FIGGIS, B. N., SKELTON, B. W. & WHITE, A. H. (1978). *Aust. J. Chem.* **31**, 1195–1199.

HERREN, F., LUDI, A. & FISCHER, P. (1979). *Acta Cryst.* B**35**, 3129–3130.

International Tables for X-ray Crystallography (1968). Vol. III, 2nd ed., pp. 197–199. Birmingham: Kynoch Press.

International Tables for X-ray Crystallography (1974). Vol. IV, pp. 270–271. Birmingham: Kynoch Press.

JAGNER, S., LJUNGSTRÖM, E. & VANNERBERG, N.-G. (1974). *Acta Chem. Scand. Ser. A*, **28**, 623–630.

KOHN, J. A. & TOWNES, W. D. (1961). *Acta Cryst.* **14**, 617–622.

LEHMANN, M. S. & WILSON, S. (1977). Internal Report, Institut Laue–Langevin, Grenoble.

RAMSDELL, L. S. (1947). *Am. Mineral.* **32**, 64–82.

REYNHARDT, E. C. & BOEYENS, J. C. A. (1972). *Acta Cryst.* B**28**, 524–529.

STEWART, J. M. (1976). The XRAY 76 system. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland.

VANNERBERG, N.-G. (1970). *Acta Chem. Scand.* **24**, 2335–2347.

VANNERBERG, N.-G. (1972). *Acta Chem. Scand.* **26**, 2863–2876.

ZACHARIASEN, W. H. (1967). *Acta Cryst.* **23**, 558–564.

Acta Cryst. (1981). B**37**, 508–513

An X-ray Diffraction Study of Tricaesium Tetrachlorocobaltate(II) Chloride at 295 K

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Abstract

An X-ray diffraction data set consisting of 1772 unique reflections (27118 measured) has been collected on Cs_3CoCl_5 at 295 K. The unit cell is tetragonal, $I4/mcm$, with $a = 9{\cdot}2315\,(15)$, $c = 14{\cdot}5535\,(24)$ Å, $Z = 4$. A free-atom form factor, harmonic model does not fit the data well. From the low-angle low-intensity data [$R(F) = 0{\cdot}022$, $R_w(I) = 0{\cdot}030$ for 54 unique reflections] charges of $+1{\cdot}27 \pm 0{\cdot}10$ e on the cobalt and $-0{\cdot}82 \pm 0{\cdot}12$ e on the tetrachlorocobaltate-anion Cl atoms are obtained. The cobalt possesses a 3*d* population of $7{\cdot}1 \pm 0{\cdot}1$ e and a much more diffuse charge of $0{\cdot}6 \pm 0{\cdot}16$ e. Comparison with neutron diffraction, polarized neutron diffraction and spectroscopic results suggests that the highest-angle data may be substantially affected by anharmonicity. 'Anharmonicity' parameters are derived.

Introduction

Tricaesium tetrachlorocobaltate(II) chloride has recently been the subject of neutron diffraction (Figgis, Mason, Smith & Williams, 1980) and polarized neutron diffraction (Figgis, Reynolds, Williams, Mason, Smith & Varghese, 1980) experiments at 4·2 K. The derived electronic spin density shows the effect of covalence in the crystal $[CoCl_4]^{2-}$ anions. Complementary charge-density studies by means of X-ray diffraction experiments are desirable. Previous photographic X-ray diffraction experiments (Powell & Wells, 1935; Figgis, Gerloch & Mason, 1964) were of limited extent in reciprocal space and neglected large absorption effects. Before collecting a low-temperature reflection data set we analysed the room-temperature data for any chemically significant information resolvable from the thermal motion. A room-temperature neutron diffraction study has been performed concurrently (Williams, Figgis & Moore, 1980).

