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Simulation of normal Rb_2ZnCl_4 near the incommensurate transition

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The purposes of the reported computer simulation of the normal (high-temperature) phase of rubidium tetrachlorozincate are to understand the disordered structure in that phase and to investigate the possibility that the transition, upon cooling, from the normal phase to one with an incommensurate modulation is associated with a change from the disordered structure to an ordered one. The simulation of the dynamics of 168 ions in a periodic structure begins from a slight perturbation of a structure that is determined by minimization of the potential energy within the constraints of the experimentally determined average symmetry. Rigid ions with short-range interactions described by the electron-gas model (with a qualification) are assumed. We find both zinc-induced and rubidium-induced instabilities in the chloride sublattices of the average experimental structure. The zinc-destabilized chloride ions move to a new sublattice in the simulation; however, a crude estimate indicates that this is caused by neglect of ionic polarizability and that these chlorides should either remain at their original sites or be disordered with chains of correlated positions. The rubidium-destabilized chloride ions form two-dimensional ordered networks in the disordered structure. We suggest that the inevitable freezing-out of disorder among the chains of zinc-destabilized chloride ions and among the networks of rubidium-destabilized chloride ions is the mechanism for the transition to the incommensurate phase.

I. INTRODUCTION

At high temperatures, the basic structural unit of rubidium tetrachlorozincate (Rb_2ZnCl_4) is four formula units in an orthorhombic cell. There is experimental evidence that the symmetry determined positions of the chloride ions in the high-temperature phase of Rb_2ZnCl_4 are unstable. The chloride ions do not lie on a perfect lattice, but are displaced from the symmetry determined lattice sites with some degree of randomness.[1] At 303 K Rb_2ZnCl_4 goes through a phase transition which is believed to be associated with a change from disordered displacements of the chloride ions from their lattice sites to periodic displacements, but the periodicity of these displacements is not commensurate with the periodicity of the lattice on which the rubidium and zinc ions lie.[2] This lower-temperature phase of the solid is called the incommensurate phase, while the phase above 303 K is called the normal or paraelectric phase.

The purposes of the study reported here are to understand, through knowledge of the theoretical forces between ions, the disordered structure of Rb_2ZnCl_4 in the normal phase and to investigate the possibility that the transition, upon cooling, from that phase to the incommensurate phase is associated with a change from the disordered structure to an ordered one. Rigid ions are assumed and the electron-gas model[3] is used to determine the short-range part of the pair potentials. Some empirical adjustment of the short-range part of the Zn^{2+}-Cl^- potential is needed to describe properly the $ZnCl_4{}^{2-}$ group in the solid. This adjustment is explained in Sec. II.

The somewhat complicated experimentally determined structure of Rb_2ZnCl_4 is discussed in Sec. III. This structure is compared to the theoretical one obtained from a static relaxation. A static relaxation is the minimization, within symmetry constraints in this case, of the potential energy of the crystal using the calculated pair potentials. This minimization locates positions at which the forces on the ions are zero, but the equilibrium can be unstable since some of the forces may vanish by symmetry, independent of the relaxation process. In this section, we identify the key role that ionic polarization plays in determining the structure of Rb_2ZnCl_4 and its isomorphs.

The method of dynamics simulation is used in Secs. IV and V to examine the stability of the static structure obtained in Sec. III, and to investigate the structure that results from any instability. A dynamics simulation is an approximate integration of the equations of motion of a collection of interacting ions over time. The simulation considers 168 ions with periodic boundary conditions. This corresponds to six orthorhombic cells of the normal phase. A short run with the ions initially close to their perfect lattice sites is used in Sec. IV to examine the stability of the static structure and to permit the system to come to equilibrium. This part of the simulation exposes what we will call the zinc-induced instabilities in the static structure. These instabilities in $\frac{1}{4}$ of the chloride positions are caused by electrostatic interactions with zinc ions.

Section V examines the positions of the ions averaged over a long time after equilibrium is established in the dy-

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namics simulation. The zinc-induced instabilities lead to an unexpected structure after the zinc-destabilized chloride ions find stable positions. Crude estimates indicate that this new structure would not appear if polarizability of the chloride ions were included. A second kind of instability, which also exists in the experimentally determined structure, exists in the "ideal" version of this new structure and leads to disorder in the positions of the other three-quarters of the chloride ions. We will call these instabilities rubidium induced because they arise from the electrostatic interactions of those chloride ions with rubidium ions.

