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First-Principles Theoretical Explanation of Incommensurate Behavior in Rb_2ZnCl_4

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We have carried out an *ab initio* theoretical study of the potential energy and molecular dynamics of Rb_2ZnCl_4. These calculations demonstrate that the incommensurate transition in this compound is caused by the relaxation of imperfect-hexagonal spirals of highly unstable $ZnCl_4^{2-}$ ions. This leads to angstrom-size displacements with essentially zero energy change. We argue that such "latent" (or imperfect) symmetry could be the general cause of incommensurate transitions in insulators.

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In 1977 Iizumi *et al.*[1] demonstrated conclusively that the 129-K phase transition in K_2SeO_4 was associated with the freezing in of a soft Σ_2 phonon with a wave vector of $\frac{1}{3}\mathbf{a}^*(1-\delta)$, where $\delta << 1$. The resultant displacement pattern is thus incommensurate and remains so until δ vanishes at 93 K, the commensurate transition temperature.

This immediately presented the problem of identifying the basic driving mechanism, since Fermi-surface instabilities[2] (the only then-known mechanism) could hardly be invoked for a large-band-gap insulator. This problem became even more perplexing as similar incommensurate phases were discovered in K_2SeO_4 isomorphs (e.g., Rb_2ZnBr_4,[3] and Rb_2ZnCl_4[4]) without however, any associated soft modes. Indeed, the attempt to find one in Rb_2ZnBr_4[5] gave results which, while not fully conclusive, indicated strongly that no such mode exists.

In this communication we wish to report the identification of the basic mechanism driving incommensurate transitions in Rb_2ZnCl_4, probably all the K_2SeO_4 isomorphs, and quite possibly all such transitions in insulators. Moreover, the mechanism appears sufficiently novel for these transitions to constitute a new and more general class, possibly embracing conventional "soft mode" transitions as a subclass.

Specifically, we find the transition to be driven by a relaxation of the quasihexagonal spirals formed by the $ZnCl_4^{2-}$ ions when viewed along the **a** axis. This symmetry would be exact if all $ZnCl_4^{2-}$ groups were equivalent. Associated with this distortion is an extremely flat area of the crystal potential surface which we demonstrate to exist by showing that during the reconstruction process drastic structural rearrangement occurs, which involves angstrom-size displacements, at virtually no cost in energy.

We were led to these findings by an attempt to apply to these systems an approach that we have previously found to be highly effective in explaining melting,[6] superionicity,[7] and, most recently, zone-boundary instabilities in halide perovskites.[8,9] The approach used the Gordon-Kim[10] technique to derive accurate potential surfaces for the systems under study. Since this appears to work well for RbCl and KCl, there appears to be no reason why these same potentials should not be equally good in the chlorozincates. The only new potential required is the zinc-chlorine interaction (all other short-range interactions involving Zn^{2+} are negligible). For this ion pair, the Gordon-Kim potential was manifestly too hard (e.g., the zinc-chlorine bond length was $\sim 10\%$ too large). However, when the prefactor in the Gordon-Kim potential was reduced, to minimize the unbalanced forces on the zinc and chlorine ions at the observed lattice positions, these forces decreased by 90% and the free-ion bond lengths were in good agreement with experiment. Subsequently, the lattice relaxed smoothly and quickly to the equilibrium *Pnam* (D_{2h}^{16}) structure with the lengths of the cell sides constrained to the experimental values. The resultant structure is shown in Fig. 1(a). Apart from the one adjustment of the *intra*molecular potential to ensure that the free ion has the correct size, all *inter*ionic potentials are parameter-free. Consequently, we regard this as an *a priori* calculation as far as the crystal is concerned.

We then proceeded to investigate the lattice dynamics of this structure. This revealed a very unstable system with 7 or 8 completely unstable branches in the disperison curves.