Experimental

The crystal used was an almost regular truncated tetragonal prism, prepared from solution (Figgis, Reynolds, Williams, Mason, Smith & Varghese, 1980). The unit cell of the tetragonal crystal was determined by a least-squares fit of ten reflections centred in the counter aperture of a Syntex $P2_1$ four-circle X-ray diffractometer. A complete sphere of data, approximately to the limit in that of observable intensities, was collected. The crystal dimensions and experimental conditions are given in Table 1. After correction for the slight change in standard intensities, the intensities of Friedel-pair-related equivalent reflections were equal, within errors in counting and standardization. These Friedel-related intensities were accordingly averaged before an absorption correction was made. An

Table 1. *Crystal, experimental and absorption data*

Crystal dimensions	(001) to $(00\bar{1})$ 0·12 mm (110) to $(\bar{1}\bar{1}0)$ 0·17 (112) to $(\bar{1}\bar{1}\bar{2})$ 0·15
X-ray data	
Radiation	Mo $K\alpha$ ($\lambda = 0{\cdot}71069$ Å)
Monochromator	graphite plate (002)
Scan mode	$\omega/2\theta$
Scan rate	variable
Scan width	2·6° + $\alpha_1\alpha_2$ splitting
Background counting time	0·5 of scan time
Number of measured reflections	27118
Number of unique reflections	1772
$2\theta_{\max}[(\sin\theta/\lambda)_{\max}]$	100° (1·08 Å^{-1})
Standard intensities	6 every 50 reflections
Absorption-correction data	
Refined crystal dimensions	(001) to $(00\bar{1})$ 0·14 (1) mm (110) to $(\bar{1}\bar{1}0)$ 0·16 (1) mm
Mean path length	0·07–0·12 mm
Transmission factor	0·222–0·342

analytical absorption correction, with crystal dimensions as input, was made using the program *ABSCOR* of the XRAY 76 system (Stewart, 1976). The dimensions used in the correction were optimized, using a small (eight unique reflections) set of representative intense reflections, to minimize the disagreement between equivalences $\{R_I = \sum \mathrm{Av}[I - \mathrm{Av}(I)]/\sum \mathrm{Av}(I)\}$. Before correction, R_I was 6·9% for the 42 intensities; after correction it was 1·9%. The crystal volume was kept constant, leaving two degrees of freedom for this crystal morphology. The refined crystal dimensions (Table 1) did not differ significantly from the measured values.

The variance between different equivalents of the same unique reflection was found to be relatively independent of θ and χ, being well approximated by

$$\sigma^2(I) = \sigma^2_{\mathrm{counting}} + p + qI^2; p = 12\,000, q = 0{\cdot}0008. \quad (1)$$

These values of p and q are consistent with machine instability (also evidenced in the standards, for which p is $\sim$12 000) together with errors in the absorption correction. The variance of our estimate of the average intensity, $\bar{I}$, we have written as

$$\sigma^2(\bar{I}) = \sigma^2_{\mathrm{counting}}(\bar{I}) + p/\sqrt{N} + (q/2)I^2, \quad (2)$$

where N is the number of different equivalents used in the averaging. The value of $(q/2)$ is a rough estimate of the residual error arising from the anisotropic part of the absorption. Since systematic errors affecting equivalent reflections equally are not considered we may expect $\sigma(\bar{I})$ to be an underestimate.

The systematically absent reflections $[0kl; l(k) = 2n + 1]$ had significant but small observable intensities, about 0·02% of the most intense reflections. This effect is presumably ascribable to multiple scattering. However, the most intense low-2θ reflections showed no detectable anomalous variations associated with multiple scattering. Although $\sigma(\bar{I})/\bar{I}$ has a minimum value of $\sim$2%, the average value over the 1772 unique reflections is 3·5%. This reflects the large number of weak reflections of high-2θ angles which were measured.

Refinement

The structure of this crystal is relatively simple. There are two independent types of caesium cations, a chloride anion, and a tetrachlorocobaltate anion. They are arranged in a layer-like structure of alternating $2Cs^+$ and Cl^- layers and Cs^+ and $CoCl_4^{2-}$ layers (Powell & Wells, 1935). The intermolecular contacts and arrangement of $CoCl_4^{2-}$ ions have been discussed in more detail, with figures, by Figgis, Gerloch & Mason (1964).