As elaborated in Sec. VI, we find that ionic polarization is responsible for a common feature of all compounds isomorphous to Rb_2ZnCl_4. We conclude that the chloride ions are indeed unstable at their perfect lattice sites, but the displacements from the lattice sites are not completely random. One-quarter of the chloride ions will occupy one of two statistically equivalent positions in the real solid and the occupied positions will be correlated in chains. Each of the other three-quarters of the chloride ions can also occupy either of two statistically equivalent positions, but there are correlations in their positions except in one direction. We suggest that the inevitable freezing-out of disorder as the temperature is lowered is the mechanism of the transition to the incommensurate phase.

II. SHORT-RANGE PAIR POTENTIALS

We use the rigid-ion model with ions Rb^+, Zn^{2+}, and Cl^-. The electrostatic interactions between point charges are treated exactly, and the electron-gas model[3] (with the qualification below) is used to determine the short-range parts of the interaction potentials from the electron densities of the isolated ions.[4]

The short-range potentials are generated over a range of separations from 2 to 12 bohrs. Points where a potential is less than about 1.0×10^{-7} hartrees are not used. A potential is accurately fitted and core and tail functions are appended in regions where the potential is not available. The function used to fit the potential is

$$u(r)=e^{-\alpha r}\sum_{n=0}^{N} c_n r^{m+n}, \quad r_c<r<r_t \ .$$

The c_n's and α are optimized for trial values of m and N. Polynomials of order $N=6$ are enough to obtain fits with errors less than 0.01% at every point. We have experimented with replacing r by r^k in the exponential function and by r^l in the polynomimal, but obtained no significant improvement in the fits.

The core function attached to the fit is

$$u(r)=A+(B/r^6) \quad r\le r_c \ ,$$

and the tail function is $u(r)=C\exp(-\beta r^2)$, $r\ge r_t$. The constants in the appended functions are determined by requiring the potential and its derivative to be continuous at the point of attachment. The cores only extend to 2 bohrs so they are almost certainly not sampled in the dynamics simulation but are included automatically as a precaution.

These potentials produced bond lengths within the $ZnCl_4^{2-}$ ion in the crystal environment that were about 10% too large. We suspect that neglect of the polarizability of chloride ions is responsible and are presently working to include this effect. However, within the rigid-ion approach, this primarily changes the Zn^{2+}-Cl^- potential, which we therefore adjust. It was discovered that almost all components of force on every chloride ion in the experimentally determined average structure of the normal phase could be nearly zeroed by reducing the short-range part of the Zn^{2+}-Cl^- potential by about 40%. The one component that could not be approximately zeroed for one of the three unique chloride positions was tending toward zero with reductions in the pair potential, but lagged behind the other components. This scaled potential produces the right bond lengths in the $ZnCl_4^{2-}$ group. The frequencies of the Raman modes that are predominantly internal motions of the tetrachlorozincate groups are also in reasonable agreement with experiment. Table I compares the ranges of calculated and observed frequencies of the four modes that are derived from stretching of the Zn^{2+}—Cl^- bonds.

TABLE I. Ranges of observed and calculated Raman frequencies in normal Rb_2ZnCl_4. The four modes listed involve predominantly stretching of the Zn^{2+}—Cl^- bonds.[a] Experimental frequencies were measured at 315 K and the theoretical values were calculated using the short-range potentials discussed in Sec. II, and the static structure described in Sec. III and shown in Fig. 2.

Raman frequencies (cm^{-1})	
Experiment	Theory
275–278	276
283–288	267–276
293–295	291–304
302–306	320–333

[a]V. Katkanant, F. G. Ullman, P. J. Edwardson, and J. R. Hardy, Technical Report, U. S. Army Research Office, Contract No. DAAG29-83-0080 (1986).

An alternative to adjustment of the Zn^{2+}-Cl^- potential that would not require intense computational effort would be to treat the tetrachlorozincate group as a rigid rotor. That would be inappropriate, however, because the low frequencies of oscillation within the group overlap the lattice phonon frequencies in Rb_2ZnCl_4. The largest phonon frequency, an internal mode of the $ZnCl_4^{2-}$ groups, is only approximately 300 cm^{-1} ($h\nu/k\sim430$ K). Consequently, vibrations of the $ZnCl_4^{2-}$ group are excited even at room temperature and should not be neglected.

