on the counting statistics.

The intensities of the five standard reflexions were measured every fifty measurements to check the stability of the incident beam and any crystal deterioration. During the period of the data collection (9 d), the intensities of the standard reflexions decreased by 1·5%. The intensity of the direct beam was also checked before and after the measurement; this decreased by 1·3%. Thus the observed structure amplitudes were corrected for the decrease in intensity of the standard reflexions.

In order to reduce the systematic errors in $|F_o|$, three to six symmetry-related reflexions were measured for each independent reflexion. The intensities were corrected for Lorentz and polarization factors. Absorption correction was made by the method of numerical Gaussian integration (Busing & Levy, 1957).

The standard deviation of each reflexion was estimated from the equation:

$$[\sigma(|F_o|)]^2 = [\sigma(\text{counting statistics})]^2$$
$$+ (k|F_o|)^2 + [\tfrac{1}{2}\mu\sigma(t)|F_o|]^2. \quad (1)$$

The value of k estimated from the least-squares calculation based on the intensity fluctuations among symmetry-related reflexions was 0·01. $\sigma(t)$ and μ are the standard deviation of the path length for each reflexion and the linear absorption coefficient respectively. The value of $\tfrac{1}{2}\mu\sigma(t)$ was estimated to be 1·0 × $t(hkl)$. Comparison of the intensities of symmetry-related reflexions revealed that five reflexions were seriously affected by multiple reflexion; these were omitted from the data set. Among the 321 independent reflexions, 273 which gave more than two non-zero values during measurements of symmetry-related reflexions were considered to be 'observed', and used for the structure refinement.

Refinement

The crystal was known to have the normal spinel structure (Greenwald, Pickart & Grannis, 1954). Refinement of the structure was carried out with the full-matrix least-squares program *RADIEL* (Becker, Yang & Coppens, unpublished). The valence-electron populations and the valence form factors were also refined (Iwata, 1977). An isotropic secondary-extinction effect was assumed. The smallest extinction factor was 0·43 for reflexion 440. The weight in the least-squares calculation was taken as $w = 1/[\sigma(|F_o|)]^2$, where $\sigma(|F_o|)$ is defined by equation (1). For the reflexions with extinction factors greater than 0·95 the averaged structure amplitudes among symmetry-

Table 1. *Experimental conditions*

Dimensions of the specimen	An octahedron, formed by {111}, of volume 8·46 × 10⁻⁷ cm³
Radiation	Mo $K\alpha$ ($\lambda = 0·71068$ Å)
Monochromator	Graphite plate
Take-off angle	5°
Scan mode	θ–2θ continuous scan
Scan rate	2° min⁻¹
Scan width	1·1° + 0·8° tan θ
Maximum number of repetitions	6 ($2\theta \le 120°$) 8 ($2\theta > 120°$)
Criterion to terminate repetition	$\sigma(|F|)/|F| \le 0·005$
$2\theta_{max}$	150°
Total number of measured reflexions	1100
Number of observed independent reflexions	273

related reflexions were used in the calculation. Positional disorder between Co and Al atoms was taken into account, and the population was included in the variable to be refined under the constraint to ensure electrical neutrality of the crystal.

The population, positional and thermal parameters and a scale factor were obtained from the high-order reflexions (sin $\theta/\lambda \geq 0.8$ Å^{-1}). In the next step, the valence-electron populations, valence form factors and an extinction parameter were refined on the basis of all the observed reflexions. These two steps were repeated alternately until the parameters converged to self-consistent values.

The atomic scattering factors for Co^{2+}, Al^{3+} and O$^-$ were taken from the values given by Fukamachi (1971) and the valence electrons were taken as follows: Co^{2+} $3d$; Al^{3+} $2p$, O$^-$ $2p$. The final parameters are given in Table 2, together with the standard deviations and the discrepancy indices.*

The discrepancies between the atomic parameters and a scale factor based on the high-order reflexions and those for all the reflexions are less than 3σ of their parameters, except for the positional parameter of the O atom. The standard deviation of the observed electron density was estimated to be 0.08 e Å^{-3} at the general position on the plane $y = x$ (Stevens & Coppens, 1976).

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33223 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Results and discussion

The site-occupancy parameter of 0.155 (9) in the expression $(Co_{1-\alpha}Al_\alpha)(Al_{2-\alpha}Co_\alpha)O_4$ indicates the presence of positional disorder of Al^{3+} and Co^{2+} ions. The Co—O distance of 1.9454 (7) and the Al—O distance of 1.9189 (7) Å agree within experimental errors with those reported previously (Barth & Posnjak, 1932).