(*A*) *Conventional refinements*

Valence contributions and anharmonic contributions to the scattering are strongly dependent on $\sin\theta/\lambda$. Accordingly, we have used the program *CRYLSQ* (Stewart, 1976) to refine only those reflections for which $\sin\theta/\lambda < 0{\cdot}6$ Å^{-1} (refinement $R1$). A second refinement ($R2$) using reflections for which $0{\cdot}8 < \sin\theta/\lambda < 1{\cdot}08$ Å^{-1} was also made. The refinement was on intensity using observed variances as weights; free-ion form factors (Co^{2+}, Cl^-, Cs^+) were used (*International Tables for X-ray Crystallography*, 1974, pp. 72–101); anomalous-dispersion corrections were made (*International Tables for X-ray Crystallography*, 1974, pp. 149–150); all data were used. The results are shown in Table 2. We define $R(F) = \sum ||F_{\mathrm{obs}}| - |F_{\mathrm{calc}}||/\sum |F_{\mathrm{obs}}|$; $R_w(I) = [\sum (1/\sigma^2_{\mathrm{obs}})(I_{\mathrm{obs}} - I_{\mathrm{calc}})^2/\sum (1/\sigma^2_{\mathrm{obs}})I^2_{\mathrm{obs}}]^{1/2}$; $\chi^2(I) = [\sum (1/\sigma^2_{\mathrm{obs}})(I_{\mathrm{obs}} - I_{\mathrm{calc}})^2/(N_{\mathrm{obs}} - N_{\mathrm{par}})$. In the low-angle refinement $R1$ we obtained $R(F) = 0{\cdot}023$, $R_w(I) = 0{\cdot}047$; $\chi(I) = 2{\cdot}4$ with $N_{\mathrm{obs}} = 327$ and $N_{\mathrm{par}} = 18$, an isotropic extinction coefficient of $4{\cdot}1(1) \times 10^3$ and an F_{rel} scale factor of 0·964 (4). For the high-angle refinement $R2$ we obtained $R(F) = 0{\cdot}127$, $R_w(I) = 0{\cdot}118$, $\chi(I) = 0{\cdot}71$ with $N_{\mathrm{obs}} = 1034$, $N_{\mathrm{par}} = 17$ (extinction held fixed) and an F_{rel} scale factor of 1·375 (5). The relatively large agreement factors for both refinements, but particularly $R2$, reflect the large number of weak reflections, often typed as 'unobserved', which we have included in the refinement to avoid any bias (Hirshfeld & Rabinovich, 1973). Fourier difference maps of $R1$, $R2$, and an all-data refinement show features around all the atoms. These features are always centrosymmetric and the largest have cylindrical symmetry around [001] with no obvious multipoles higher than quadrupolar (with the exception of Co).

Table 2. *Atomic positional coordinates and thermal parameters for* Cs_3CoCl_5 *by conventional refinements*

The low-angle, *R*1, refinement is the first line, the high-angle the second, and the 295 K neutron refinement the third. *U* is in $Å^2 \times 10^3$. The anisotropic thermal parameters given by $T = \exp(-2\pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^*)$ $(a_1^* = h/a, a_2^* = k/b, a_3^* = l/c)$.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co	0	$\frac{1}{2}$	$\frac{1}{4}$	32·1 (4)	32·1 (4)	26·7 (6)	0	0	0
	0	$\frac{1}{2}$	$\frac{1}{4}$	27·4 (15)	27·4 (15)	17·6 (17)	0	0	0
	0	$\frac{1}{2}$	$\frac{1}{4}$	26·7 (6)	26·7 (6)	19·3 (8)	0	0	0
Cs(1)	0	0	$\frac{1}{4}$	46·6 (3)	46·6 (3)	44·3 (4)	0	0	0
	0	0	$\frac{1}{4}$	40·0 (17)	40·0 (17)	34·3 (18)	0	0	0
	0	0	$\frac{1}{4}$	40·3 (3)	40·3 (3)	34·1 (5)	0	0	0
Cs(2)	0·66577 (4)	0·16577 (4)	0	31·4 (2)	31·4 (2)	41·2 (3)	−1·7 (2)	0	0
	0·66579 (20)	0·16579 (20)	0	25·9 (13)	25·9 (13)	34·9 (15)	−0·7 (7)	0	0
	0·66565 (5)	0·16565 (5)	0	24·9 (2)	24·9 (2)	32·4 (3)	−0·14 (2)	0	0
Cl(1)	0	0	0	34·0 (7)	34·0 (7)	52·6 (15)	0	0	0
	0	0	0	28·4 (24)	28·4 (24)	38·8 (45)	0	0	0
	0	0	0	27·1 (2)	27·1 (2)	42·8 (3)	0	0	0
Cl(2)	0·13949 (10)	0·63949 (10)	0·15760 (11)	49·0 (5)	49·0 (5)	42·5 (8)	−11·1 (5)	6·6 (5)	6·6 (5)
	0·13984 (75)	0·63984 (75)	0·15783 (78)	39·5 (23)	39·5 (23)	32·9 (31)	−10·6 (22)	4·8 (13)	4·8 (13)
	0·13945 (2)	0·63945 (2)	0·15738 (2)	40·3 (1)	40·3 (1)	34·7 (1)	−11·7 (1)	6·5 (1)	6·5 (1)