III. STATIC β-K_2SO_4-TYPE STRUCTURE

A logical first step toward simulation of the dynamics of Rb_2ZnCl_4 is to use the pair potentials obtained in Sec. II to find a structure that has the experimentally determined average symmetry and in which the forces on the basis ions are zero. A comparison of the positions of the ions obtained from this static relaxation to the positions determined by analysis of x-ray diffraction data will intro-

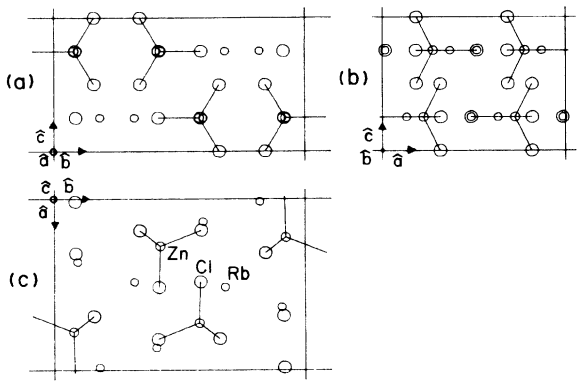

FIG. 1. Projections of the experimentally determined average structure of Rb_2ZnCl_4 in the normal phase. Unit vectors indicate the directions of the lattice basis vectors. A unit vector pointing out of the page is represented by a circle and one pointing into the page is represented by a dot. Bonds (straight lines) connect each zinc and the nearest four chloride ions.

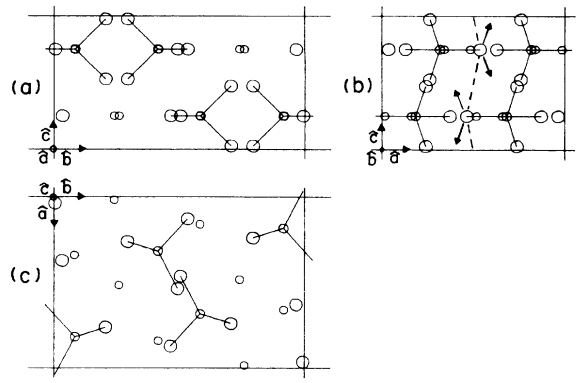

FIG. 2. Projections of the theoretical static structure. Destabilizing forces from neighboring zinc ions point away from the unstable chlorides in the view along the **b** direction. The chloride-chloride interactions that cause rows of those ions to move collectively in the dynamics simulation are indicated with broken lines.

duce the complicated structure and provide clues as to which interactions could cause the structure to be unstable.

Figure 1 shows projections of the experimental positions parallel to each of the three orthorhombic axes ($a=9.261$ Å, $b=12.725$ Å, and $c=7.280$ Å).[5] The prototype for this structure is that of β-K_2SO_4, and the space group is *Pnam* (D_{2h}^{16}), but we have translated the basis ions by **b**/2 in all figures. In this structure, the rubidium, zinc, and two of every four chloride ions are constrained to lie in mirror planes that are perpendicular to the c axis and intersect it at z/c equal to $\frac{1}{4}$ and $\frac{3}{4}$. The point symmetry for all of these sites is $4(c)$ in the Wyckoff notation. The other two of every four chloride ions are each the image of the other in a mirror plane. The point symmetry of these sites is $8(d)$. The two mirror planes in a unit cell are made equivalent by a center of inversion at the center of the cell. These constraints are used in the analysis of experimental data in order to be consistent with the fact that the polarization of the crystal in the normal phase is zero.

Itoh *et al.*[1] used a split-atom analysis of x-ray diffraction data to check for disorder in Rb_2ZnCl_4. That analysis produced a better fit to the diffraction data than was obtained when the chlorides were constrained to only one position. The two positions of each split chloride were constrained to be consistent with the mirror planes of the space group *Pnam* and each site was given a 50% probability of occupancy in order to preserve the zero polarization. Their results strongly suggest that there are two equivalent orientations for each tetrachlorozincate group, and they postulated that each group moves between the two possible orientations with librations about the zinc ion. The structure is disordered, i.e., there is no three-dimensional translational symmetry if correlation in the orientations of every pair of $ZnCl_4^{2-}$ groups is lacking. Raman-scattering data for this and related extrinsic ferroelectrics also suggest that the solids are disordered.[6]

Projections of the positions resulting from a static relaxation are shown in Fig. 2. The lattice constants were not allowed to vary during the relaxation and the ions were constrained to positions described by the space group *Pnam*. The relaxation began from the experimental β-K_2SO_4-type structure and all forces on the basis ions, including forces of constraint, are zero. The projection of the zinc and rubidium ions parallel to **a** can form a two-dimensional hexagonal structure if the ratio of b to c is 1.73 ($\sqrt{3}$). The experimental ratio and the value in the constrained relaxation are 1.75. If the lattice vectors are allowed to vary during the relaxation in order to zero the stresses, the cell remains orthorhombic with slightly shrunken a and c axes and a slightly expanded b axis. The resulting ratio of b to c is 1.81. These changes in lattice vector lengths from their values in the experimental structure are to be expected because that is an average structure rather than one that is in stable equilibrium.

