

Rubidium Tetrachlorocadmate: X-Ray Diffraction Measurements and an Electronic Structure Study

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The structure of Rb_2CdCl_4 single crystal at room temperature has been determined from X-ray diffraction of the $\text{MoK}\alpha$ line ($\lambda = 0.7107 \text{ \AA}$). After refinement through blocked least-squares methods, the reliability factor R in the final cycle is 3.07%. The following results have been obtained: tetragonal system, space group $I4/mmm$, $a = b = 5.195(1) \text{ \AA}$, $c = 16.130(1) \text{ \AA}$; $F(000) = 380$; $Dm = 3.243 \text{ g/cm}^3$; $Z = 2$. The structure can be viewed as made of layers of CdCl_6 octahedra chains ($\text{Cd}-\text{Cl}(1) = 2.597(1) \text{ \AA}$ and $\text{Cd}-\text{Cl}(2) = 2.572(1) \text{ \AA}$) separated by double slabs of rubidium atoms perpendicular to the c direction. First-principles density functional theory calculations have been carried out to determine the electronic density distribution. The calculated equilibrium structure is in satisfactory agreement with the experimental data. Electronic density maps have been drawn from *ab initio* wavefunctions calculated both at the experimental and theoretical equilibrium geometries. Analysis of the calculated atomic populations confirms the highly ionic character of the electronic charge distribution in the crystal. © 1998

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1. INTRODUCTION

The A_2BX_4 crystals can be separated into two principal families. In the first family, the compounds are isostructural to $\beta\text{-K}_2\text{SO}_4$, and in the second family, they are isostructural to K_2NiF_4 . From the point of view of phase dynamics, the $\beta\text{-K}_2\text{SO}_4$ -type compounds are especially interesting because they exhibit a cascade of phase transitions with the formation of incommensurately and commensurately

modulated phases, whereas the K_2NiF_4 -type compounds are characterized by "classical" phase transitions.

Among the A_2BX_4 crystals, the class of compounds in which X is a halogen ion and B belongs to the zinc column ($B = \text{Zn, Cd, Hg}$) contains mostly species of the $\beta\text{-K}_2\text{SO}_4$ -type structure (1). However, essentially because of steric effects, a few of them, such as Cs_2CdCl_4 (2), crystallize in the K_2NiF_4 -type structure.

Rb_2CdCl_4 is one of the few members of this class the structure of which has not yet been determined. This is undoubtedly due to the difficulties encountered in crystallizing this compound. Even its very existence has been controversial (3, 4). Thermal measurements by Bohac *et al.* were not able to conclude whether the Rb_2CdCl_4 crystal melts congruently at 454°C or incongruently between 434 and 454°C (3). The $\text{RbCl}-\text{CdCl}_2$ phase diagram was reexamined by Yada *et al.* in view of understanding the melting process (5). More specifically, only the $\text{RbCl}-\text{RbCdCl}_3$ part of the system was studied. This work allowed one to conclude definitely that Rb_2CdCl_4 melts congruently. This result was used to carry out the crystallization of Rb_2CdCl_4 single crystals in our laboratory using the Bridgman method in a capillary. Compounds were heated until the fusion temperature (450°C) is reached. Then on slowly decreasing the temperature, crystallization of Rb_2CdCl_4 was obtained at about 50°C below the fusion temperature. Moreover, severe drying conditions were required because of the very high hygroscopic properties of RbCl and CdCl_2 .

This paper reports X-ray diffraction determination of the structure of Rb_2CdCl_4 at room temperature. After the cell parameters and internal coordinates of the nuclei have been experimentally determined, an attempt has been made to visualize the valence electronic charge distribution (VECD)

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in the material. With so heavy atoms a direct experimental determination of VECD via X-ray diffraction, as done previously for crystals made of lighter elements [6], is not easily tractable. Therefore the VECD was deduced theoretically from ab initio crystalline wavefunctions.

2. X-RAY DIFFRACTION MEASUREMENTS

2.1. Experimental Setup

A cylindrical crystal was mounted on an Enraf–Nonius CAD-4 diffractometer with graphite-crystal monochromator MoK α radiation ($\lambda = 0.7107 \text{ \AA}$) using an ω - 2θ scan in the range $2.53 < \theta < 33.92^\circ$. A total of 3665 reflections were collected, among which only 1820 reflections, namely those for which $I \geq 2\sigma(I)$, were used to determine and solve the structure. Accurate lattice parameters were obtained from a least-squares fitting to the angular settings of 25 selective reflections. The structure was solved using the Patterson method with the *SHELXS86* program (7, 8), and a cylindrical absorption correction was made. The refinement was carried out using anisotropic temperature factors for the atoms (*SHELXL93*) (9).