(*B*) *Low-angle refinement*

At low angles the resolution of the data will be insufficient to determine more than atomic charges and/or any diffuse features. Conversely for sufficiently low-angle data thermal motion is not important and any reasonable values of the thermal parameters will not noticeably bias the results. Extinction seriously affects intense reflections, and multiple scattering may also affect very weak ones. We used all the data with $\sin\theta/\lambda < 0{\cdot}35$ Å^{-1}, in which the intensity is not reduced by extinction in *R*1 by more than 4% and which are not systematically absent. 54 unique reflections remain. We have used these to refine form factors, using the thermal and extinction parameters of *R*1, to which the data are insensitive. In the program *ASRED* (Figgis, Reynolds & Williams, 1980) we have refined a chemically reasonable model. We used free-ion form factors for Cs(1), Cs(2) and Cl(1) (the free chloride ion); while in the tetrachlorocobaltate anion the Cl(2) had a fixed neon core and a variable 3*s* + 3*p* population, and the Co(1) had a fixed argon core and variable 3*d* and more diffuse populations. The cobalt diffuse component had a radial extent fixed at 2·5 times the radial exponent of the 3*d* orbital. This is suggested by the polarized neutron diffraction results. Appropriate form factors were obtained from *International Tables for X-ray Crystallography* (1974, pp. 103–146). Variation of these three extra population parameters reduced $R(F)$ from 0·032 to 0·022, $R_w(I)$ from 0·045 to 0·030 and $\chi(I)$ from 3·5 to 2·4.

We obtain a charge on Cl(2) of −0·82 ± 0·12 e and a net charge on cobalt of +1·27 ± 0·10 e. The latter may be divided into a '3*d*' population of 7·13 ± 0·10 e and a diffuse population of 0·60 ± 0·16 e. It is pleasing that the refined charge on the tetrachlorocobaltate anion is −2·01 ± 0·10 e, thus maintaining crystal electroneutrality, which was not constrained. Allowing valence populations on Cl(1) and Cs(1) to vary gives charges of −0·98 ± 0·1 and +0·99 ± 0·10 e respectively.

(*C*) *Restricted multipole refinement*

In the light of the above difference Fourier maps we decided to analyse the data in terms of two (scalar and quadrupolar) functions per atom whose wavevector dependence we would refine. We write

$$|F_{\mathbf{h}}| = \Big| \sum_{\text{atoms}} [a_i(|\mathbf{s}|) + \cos^2(\varphi) b_i(|\mathbf{s}|)] f_i(|\mathbf{s}|) \times \exp(2\pi i \mathbf{h}\mathbf{x}_i) T^i_{\mathbf{h}} \Big|, \qquad (3)$$

where $|F_{\mathbf{h}}|$ is the observed structure factor, $T^i_{\mathbf{h}}$ the atomic harmonic thermal parameter, $f_i(|\mathbf{s}|)$ the theoretical atomic form factor, and $a_i(|\mathbf{s}|)$ and $b_i(|\mathbf{s}|)$ the required corrections to obtain the best fit to the actual atomic form factor in the crystal together with any anharmonic effects. φ is the angle between *c* and the scattering vector **s**. If we use the 'harmonic thermal parameters' of *R*1 to calculate $T^i_{\mathbf{h}}$ then *a* and *b* will contain some harmonic thermal information, as well as electronic and anharmonic effects. This also incidentally constrains the first and second derivatives of *a* and *b* with respect to $|\mathbf{s}|$ to be zero. If the effects contained in *a* and *b* are small then we can hope to extract empirically their $|\mathbf{s}|$ dependence by refining successive thin shells of data, assuming *a* and *b* are invariant in a small range $s_1 - \Delta < |\mathbf{s}| < s_1 + \Delta$.

We have divided the data into 14 shells, each containing slightly more than 100 unique reflections. In each shell there are five $a_i(|\mathbf{s}|)$ and five $b_i(|\mathbf{s}|)$ to refine. The results are shown in Table 3(*a*, *b*). The goodnessof-fit, $\chi(I)$, varies from 1·5 at low angle to 0·6 at high angle, showing that for intense reflections we have probably underestimated the errors.