Comparison of Fig. 2(c) with Fig. 1(c) reveals that the primary differences between the experimental average structure and the theoretical static structure are rotations of the tetrachlorozincate groups about the c axis. Those are the only rotations allowed by the symmetry constraints. A rotation of a $ZnCl_4^{2-}$ group is driven by electrostatic attractions, indicated in Fig. 2(b), between a particular one of the group's chloride ions that is constrained to lie in a mirror plane and the zinc ions of two other groups that lie in adjacent mirror planes. One way, which we believe to be erroneous, to prevent these rotations is to transfer enough charge within each $ZnCl_4^{2-}$ group to make the charge on the zinc ion $1+$ rather than $2+$. How this charge transfer prevents the rotations can be understood by considering Fig. 1(c). The labeled zinc and rubidium ions are in one mirror plane and the labeled chloride ion is in the other mirror plane. If the charges on the zinc and rubidium ions are equal, then they attract the chloride ion equally and the position of the chloride ion in fig. 1(c) is stable against displacements in the mirror plane. However, if the zinc charge is raised slightly above

TABLE II. The potential energy (eV per formula unit), the energy that polarizable chloride ions would have ($-\alpha E^2/2$ with $\alpha = 2.97\times10^{-24}$ cm^3), and the sum of the two for the experimental β-K_2SO_4-type structure (Fig. 1), the corresponding relaxed static structure (Fig. 2), and the relaxed structure with *Pnam* symmetry that corresponds to the dynamics simulation (Fig. 5) but without relaxation of the rubidium-induced instabilities.

Structure	Potential	+	Polarization	=	Total
Experimental[a]	−38.61		−5.38		−43.99
Static[b]	−39.12		−3.05		−42.17
Dynamic[c]	−39.60		−1.50		−41.10

[a]Figure 1.
[b]Figure 2.
[c]Figure 5.

1 + the balance is removed and the chloride moves into its position in Fig. 2(c). Very indirect evidence for the hypothesis of charge transfer comes from analyses of nuclear quadrupole resonance data to determine what monopoles should be put into the experimental average structure to best reproduce the derived electromagnetic field gradients at chloride[7] and at rubidium[8] sites.

There are many compounds related to Rb_2ZnCl_4 with β-K_2SO_4-type structures, and all of them that we are aware of have one bond of each tetrahedral group nearly aligned with the *a* axis, i.e., the rotation about **c** seen in the static relaxation is not present. It is implausible that charge transfer and short-range forces are exactly in balance in all of these compounds to cause the bond alignment. A mechanism that depends more on crystal symmetry than on the particular constituents of the solid, and one which could mimic charge transfer in some experiments is ionic polarization. As the first two rows of Table II show, the energy of the relaxed structure (Fig. 2) is only 0.5 eV per formula unit lower than the energy of the experimental structure (Fig. 1), but the energy that polarizable chloride ions would have in the fields at their sites in the relaxed structure is 2.3 eV per formula unit higher than they would have in the fields at their sites in the experimental structure. A self-consistent inclusion of ionic polarizability would predict a considerably smaller energy difference than this zero-order approximation, but would not change the qualitative conclusion that the experimental structure is definitely the more stable of the two.

Lattice-dynamical calculations reveal several flat imaginary branches in the vibrational spectrum of the relaxed structure. That this structure might be unstable is understandable since the **c** components of forces on all ions in the mirror planes are zero by constraint rather than by relaxation. The dispersionless character of the unstable branches suggests that the instability will lead to disorder, i.e., the ions will fall from their sites individually rather than collectively. An obvious example of a possible instability that could lead to disorder is the chlorides whose attraction by zinc ions caused the rotations of the $ZnCl_4^{2-}$ groups in the static relaxation. The distance from one of these possibly unstable chloride ions to either zinc ion in adjacent mirror planes is 4.05 Å. If the only interactions determining the stability of one of these chloride positions were between the chloride ion and those zinc ions, then that distance is large enough to mandate instability because the destabilizing electrostatic force is dominant. The rubidium ions corresponding to the labeled one in Fig. 1(c) would also participate in destabilizing these chloride ions in the experimental structure.