2.2. Structure Determination

At room temperature, the monocrystalline compound crystallizes in the tetragonal phase with two molecules per unit cell. The space group is found to be *I4/mmm* from the systematic extinctions of the reflections. The following tetragonal lattice constants have been obtained: $a = b = 5.195(1) \text{ \AA}$ and $c = 16.130(1) \text{ \AA}$ (see Table 1). The fractional atomic coordinates are given in Table 2. The structure was solved as usual using first the Patterson function to localize heavy atoms and then carrying out an electron density synthesis, and finally performing a difference electron density synthesis to refine and to optimize the position of the remaining atoms. The crystal structure of Rb_2CdCl_4 is given in Fig. 1 (10). The rubidium atoms occupy the $4e$ sites, $z = 0.359 \text{ \AA}$, and the cadmium atoms the $2a$ sites. The chlorine ions have two different coordinations. The two independent chlorine atoms, Cl(1) and Cl(2), fully occupy the $4c$ and the $4e$, $z = 0.159 \text{ \AA}$ sites, respectively. The reliability index R was 3.07% based on 304 independent reflections. The largest peaks in the final difference map were -1.68 and 0.76 e\AA^{-3} . As evidenced by the space group and the coordinates, this form of Rb_2CdCl_4 is isostructural with the K_2NiF_4 -type structure (11).

In this tetragonal phase, each Cd atom is bonded to six chlorine neighbors that nearly form a regular octahedron. Each octahedron is formed by a square base built on four Cl(1) atoms ($\text{Cd}-\text{Cl}(1) = 2.597(1) \text{ \AA}$) and by two Cl(2) atoms on each side of this base ($\text{Cd}-\text{Cl}(2) = 2.572(1) \text{ \AA}$). For chlorine atoms in a plane at the same z coordinate, $\text{Cl}(1)-\text{Cl}(1) = 3.673(1) \text{ \AA}$, while in the xz plane,

TABLE 1
Crystal Data and Structure Refinement

Empirical formula	Rb_2CdCl_4
Formula weight	425.14
Temperature	293 (2) K
Wavelength	0.7107 \AA
Crystal system	Tetragonal
Space group	<i>I4/mmm</i>
Unit cell dimensions	$a = 5.195(1) \text{ \AA}$, $\alpha = 90^\circ$ $b = 5.195(1) \text{ \AA}$, $\beta = 90^\circ$ $c = 16.130(1) \text{ \AA}$, $\gamma = 90^\circ$
Volume	$435.32(12) \text{ \AA}^3$
Z	2
Density (calculated)	3.243 g/cm^3
Absorption coefficient	14.758 mm^{-1}
F(000)	380
Crystal shape	Cylindrical
θ range for data collection	2.53° to 33.92°
Index ranges	$-8 \leq h \leq 8$, $-8 \leq k \leq 8$, $0 \leq l \leq 25$
Collected reflections	3665
Independent reflections	304 [$R(\text{int}) = 0.0337$]
Refinement method	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	1.291
wR2 reliability factor	0.0777
Final R indices [$I > 2\sigma(I)$]	0.0307
Difference density maximum	0.76 e/\AA^3
Difference density minimum	-1.68 e/\AA^3

$\text{Cl}(1)-\text{Cl}(2) = 3.655(1) \text{ \AA}$. The octahedra are linked in endless chains running along the $a(b)$ axis (see Fig. 2 (12)), with four corners shared by four adjacent octahedra.

The rubidium atoms are surrounded by four chlorines in the four-fold positions ($4c$ sites) with a $\text{Rb}-\text{Cl}(1)$ distance of $3.453(1) \text{ \AA}$ and by five chlorines in the $4e$ sites with unequal $\text{Rb}-\text{Cl}(2)$ distances, four equal to $3.685(1) \text{ \AA}$ and one equal to $3.218(2) \text{ \AA}$ (Table 3).

Interatomic distances and angles for Rb_2CdCl_4 are summarized in Table 3. Such a layered structure may lead in an instability of single layer planes of CdCl_6 octahedra and give rise to phase transitions (13). So the next step in the future will be to investigate the possible occurrence of a phase transition sequence on a Rb_2CdCl_4 monocrystal.