It is evident from these results why a harmonic, free-atom model is inadequate to parametrize the data. For $\sin\theta/\lambda > 0\cdot8$ Å^{-1} with Co, Cs(1) and Cl(2) $a_i(|\mathbf{s}|)$ increases significantly above one, while Cs(2) shows the opposite effect. For Co and Cs(1) $b_i(|\mathbf{s}|)$ becomes markedly negative at high $\sin\theta/\lambda$.

(*D*) *'Series-expansion' refinement*

We write a series expansion of the form factors, truncated in a way suggested by the difference Fourier maps, and using $|\mathbf{s}|$-independent parameters

$$|F_{\mathbf{h}}| = |\sum_i f_i(|\mathbf{s}|)\exp(2\pi i\mathbf{hx}_i)\exp\{-2\pi^2 \times [\sum_n\sum_m U^i_{nm}a^*_n a^*_m - \gamma^i_{hh}(a^*_1)^4 - \gamma^i_{ll}(a^*_3)^4 - \gamma^i_{hl}(a^*_1 a^*_3)^2]\}|. \quad (4)$$

This provides an empirical, parametrized fit to the data. Trial refinement shows that γ^i_{hl} is highly correlated with γ^i_{hh} and γ^i_{ll}. Accordingly, we have rewritten the fourth-order terms in a^* as $-\gamma^i_s|\mathbf{s}|^4 - \gamma^i_{ll}(a^*_3)^4$. Refinement of this model, using *ASRED* and the atomic form factors used in part (*B*), gave $R(F) = 0\cdot05$, $R_w(I) = 0\cdot078$, $\chi(I) = 1\cdot8$, $N_{\rm obs} = 1749$, $N_{\rm par} = 28$. 23 reflections which were highly affected by extinction were omitted from the refinement.

The refined values of the parameters are given in Table 4. The derived $[\mathrm{CoCl_4}]^{2-}$ geometry is given, together with the neutron results, in Table 5.† As might be expected from the form of equation (4), the U's resemble those from the low-angle refinement; while the γ's have adjusted to fit the high-angle data. The only correlation coefficients above 0·5 were some of those connecting γ's and the corresponding diagonal elements of U for a given atom. The maximum value of a correlation coefficient is 0·76 with the majority ~0·6. Such correlation, while large, is acceptable. In other cases (Cooper & Rouse, 1973) the correlation has been

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† A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35728 (30 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Form-factor correction parameters*

(*a*) Values of the spherical form-factor correction parameter $a_i(|\mathbf{s}|)$: these are derived by refinement in shells between the $\sin\theta/\lambda$ limits tabulated.

$\sin\theta/\lambda$ limits (Å^{-1})	Co	Cs(1)	Cs(2)	Cl(1)	Cl(2)
0·1					
0·3	1·003 (3)	1·002 (2)	1·000 (2)	1·004 (5)	0·988 (4)
0·4	0·993 (6)	1·004 (4)	0·997 (3)	1·034 (14)	0·978 (9)
0·5	1·008 (8)	0·991 (5)	0·988 (3)	1·010 (18)	0·997 (9)
0·575	0·997 (10)	0·992 (6)	0·978 (4)	1·001 (10)	0·992 (12)
0·625	1·015 (16)	0·982 (10)	0·954 (5)	0·969 (34)	0·999 (17)
0·675	0·987 (16)	0·973 (11)	0·929 (5)	1·014 (40)	1·010 (20)
0·725	0·979 (19)	0·947 (14)	0·895 (6)	0·990 (50)	1·028 (26)
0·775	1·010 (22)	1·004 (18)	0·906 (6)	1·072 (61)	0·974 (37)
0·825	0·945 (25)	0·984 (20)	0·905 (6)	0·998 (67)	0·967 (34)
0·875	1·034 (34)	0·885 (34)	0·889 (10)	1·329 (112)	1·132 (57)
0·925	0·917 (39)	1·089 (40)	0·911 (27)	1·007 (130)	1·122 (82)
0·975	1·140 (66)	0·937 (77)	0·893 (32)	1·780 (264)	1·488 (146)
1·025	1·040 (84)	1·188 (110)	0·973 (35)	1·166 (352)	1·332 (172)