IV. ZINC-INDUCED INSTABILITIES

The sample for simulation of the normal phase of Rb_2ZnCl_4 consists of six of the structural unit cells of that phase, i.e., 168 ions. This supercell was obtained by first tripling the unit cell in the **a** direction to obtain a cell which is the size of the unit cell of the commensurate phase (the ferroelectric phase at temperature between 72 and 192 K).[2] The tripled cell was then doubled in the **c** direction in order to lessen intrinsic correlation along the very short *c* axis. The simulated crystal is made quasi-infinite by applying periodic boundary conditions. The volume and shape of this $27.783\times12.725\times14.560$ Å^3 cell are held constant during the simulation because the basis ions start far from stable equilibrium and the cell may overreact to the large initial internal stresses if external forces are not applied to prevent this. The sample was further prepared by adding kinetic energy equivalent to 50 K, and adding random displacements of magnitude less than $|\mathbf{a}+\mathbf{b}+\mathbf{c}|/1000$ to the ion positions. These perturbations of the static structure were made intentionally very small because additional kinetic energy is extracted during stabilization of the structure.

Figure 3 shows the potential and total energies during the first 128 evenly spaced sampling times in the simulation. The interval between successive sampling times is 0.01033 psec, which is 10 times the unit of time required when amu is used for mass, bohr for length, and hartree for energy. The position updates are accurate through $O(\Delta t^3)$ and the velocity updates are accurate through $O(\Delta t^2)$.

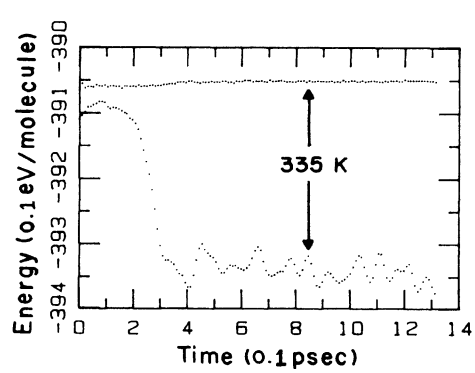

FIG. 3. Total and potential energies per molecule vs time for the first 128 steps (1.3 psec) of the dynamics simulation. There are 24 molecules, i.e., formula units in the supercell. The temperature shown is determined from the average kinetic energy per ion during the subsequent 512 steps (5.3 psec).

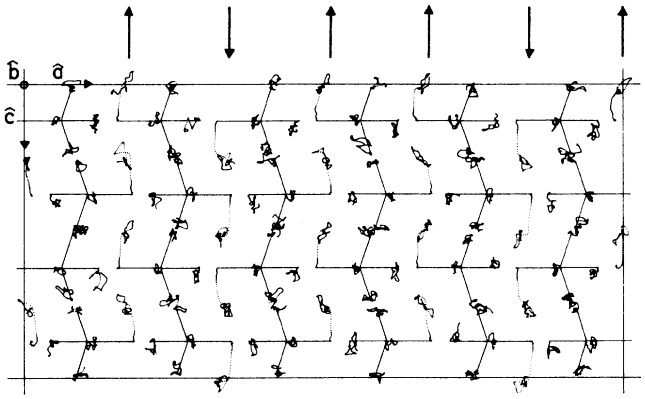

FIG. 4. Projected trajectories, viewed along $-\mathbf{b}$, of the zinc and chloride ions at each of the first 128 steps in the dynamics simulation. Straight lines connect the initial position of each zinc ion to the initial positions of the four nearest chloride ions. The four zinc-destabilized chlorides below each arrow move collectively away from their unstable positions in the direction indicated by the arrow.

Figure 4 is a view parallel to **b** of the zinc and chloride positions at each of the first 128 steps. The chlorides, one from each formula unit, whose sites in the static structure were suspected of being unstable are indicated by arrows above their positions in Fig. 4. This certainly was the case, and the sharp drop in the potential energy versus time in Fig. 3 is caused by the motion of these zinc-destabilized chlorides away from their unstable sites. Examination of the trajectories of these chlorides reveals that they moved in one of two equivalent directions. Furthermore, those unstable chlorides that have nearly equal **a** coordinates moved together in a cascade. This is true for all six such groups. This collective motion is caused by electrostatic repulsions, indicated in Fig. 2(c), between chlorides in adjacent $ZnCl_4^{2-}$ groups.

The cascades of zinc-destabilized chlorides stop with each of those ions at equilibrium positions that are exactly between mirror planes. The electric field at one of these chlorides decreases as it moves from the mirror plane and becomes zero at the new sites, so the inclusion of ionic polarizability would attenuate the zinc-induced instabilities and would place the equilibrium positions of those chloride ions closer to the mirror planes if not on them. If the equilibrium positions of the zinc-destabilized chloride ions are neither on the mirror planes nor exactly between them, a situation very much like that suggested by the split-atom analysis of Itoh *et al.* would exist. Each of those chlorides would move between two equivalent positions at high temperatures and chains of correlation in their positions would develop parallel to **c** at low temperatures.