TABLE 2
Fractional Atomic Coordinates ($\text{\AA} \times 10^3$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$)

	Wyckoff notation	X/A	Y/B	Z/C	U(eq)
Rb	$4e$	0	0	359 (1)	350 (3)
Cd	$2a$	0	0	0	124 (2)
Cl(1)	$4c$	0	500	0	321 (4)
Cl(2)	$4e$	0	0	159 (1)	420 (6)

Note. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

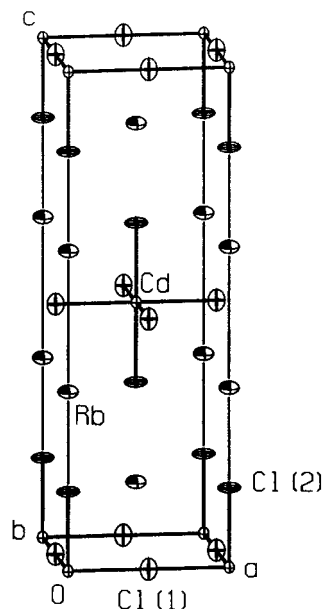


FIG. 1. Crystal structure of Rb_2CdCl_4 (conventional unit shell).

3. ELECTRONIC CHARGE DENSITY MAPS

In addition to the experimental work described above, first-principles density functional theory calculations were performed to get the electronic structure using the *CRYSTAL95* code (14). This program provides self-consistent field solutions either to the Hartree–Fock–Roothaan equations or to the Kohn–Sham equations (15, 16). These solutions are given in terms of Bloch orbitals expanded onto a basis set of Gaussian functions localized on atomic centers. Details of the mathematical formulation of the method can be found elsewhere (17). Here the Perdew–Wang Generalized-Gradient-Approximation exchange–correlation functional (18) was used for the calculations. Small-core pseudopotentials (19–21) for Rb, Cd, and Cl were used and a total of 134 Gaussian functions partially contracted into 83 basis atomic orbitals per cell served to describe the valence orbitals. This basis set was optimized by minimizing the electronic energy at the experimental equilibrium geometry. It is given in Table 4.

The calculated wavefunction contains all the information needed to determine the mean distribution of the valence electronic charge within the crystal. In principle, two different points of view can be adopted relating to the choice of the geometry for which the theoretical density maps are plotted. One can prefer to work either at the experimental equilibrium geometry (provided it is known) or at the theoretical equilibrium geometry. The theoretical equilibrium geometry is defined as the geometry that is obtained through internal energy minimization in the tetragonal phase. However, as discussed later on, it will be found

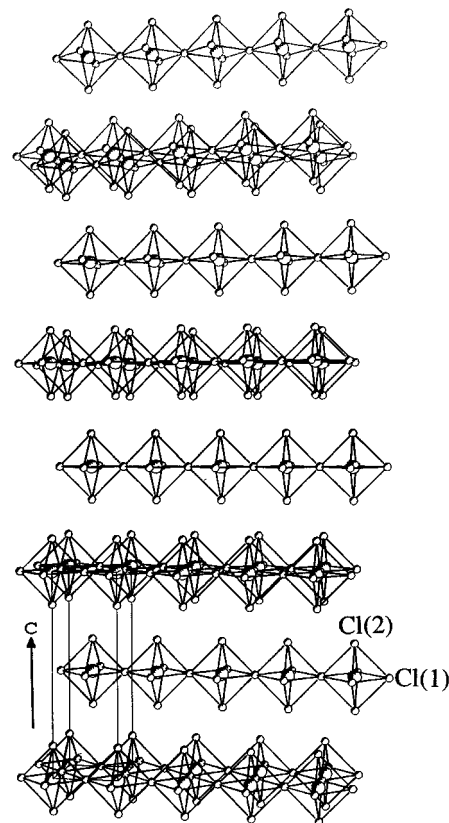


FIG. 2. Visualization of layers made of chains of CdCl_6 octahedra built along the a direction.

ultimately that the charge density distribution is not very sensitive to the choice of one point of view or the other.

In the present case, the determination of the theoretical equilibrium geometry requires the minimization of a function of four parameters: the cell parameters a and c and the internal general coordinates z_{Rb} and $z_{\text{Cl}(2)}$ defined in Table 2 (all other coordinates correspond to special positions). The final results are given in Table 5, where they are compared to experiment. The fairly good agreement between the theoretical parameter values and their experimental counterparts is revealing the good quality of the calculation. This in turn gives confidence in using the wavefunctions thus obtained for determining the charge distribution within the crystal.