(*b*) Values of the quadrupolar form-factor correction parameter $b_i(|\mathbf{s}|)$

$\sin\theta/\lambda$ limits (Å^{-1})	Co	Cs(1)	Cs(2)	Cl(1)	Cl(2)
0·1					
0·3	0·002 (3)	0·002 (2)	−0·001 (2)	−0·006 (6)	−0·001 (4)
0·4	−0·001 (5)	−0·009 (3)	−0·002 (2)	−0·017 (13)	−0·013 (7)
0·5	−0·007 (7)	−0·006 (4)	−0·002 (3)	0·019 (17)	0·007 (9)
0·525	0·005 (9)	−0·001 (6)	−0·005 (4)	−0·006 (20)	−0·002 (10)
0·625	−0·024 (12)	−0·017 (8)	−0·009 (5)	0·035 (30)	0·016 (13)
0·675	0·019 (12)	−0·017 (9)	−0·016 (5)	0·030 (30)	0·023 (16)
0·725	−0·013 (15)	0·047 (13)	−0·041 (6)	0·081 (60)	0·027 (23)
0·775	−0·026 (19)	−0·015 (16)	−0·023 (6)	0·039 (61)	0·020 (34)
0·825	−0·042 (21)	−0·056 (19)	−0·022 (7)	−0·028 (67)	−0·025 (25)
0·875	−0·063 (80)	−0·057 (30)	−0·005 (11)	−0·373 (122)	−0·095 (57)
0·925	−0·098 (31)	−0·037 (38)	−0·034 (30)	−0·337 (129)	−0·012 (75)
0·975	−0·054 (54)	−0·016 (59)	−0·012 (24)	−0·454 (264)	0·070 (128)
1·025	−0·118 (78)	−0·123 (100)	0·15 (36)	0·303 (362)	−0·170 (149)

Table 5. *Bond lengths* (Å) *and angles* (°) *in the* $\mathrm{CoCl_4^{2-}}$ *ion of* $\mathrm{Cs_3CoCl_5}$ *at* 295 K, *corrected for rigid-body-libration effects by the* **TSL** *method of Schomaker & Trueblood* (1968)

	X-ray, 295 K		Neutron, 295 K*	
	Uncorrected	Corrected	Uncorrected	Corrected
Co–Cl(2)	2·260 (1)	2·271 (1)	2·2652 (3)	2·2754 (3)
Cl(2)–Co–Cl(2$^{\rm I}$)†	106·98 (4)	106·94 (4)	106·97 (1)	106·92 (1)
Cl(2)–Co–Cl(2$^{\rm II}$)†	110·75 (3)	110·76 (3)	110·74 (1)	110·76 (1)

* Values taken from Williams, Figgis & Moore (1980).

† Coordinates of 2$^{\rm I}$ are related to those of 2 by the transformation $-x$, $1-y$, z, and 2$^{\rm II}$ by the transformation x, $1-y$, $\frac{1}{2}-z$.

Table 4. *First-, second- and fourth-order coefficients obtained by 'series-expansion' refinement*

U is in Å$^2\times10^3$, γ in Å$^4\times10^3$.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	γ_s	γ_{ll}
Co	0	$\frac{1}{2}$	$\frac{1}{4}$	30·6 (4)	30·6 (4)	27·1 (6)	0	0	0	15 (3)	−1 (6)
Cs(1)	0	0	$\frac{1}{4}$	44·8 (3)	44·8 (3)	43·1 (5)	0	0	0	5 (3)	3 (6)
Cs(2)	0·66575 (5)	0·16575 (5)	0	29·4 (2)	29·4 (2)	40·0 (4)	−2·1 (1)	0	0	−5 (2)	1 (4)
Cl(1)	0	0	0	33·9 (9)	33·9 (9)	50·2 (18)	0	0	0	39 (6)	−48 (19)
Cl(2)	0·13915 (10)	0·63915 (10)	0·15760 (11)	49·6 (7)	49·6 (7)	42·4 (10)	−11·6 (3)	6·2 (1)	6·2 (1)	32 (5)	−39 (11)

greater. Our correlation is reduced by the presence of much low-intensity high-angle data. The minimum Debye–Waller factor is about 0·05 Å^2 as against about 0·15 Å^2 in Cooper & Rouse's potassium chloride data.