A section of the difference Fourier map through the plane $y = x$ is presented in Fig. 1. In the calculation of the map, six reflexions with extinction factors less than 0.7 were excluded in view of the large errors in the observed F values. Inclusion of these reflexions gave essentially the same features; however, a number of spurious peaks appeared in the region between the atoms. All the crystallographically independent atoms and chemical bonds are contained in this map. A remarkable feature is the distribution of residual electron density around Co^{2+} on the tetrahedral site: two positive peaks of 1.3 e Å^{-3} appear on the a_3 axis at 0.40 Å from the nucleus. In all, six peaks are located at the apices of an octahedron centred at the Co nucleus. On the other hand, four negative peaks appear on the threefold axes through the Co and O atoms. Two of the four negative peaks are at 0.40 Å from the Co towards the O atoms with peak heights of -1.0 e Å^{-3}. The remaining two with peak heights of -0.5 e Å^{-3} are situated on the extension of the O—Co bond at about 0.5 Å from the Co nucleus. These negative peaks are arranged at the eight corners of a cube centred at the Co nucleus. The arrangement of positive and negative
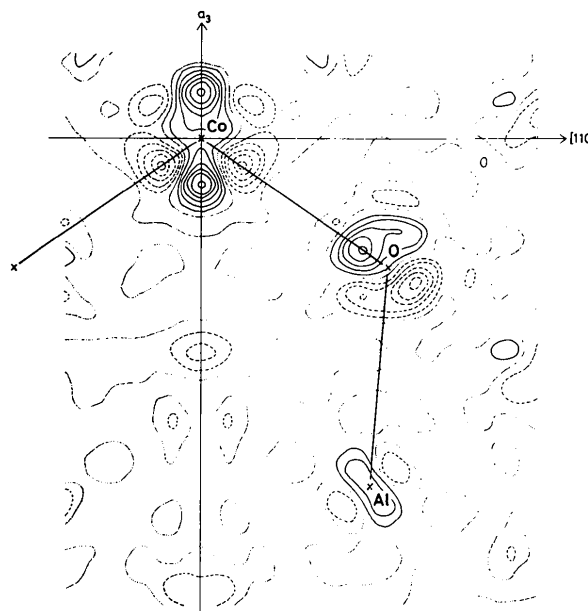
Table 2. The final parameters and discrepancy indices

The values of the positional and thermal parameters are multiplied by 10^5 and those of the populations by 10^3. The temperature factors are as follows: $\exp\{-2\pi^2 a^{*2}[U_{11}(h^2 + k^2 + l^2) + 2U_{12}(hk + hl + kl)]\}$.

Population		$x(=y=z)$	U_{11}	U_{12}
Tetrahedral sites				
Co	845	0	431 (7)	0
Al	155 (9)			
Octahedral sites				
Al	922	62500	386 (13)	−17 (3)
Co	78			
Oxygen sites		38875 (5)	693 (8)	−9 (6)

	Co	Al	O
Number of electrons	25·47 (11)	10·18 (5)	9·79
Valence form factor κ defined by $f(s/\kappa)$	1·065 (10)	1·018 (4)	0·974 (9)

Scale factor	2·296 (13)
G ($\times 10^4$)	1·11 (4)
$R_w(F)$	0·0213
$R_w(F^2)$	0·0422
$R(F)$	0·0168
$R(F^2)$	0·0297
$S = [\Sigma w(|F_o| - |F_c|)^2/(n - p)]^{1/2}$	1·201

Fig. 1. Section of the difference Fourier map through the plane $y = x$. Contours are at intervals of 0.2 e Å^{-3}. Zero contours are in dotted lines, and negative contours broken.

peaks is contrary to the result obtained for the transition-metal ions in an octahedral environment {e.g. [Co(NH$_3$)$_6$][Co(CN)$_6$]: Iwata & Saito, 1973; [Co(NH$_3$)$_6$][Cr(CN)$_6$]: Iwata, 1977; γ-Ni$_2$SiO$_4$: Marumo, Isobe, Saito, Yagi & Akimoto, 1974; and γ-Co$_2$SiO$_4$: Marumo, Isobe & Akimoto, 1977}. In all these structures, eight positive peaks were observed at the corners of a cube surrounding the transition-metal atom.

According to the simple crystal-field model, the energy level of the 3d electrons in a transition-metal atom placed in a tetrahedral environment splits into a lower doublet e and a higher triplet t_2. Thus, four of the seven d electrons of the Co^{2+} ion occupy the e orbital and the remaining three occupy the t_2 orbital in the ground state. In other words, two electrons are added in the e orbital to the half-closed shell ground state with spherical symmetry, $(e)^2(t_2)^3 + (e)^2$. Thus the expected deformation density around Co^{2+} may be a positive charge density in the direction of the e orbital and a negative charge density in the direction of the t_2 orbital. The observed deformation density shown in Fig. 1 exactly agrees with that expected, as described above.

The refinement of the valence-electron population gives the effective charges for the Co, Al and O atoms as +1·5, +2·8 and −1·8 e respectively. This result seems to suggest the ionic character of the compound. It is to be noted that the Co atom is somewhat neutralized.

No significant residual density is observed around the Al^{3+} ion, indicating a spherical charge density around Al^{3+}. Thus the 16% migration of Al^{3+} in the tetrahedral site may not cause any bias to the deformation density around the Co^{2+} ion.

Residual density is observed around the O^{2-} ion on the Co—O bonds. The positive peaks are directed towards Co^{2+} and the negative peaks are at the opposite side of the O atom with respect to the Co atom. They are at about 0·3 Å from the O nucleus, the peak height being ±1·0 e Å^{-3}. The electron-density distribution around the O atom will be biased by the positional disorder of the Co and Al sites. When 16% of the O^{2-} ion was assumed to be shifted towards the Co^{2+} ion by 0·03 Å (the difference between the Co—O

and Al—O distances), the heights of the residual peaks were reduced by about one third in the resulting difference synthesis. The general features were, however, retained. If the shift is increased to greater than 0·05 Å, a number of spurious peaks appear on the difference synthesis and the R value begins to increase. Accordingly, the residual charge density around the O atom is at least qualitatively meaningful, which appears to indicate some covalent character of the Co—O bond, being consistent with the slightly neutralized charge of the Co^{2+}. This differs markedly from silicate spinels, γ-M$_2$SiO$_4$ (M = Ni, Fe or Co), where the excess densities due to bonding electrons were localized between the Si and O atoms.

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