V. ANOTHER STRUCTURE AND RUBIDIUM-INDUCED INSTABILITIES

The motion during the first 1.3 psec of the simulation did not stop at simple librations of each tetrachlorozincate group to one of two equivalent orientations. Each zinc-destabilized chloride ion stretched the bond with its original zinc ion and moved into a stable position between that zinc and one of the two that destabilized the initial position of the chloride.

Figure 5 shows three perspectives of the average positions during time steps 129 through 640 (duration 5.3 psec) of the simulation. The temperature of the simulated crystal during this time interval is 335 K. An ellipse in Fig. 5 has major and minor axes equal to the square roots of the average squares of the projected deviations of the ion from its average position. The coordinate system used to collect the rms deviations, thus the orientation of the ellipse, is that which results in a minimum area.

The rubidium and zinc sublattices are still described by the space group *Pnam* and can be divided into six equivalent subcells. This is consistent with the experimental fact that these ions do not participate in the disorder and is quite striking in view of the changes that have occurred in the chloride sublattices. The average positions of the rubidium ions are almost identical to the static positions, and the excursions from those positions are greater than the corresponding excursions of the zinc ions. There is a slight distortion of the near hexagonal projection of the zinc sublattice caused by the relocation of the zinc-destabilized chloride ions, but that distortion is the same in every subcell and does not alter the symmetry of the sublattice.

We shall henceforth call those chloride ions whose positions in the static structure were destabilized by zinc ions the shared chloride ions because they are no longer bonded exclusively to one zinc ion but are equally shared by two. The other three of every four chloride ions, which remain bonded to only one zinc ion and move as a group, will be called a triplet of unshared chloride ions.

The shared chloride ions reside on an ordered sublat-

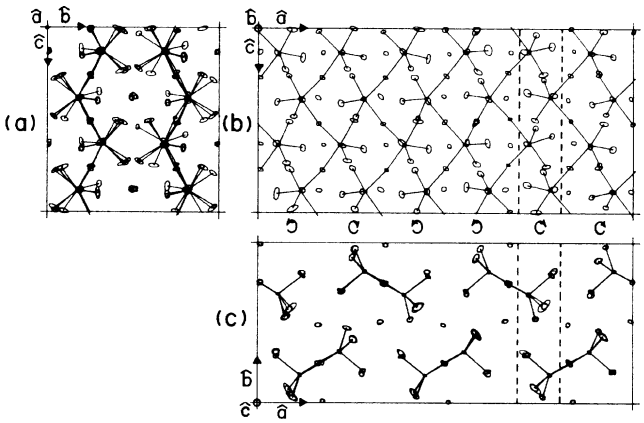

FIG. 5. Average positions during steps 129–640 (5.3 psec) of the dynamics simulation. Bonds connect the average positions of each zinc to those of the nearest five chlorides. Correlation exists between triplets of unshared chlorides in the senses of their rotations about **a**. One such group lies between dashed lines in (b) and (c), and the sense of rotation of each group when viewed along $-\mathbf{a}$ is indicated by a curled arrow that is between the two views of the group in (b) and (c).

tice. Each site is equivalent to every other regardless of the direction from which the chloride ion entered its equilibrium position. The group of the sublattice on which these shared chloride ions reside is *Pnam* and the unit cell is the same as that of the zinc and rubidium ions, i.e., the unit cell contains four formula units. The point symmetry of the new positions of the shared chloride ions is now 4(*b*) in the Wyckoff notation rather than 4(*c*), which was the designation of their sites in the β-K_2SO_4-type structure. Table II shows that the static version of this new structure has an energy that is 1.0 eV per formula unit lower than the energy of the experimental structure, but the energy of polarization of the chloride ions in the fields of this structure is 3.9 eV per formula unit higher than the corresponding energy in the fields of the experimental structure. This indicates that a self-consistent inclusion of ionic polarizability in the simulation would prevent the formation of the new structure and that the shared chloride ions would move as described in the final paragraph of Sec. IV.

Only the sublattices of unshared chloride ions are disordered in this structure, as can be seen in Fig. 5(a). The zinc and shared chloride ions form rigid chains while each triplet of unshared chlorides is rotated either clockwise or counter-clockwise about **a**. However, the directions of rotation are correlated in groups of four, which the periodic boundary conditions translate into two-dimensional networks. All triplets that have approximately equal **a** coordinates are rotated in the same direction. One such group of four triplets is shown between two dotted lines in Figs. 5(b) and 5(c).