For that purpose, electronic density maps in two mutually orthogonal sections corresponding to the (110) plane and to the (ab) plane have been plotted in Fig. 3. Quantitative details about the isodensity curves are given in the caption of this figure. It is worthwhile emphasizing that practically no perceptible difference in the internal structure of the maps plotted for the experimental equilibrium geometry compared to those plotted for the theoretical equilibrium geometry is noticeable with the eye (only the volume is

TABLE 3
Interatomic Distances (Å) and Angles (°) with e.s.d.'s
in Parentheses

Rb-Cl(2)	3.218 (1)
Rb-Cl(1) #4	3.453 (1)
Rb-Cl(2) #5	3.685 (1)
Rb-Cd #2	4.321 (1)
Cd-Cl(2)	2.572 (1)
Cd-Cl(1)	2.597 (1)
Cd-Cl(1) #1	2.597 (1)
Cl(2)-Rb-Cl(1) #4	131.215 (10)
Cl(1)-Rb #4-Cl(1) #3	64.270 (11)
Cl(2)-Rb-Cl(2) #5	85.39 (3)
Cl(1)-Rb #4-Cl(2) #5	61.50 (2)
Cl(2)-Rb-Cd #2	121.772 (8)
Cl(1)-Rb #4-Cd #2	36.952 (4)
Cl(2)-Cd-Cl(1) #1	90.0
Cl(2)-Cd-Rb #5	58.228 (9)
Cd-Cl(2)-Rb #5	85.39 (3)

Note. Symmetry transformations used to generate equivalent atoms: #1, $-y, x, z$; #2, $x + \frac{1}{2}, y + \frac{1}{2}, z + \frac{1}{2}$; #3, $x + \frac{1}{2}, y - \frac{1}{2}, z + \frac{1}{2}$; #4, $-y + \frac{1}{2}, x + \frac{1}{2}, z + \frac{1}{2}$; #5, $-x + \frac{1}{2}, -y + \frac{1}{2}, -z + \frac{1}{2}$.

appreciably different). The essentially ionic character of the compound clearly appears on these maps; it results in well-separated, almost spherical charge distributions around the nuclei. This is especially the case for the rubidium ions; these ions have lost all of their valence charge and their shape is very close to that of a sphere. However, for Cl centers and even more for Cd centers, slight anisotropies along directions connected with the site octahedral symmetry are observed. Such deviations from spherical symmetry are the mark of a small covalent component in the merely ionic Cd-Cl bonds.

These observations are reflected in the values of the net charges evaluated according to a Mulliken scheme (22). Using the wavefunction calculated at the experimental geometry, these charges are found to be +0.989, +1.247, -0.779, and -0.831 for Rb, Cd, Cl (1), and Cl (2), respectively. These values are hardly changed if one uses the wavefunction calculated at the theoretical geometry: +0.988, +1.181, -0.766, and -0.813. These values should be compared to the nominal charges expected for the ideally ionic structure: +1, +2, -1, and -1. The deviations from the nominal Cd and Cl charges provide an estimate of the part of covalency that is contained in the otherwise essentially ionic Cd-Cl bonds. The covalent character is slightly stronger for the bonds pointing in the *c* direction than for those pointing in the (*a*, *b*) plane. This is a consequence of steric effects that favor a greater bond length between the Cd and the four Cl(1) ions compared to that between the Cd and the two Cl(2) ions. On the other hand, the rubidium atoms are fully ionized. Consequently Rb₂CdCl₄ can be regarded as a fully ionic insulator made of

TABLE 4
Exponents α (in Bohr⁻²) and Contraction Coefficients *C* of the
Gaussian Functions Used for the Calculations of Structural
Properties of Rb₂CdCl₄

Atom		Gaussian basis set	
		α	<i>C</i>
Rb, [Zn ²⁺]4s ² 4p ⁶ 5s ¹	<i>s</i>	1.358	-1.369202
		0.9859	1.459953
	<i>s</i>	0.2822	1.0
	<i>p</i>	3.070	-0.082929
		0.6119	0.629902
Cd, [Kr]5s ² 4d ¹⁰	<i>p</i>	0.2125	1.0
	<i>s</i>	0.4922	-0.480780
		0.2273	0.572371
	<i>s</i>	0.12	1.0
	<i>p</i>	0.1129	1.0
	<i>d</i>	2.4823	0.361719
		1.0199	0.468259
	<i>d</i>	0.4190	0.291373
		0.1639	1.0
	Cl, [Ne]3s ² 3p ⁵	<i>s</i>	21.51
		2.145	-0.312937
		0.5119	0.712432
<i>s</i>		0.1799	1.0
<i>p</i>		14.55	-0.008368
		4.179	-0.020126
		0.6291	0.549503
<i>p</i>		0.1830	1.0
<i>d</i>		0.75	1.0

CdCl₆²⁻ octahedra embedded in a sublattice of rubidium ions completely stripped of their valence electron.