Results

(*A*) *Atomic charges*

Naively, the only deviation from a completely ionic structure in Cs_3CoCl_5 which we would expect is some small charge redistribution in the weakly covalent tetrachlorocobaltate anion. We observe this in the low-angle data: a charge of −0·82 ± 0·12 e on the chlorine and +1·27 ± 0·1 e on the cobalt. If we use the covalency parameters obtained from polarized neutron diffraction, then a simple ligand-field MO model predicts a charge of −0·86 ± 0·05 e on the chlorine and +1·44 ± 0·2 e on the cobalt (Figgis, Reynolds & Williams 1980). The agreement between X-ray and polarized neutron diffraction (p.n.d.) extends further. The p.n.d. experiments also reveal an essentially unchanged 3*d* population, together with extra charge density in diffuse orbitals. The X-ray charge of 0·6 ± 0·16 e may be compared to the p.n.d. diffuse spin density of 0·5 ± 0·1 e. This suggests that the charge we observe is due to 'unpaired' electrons in the diffuse region.

(*B*) *Harmonic thermal parameters*

The disagreement of the various refinements with a simple free-atom form factor, harmonic model can be attributed to thermal diffuse scattering, anharmonicity, or the use of incorrect form factors caused by electronic rearrangement within the crystal. The separation of these factors requires more experimental information. In particular, the *reliable* separation of anharmonicity and electronic rearrangement requires temperature-dependent X-ray data and neutron data.

The TDS correction to the observed intensities may be calculated using the spherical approximation (Pryor, 1966), the experimental conditions, and elastic constants estimated from the infrared spectrum (Brown-Acquaye & Lane, 1977). The error in using an 'average' elastic constant, and in the assumption of a sinusoidal shape for the appropriate phonon-dispersion curves, is considerable. We obtain a TDS correction to the diagonal elements of U^i of 0·015 ± 0·005 Å^2. TDS correction to terms of higher order in a^* cause a slight downward curvature in $a_i(|s|)$ at higher $|s|$. The magnitude is smaller than the observed curvature and generally of the opposite sign.

A similar correction to the room-temperature neutron data results in addition of 0·025 ± 0·009 Å^2 to the diagonal elements of U^i. The larger correction is a result of more relaxed collimation in the neutron experiment (Williams, Figgis & Moore, 1980). If we compare the neutron results with the lower-angle refinement *R*1 we find that the mean ratio of the independent diagonal elements of the TDS-corrected *U* (for the refinement *R*1) and the corresponding neutron values is 0·96 ± 0·04. The corresponding ratio for *R*2, the high-angle X-ray refinement, and the neutron refinement is 0·81 ± 0·05. This implies that the high-angle X-ray data are not well described by a harmonic model with free-atom form factors, but that the low-angle data are so described well.

The disagreement of neutron and high-angle X-ray data implies anharmonicity in the crystal. At these high angles the X-ray data are sensitive only to motion of the core electrons, whose form factor is insensitive to chemical effects. The agreement of the neutron and low-angle data is more surprising: it implies only small changes from free-ion values in the valence-electron form factor. The agreement between *U* in the conventional free-atom form-factor refinement *R*1 and the valence-electron modified form factor in the 'series-expansion' refinement, 1·02 ± 0·02, shows that the effect of the slight changes made to the Cl 3*p*, Co 3*d* and Co diffuse populations on the thermal parameters is small. This is partly due to the large fraction of core electrons in Cs_3CoCl_5 ($\sim\frac{2}{3}$) compared to a typical organic compound ($\sim\frac{1}{3}$), and partly due to the relatively ionic nature of this compound. The small changes we have made to form factors for free ions also well describe the polarized-neutron spin-density results. This is further evidence for our conclusion that valence-electron form-factor changes are insignificant in the derivation of *U*'s. A 'traditional' use of *U*'s derived from high-angle X-ray data, with the assumption of harmonic core motion, forces large changes of up to 20% from the free-ion form factors at medium and low angles. Such large changes, presumably to valence electrons, seem to be incompatible with other results (Figgis, Reynolds & Williams, 1980, and references therein).

(*C*) *Anharmonicity*

If we accept that the TDS-corrected quadratic parameters in the 'series refinement' may be the true harmonic thermal parameters, then the ten γ parameters can be *tentatively* labelled as quartic anharmonic thermal parameters. Their values are not well defined so we will only make some general points. Given the large TDS correction to both X-ray and neutron diffraction data a more detailed discussion would only be warranted by temperature-dependent studies to higher angle using short-wavelength neutrons (to minimize TDS correction).