The ions between the dotted lines in Fig. 5 are shown in Fig. 6. The ordered structure that corresponds to the simulated disordered one would have the unshared chlorides in positions described by the space group *Pnam*, just as they are in the experimental average structure. Each triplet of unshared chloride ions is inside a triangle

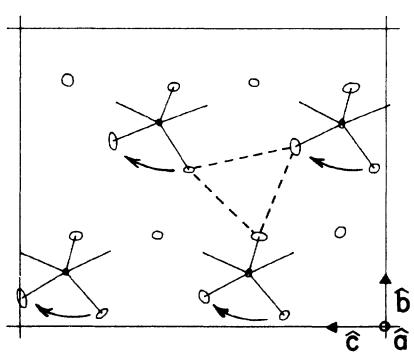

FIG. 6. View along $-\mathbf{a}$ of the two-dimensional network of triplets that lies between the dashed lines in Fig. 5. The bonds of each zinc to two shared chloride ions are shown but those chloride ions are omitted. The upper two triplets of unshared chloride ions are attached to zinc ions that lie below the page, and the lower two triplets are attached to zinc ions that lie above the page. The interactions which provide the tendency toward correlated rotations of the triplets are indicated with dotted lines, and the sense of rotation of each triplet away from the rubidium-destabilized orientation is indicated by an arrow.

of rubidium ions. The separation of rubidium and chloride ions is apparently large enough so that electrostatic interactions dominate short-range interactions and the "ideal" positions of those chlorides are unstable, particularly those positions in the mirror planes. These rubidium-induced instabilities are present also in the experimentally determined β-K_2SO_3-type structure. Interactions between unshared chlorides cause the tendency of their displacements away from their rubidium-destabilized positions to be correlated. Thus, the unshared chloride ions can be sorted into two-dimensional ordered networks.

The spirals between Fig. 5(b) and Fig. 5(c), which show the sense of the rotations of the triplets in the two-dimensional correlation networks, suggest that correlation parallel to **a** between the networks is absent. Thus, the truly infinite version of this new structure is disordered. One network of unshared chlorides could contribute to the polarization of the crystal, but the total contribution of all networks would be zero. This is so because the two possible orientations of the triplets are equally probable, so each network can be obtained by an inversion of another through the center of some unit cell (one-sixth of the simulated supercell). Thus, the truly infinite version of this new structure has no macroscopic spontaneous polarization.

VI. CONCLUSIONS

Our first conclusion from this investigation is that the β-K_2SO_4-type structure may show two types of instability as illustrated by Rb_2ZnCl_4. Electrostatic interactions with zinc ions destabilize the positions of one-quarter of the chloride ions. The positions of the other three-quarters of the chloride ions are destabilized by electrostatic interactions with rubidium ions.

Relaxation of the zinc-induced instabilities produces a new structure in which each zinc-destabilized chloride ion is shared by two zinc ions. While this new structure still has the space group *Pnam* (plus Cl^- partial disorder) the point symmetry of the sublattice of shared chlorides is not the same as that in the β-K_2SO_4-type structure.

Experimental data clearly show that none of the β-K_2SO_4 isomorphs ever assumes this new structure. Furthermore, the symmetry-allowed rotation of the tetrahedral groups about **c** that were seen in the static relaxation are not present in any of these compounds, i.e., each tetrahedral group has one bond nearly aligned with the **a** axis.

Evidently, there is something missing from our present lattice energy expressions; some global feature since it appears to operate in any β-K_2SO_4 isomorph. Covalency within the $ZnCl_4^{2-}$ ion is clearly not such a property, since there is no reason to assume that the central ion of every type of XY_4^{2-} radical carries the charge of almost exactly $1+$, necessary to prevent the rotations about **c**. Experimentation with charge transfer and short-range forces has convinced us that charge transfer can prevent the rotations about **c** while the constraints of the space group *Pnam* are maintained, but the new structure that appeared in the simulation, with shared chloride ions, is

still preferred over the experimental one. Therefore, charge transfer alone can not explain the structure of these compounds.

Another effect missing from our treatment of the ionic interactions is polarizability of the ions. In the β-K_2SO_4-type structure, the resultant electric fields at the average sites of the Cl^- ions do not vanish, nor are they caused only by the central Zn^{2+} ion of each $ZnCl_4^{2-}$ group. Thus, there exists the possibility that inclusion of polarizability could stabilize an otherwise unstable site. This could be the case at sites that are maxima of the self-consistent electric field. This possibility is just the reverse of that in structures like rocksalt, in which ionic polarizability is a potentially destabilizing effect because the electric field vanishes at the equilibrium sites of the ions.