According to this discussion the interest of the present study has then been twofold. First, as a primary objective, the as yet unknown structure of one of the members of the *A*₂*BX*₄ series, Rb₂CdCl₄, has been determined. Second, the distribution of the electronic charge in the crystal has been quantitatively displayed and the nature of the chemical bond in the CdCl₆ octahedra has been discussed on the grounds of accurate ab initio calculations. The results are in agreement with the commonly accepted view for this family of compounds belonging to the *A*₂*BX*₄ series and in which

TABLE 5
Calculated versus Experimental Structure of Rb₂CdCl₄

	Experiment	Theory	Δ (%)
<i>a</i> parameter (Å)	5.195	5.351	3.0
<i>c</i> parameter (Å)	16.130	16.463	2.1
<i>z</i> _{Rb} coordinate	0.359	0.362	0.8
<i>z</i> _{Cl(2)} coordinate	0.159	0.162	1.9

Note. Δ is the difference in percent between experimental and calculated values.

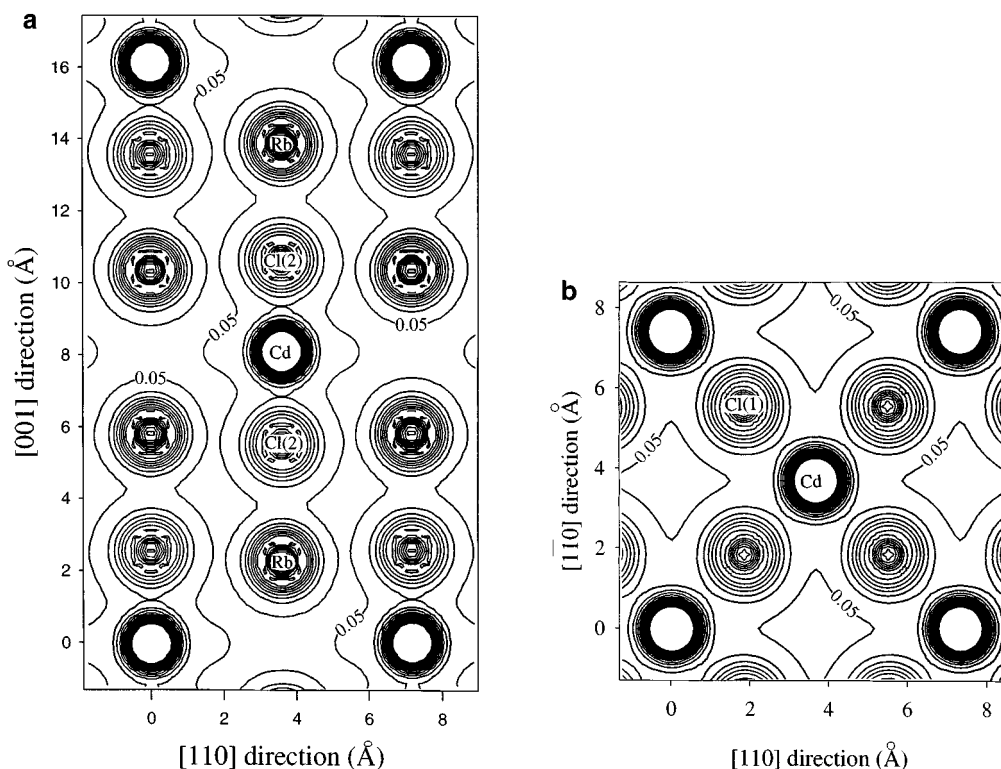


FIG. 3. Electron density maps (from ab initio calculations): (a) in the (110) plane, (b) in the ab plane. The curves closest to atomic centres correspond to a density of 4.50 \AA^{-3} (maximum density value plotted, which eliminates visualization of the cores). The 0.05 \AA^{-3} isodensity curves (corresponding to the minimum density value plotted) are explicitly specified on the map. The value for the other curves can then be deduced, knowing that the separation between isodensity curves is 0.25 \AA^{-3} .

the B cation is located in a site of octahedral symmetry (the K_2NiF_4 -type structure). Here, the interest of the ab initio study has been to give a nonempirical basis to this description, which has made possible a quantitative description of the bonding mechanisms in the crystal. Nevertheless this description relies on first-principles simulation. Even though this kind of calculation has now attained an excellent level of accuracy, it would be nice and really useful to be able to obtain density maps directly from experiment. This is interesting in itself of course, but also this would allow one to test the reliability of such simulations. However, as pointed out above, obtaining valence electronic density experimentally would be very problematic with heavy ions as in Rb_2CdCl_4 and, in this case, the ab initio method we have used is an interesting alternative for getting information about the mean distribution of the charge within the crystal.

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