The anharmonic force constants which may be derived from these data are of the same size as those obtained in KCl by Cooper & Rouse. The effect of these anharmonic force constants is much larger in Cs_3CoCl_5 since it is such a relatively soft material with high $\langle u^2 \rangle$ values. It is interesting to note that we obtain large positive values for γ only for those atoms for which both $\langle u^2 \rangle$ is large and there is a short intermolecular contact [Cs(2)–Cl(1) and Cs(2)–Cl(2)]. Moreover, the coefficients for Cs(1) are small, even though its $\langle u^2 \rangle$ is large, which might suggest that it is too small for the 'hole' that it occupies in the lattice. Perhaps the instability of Rb_3CoCl_5 and the non-existence of K_3CoCl_5 may be due to their even smaller cation sizes.

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References

Brown-Acquaye, H. A. & Lane, A. P. (1977). *J. Inorg. Nucl. Chem.* **39**, 2277–2282.

Cooper, M. J. & Rouse, K. D. (1973). *Acta Cryst.* A**29**, 514–520.

Figgis, B. N., Gerloch, M. & Mason, R. (1964). *Acta Cryst.* **17**, 506–508.

Figgis, B. N., Mason, R., Smith, A. R. P. & Williams, G. A. (1980). *Acta Cryst.* B**36**, 509–512.

Figgis, B. N., Reynolds, P. A. & Williams, G. A. (1980). *J. Chem. Soc. Dalton Trans.* pp. 2339–2347.

Figgis, B. N., Reynolds, P. A., Williams, G. A., Mason, R., Smith, A. R. P. & Varghese, J. N. (1980). *J. Chem. Soc. Dalton Trans.* pp. 2333–2338.

Hirshfeld, F. L. & Rabinovich, D. (1973). *Acta Cryst.* A**29**, 510–513.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

Powell, H. M. & Wells, A. F. (1935). *J. Chem. Soc.* pp. 359–362.

Pryor, A. W. (1966). *Acta Cryst.* **20**, 138–140.

Schomaker, V. & Trueblood, K. N. (1968). *Acta Cryst.* B**24**, 63–76.

Stewart, J. M. (1976). The XRAY system – version of 1976. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland.

Williams, G. A., Figgis, B. N. & Moore, F. H. (1980). *Acta Cryst.* B**36**, 2893–2897.

Acta Cryst. (1981). B**37**, 513–518

X-ray Determination of Electron Distributions in Forsterite, Fayalite and Tephroite

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Abstract

Atomic net charges and electron density distributions of the olivine structures forsterite (α-Mg_2SiO_4), fayalite (α-Fe_2SiO_4) and tephroite (α-Mn_2SiO_4) have been determined from accurate single-crystal X-ray data on the respective synthetic crystals. The atomic net charges were obtained from the direct integration of the electron density within the sphere of a newly defined radius, the *effective distribution radius*, around each cation. Such net charges revealed that the tetrahedral Si atom is less ionic than the octahedral cations and the transition-metal Fe and Mn are less ionic than Mg. These charges also showed that the $M(1)$-site cation is less ionic than the $M(2)$-site cation when the cations of the same kind occupy both $M(1)$ and $M(2)$ sites. Radial distributions of valence electrons outside the Ar cores of the transition metals show that the $3d$ electrons have their maximum densities about 0·4 ~ 0·5 Å from the centre of the atom. In three-dimensional difference Fourier maps of forsterite the positive peaks appeared 0·96 Å, on average, from the centre of the Si atom along each of the four Si—O directions. [Crystal data: forsterite: a = 4·7534 (6), b = 10·1902 (15), c = 5·9783 (7) Å, space group *Pbnm*, final R = 0·0209; fayalite: a = 4·8195 (6), b = 10·4788 (17), c = 6·0873 (8) Å, space group *Pbnm*, final R = 0·0255; tephroite: a = 4·9023 (6), b = 10·5964 (16), c = 6·2567 (9) Å, space group *Pbnm*, final R = 0·0310.]

Introduction

We have previously described (Sasaki, Fujino, Takéuchi & Sadanaga, 1980) a procedure for deter-

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