While the absolute magnitude of the effect of polarization is very uncertain, a qualitative estimate can be made by examining the electric fields at the various Cl^- ion centers (to lowest-order polarization effects are quadratic in the field). The results of this estimate, shown in Table II, clearly indicate that the β-K_2SO_4-type structure is resistant to the rotations of tetrahedral groups about **c** that were seen in the static relaxation, and is also resistant to the formation of the new structure that was seen in the simulation. Obviously, this is an overestimate of the effects of polarization, but even if those effects are overestimated by nearly an order of magnitude, the qualitative conclusion is the same: The bond alignment in every β-K_2SO_4 isomorph is favored by polarizable anions.

At first sight this finding appears to cast doubt on the qualitative validity of our other findings concerning zinc- and rubidium-induced instabilities. However, further consideration reveals that this is virtually impossible. As we have examined these instabilities, it has emerged that they both have the same basic origin. The interactions that affect the orientation of a $ZnCl_4^{2-}$ group are between its Cl^- ions and pairs of symmetrically placed cations. These interactions occur at such large distances that the monopole contributions are much greater than the short-range or even the dipole contributions. Thus, if we constrain the structure to *Pnam* symmetry, the Cl^- ions are placed at unstable sites, and the rotations about **a** or **b** that would relax the instabilities are forbidden. The one rotation that is permitted, that about **c**, naturally occurs in order to reduce the potential energy as much as possible within the constraints. All three rotations occur when symmetry constraints are relaxed, but when polarization is included the magnitudes of the rotations about **b** and **c**, and perhaps those about **a**, are reduced. However, the rotations about **a** and **b**, which are, respectively, consequences of the rubidium- and zinc-induced instabilities, cannot be eliminated completely. This is entirely in accord with experiment since the split-atom structure from Ref. 1 indicates that the zinc- and rubidium-induced instabilities are both present in the normal phase of Rb_2ZnCl_4.

It must be remembered that the periodic boundary conditions could either favor correlations among the positions of ions that might be uncorrelated at the same temperature in the real solid, or they could prevent correlations that would exist in the real solid but are not commensurable with the simulated supercell. It is gratifying, in light of the former possibility, that the disorder among the networks of rubidium-destabilized chlorides could be observed in this simulation. Nevertheless, it may be argued that the extra length of our supercell in the **a** direction, relative to the **b** and **c** directions, favors lack of order parallel to **a** and may precipitate order in the other two directions. This appears not to be the case, because any pattern of orientations of the networks can be obtained in simulations with the length of the supercell reduced from $3a$ to $2a$, or even a. This disorder exists because the Cl^--Cl^- interactions that could cause correlation among the networks occur at relatively large distance ($\sim$4.9 Å) and, consequently, are weak. Indirect interactions between networks could occur in the real solid through intermediate chains of zinc-destabilized chlorides, but should also be weak. Furthermore, we think it unlikely that the periodic boundary conditions in the **b** and **c** directions precipitated the correlations seen in those directions. The Cl^--Cl^- interactions responsible for the ordering of the rubidium-destabilized chloride ions within a network and those that favor ordering of the zinc-destabilized chlorides within a chain are strong because they occur at relatively short distances (4.0-4.2 Å). Thus, the ordered substructures should appear with any choice of boundary conditions in the **b** and **c** directions.

The authors of Ref. 2 present experimental evidence that the disorder in the normal phase of rubidium tetrachlorozincate is transformed into the structural modulation of the incommensurate phase. This simulation seems to support that conclusion. A zinc-induced instability causes a $ZnCl_4^{2-}$ group to rotate about **b** and rubidium-induced instabilities cause the group to rotate about **a**. Strong tendencies of the rotations about **b** to be correlated in chains parallel to **c** and of the rotations about **a** to be correlated in two-dimensional networks parallel to the *bc* plane were seen in the simulation, and will be present in the real crystal since they arise almost entirely from electrostatic interactions among monopoles. (Both of these types of correlation exist in the ferroelectric phase shown in Fig. 2 of Ref. 2.) A transition to an ordered structure will inevitably occur as the temperature is lowered when correlation among the chains and among the networks develops.

We leave for later discussion the question of whether both types of instability observed in this simulation are required in order for a β-K_2SO_4 isomorph to have an incommensurate phase, i.e., the incommensurate modulation might be a pattern in the twists of the rubidium-destabilized triplets from one network to the next, or it might be a pattern in the canting of the zinc-destabilized chlorides from one chain to the next, or both (as Table I of Ref. 2 seems to indicate). A detailed discussion of the unique significance of the pattern of rotations that emerges will be presented elsewhere in the context of a study of the transition mechanism itself.

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