Evidently, given the results for other systems which indicate that our potentials are reliable, we must be dealing with a novel situation. In particular, it would appear unlikely that conventional soft-mode theory can be applied. Consequently, we then proceeded to examine the energy of the low-temperature phase in which the unit cell is tripled along the **a** axis. We do

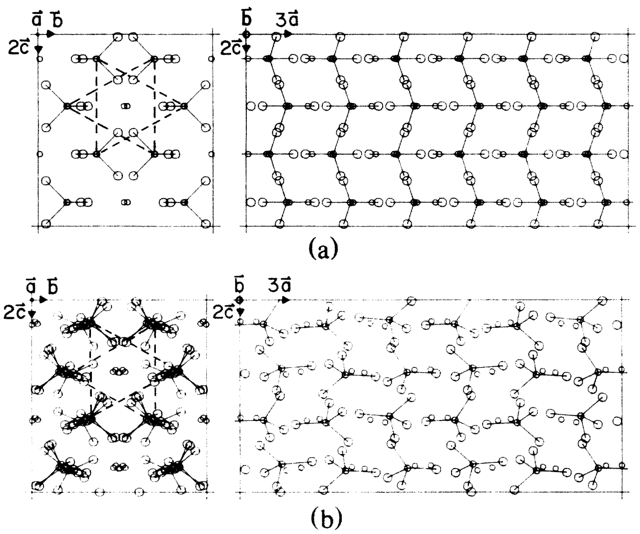

FIG. 1. (a) **a**-**c** and **b**-**c** cross sections of the relaxed static-*Pnam* structure of Rb_2ZnCl_4. The two triangles join the triplets of zincs of width $\sim a/7$ along **a** (in this and subsequent figures all $ZnCl_4{}^{2-}$ tetrahedra are shown but not all Rb^+ ions). Note: $a = 9.257$ Å, $b = 12.726$ Å, and $c = 7.282$ Å. (b) **a**-**c** and **b**-**c** cross sections of the relaxed $Pna2_1$ structure of Rb_2ZnCl_4—note the relative torsional movement of the $ZnCl_4{}^{2-}$ triplets in the other two cells with respect to the two triangles of triplets shown for the first of the three cells.

not address the incommensurate phase directly, since we need a periodic structure for our computations. As we shall see, this is unimportant.

Once again the system relaxed smoothly and quickly to the final configuration shown in Fig. 1(b).

In this new structure approximately half the unstable normal modes for the *Pnam* phase had stabilized, but the most striking feature was that the energy per molecule had changed by only 0.0037 eV. This result is particularly striking when one compares the ionic positions in the *Pnam* and $Pna2_1$ (C_{2v}^9) structures, as shown in Figs. 1(a) and 1(b). It can be seen that the ionic positions are very different and, in particular, the $ZnCl_4{}^{2-}$ tetrahedra have displaced and rotated through *angstrom*-size distances.

Evidently, this implies that the potential energy surface in the hyperspace of ionic coordinates is extremely flat, so much so that the two configurations are effectively degenerate with one another, and with the large volume of hyperspace between them.

Examination of Figs. 1(a) and 1(b) provided a qualitative explanation of this most unusual behavior. It would appear that the apparently hexagonal array of $ZnCl_4{}^{2-}$ ions can rotate synchronously over large angles with little appreciable change in energy. However, the apparent near-hexagonal symmetry in projection is revealed in three dimensions as an *approximate sixfold screw axis along* **a**. This imperfect symmetry, which we choose to call "latent symmetry," is the origin of incommensurate behavior.

The true situation is that there are two trigonal arrays of tetrahedra, as indicated in Fig. 1(a), rotated with respect to one another by π about **a**. However, while the two layers within each array are separated by $\sim a/7$ along the **a** axis, the two arrays are $a/2$ apart. Thus, what has taken place in the transformation between the two *ideal* lattices, shown in Fig. 1, can be decomposed into two components: (a) synchronous rotations *within* the trigonal layers, which cost virtually no energy until the rotational displacements are a significant fraction of the distance between first-neighbor tetrahedra; and (b) correlated motion between adjacent trigonal layers, again at a low cost in energy.

In addition to these primary motions, there are secondary (but still angstrom-size) displacements, transverse to the **a** axis, of the Zn^{2+} and Rb^+ ions. This type of motion provides a very efficient means of relaxing any significant accumulation of energy due to the rotations; it does so because the $ZnCl_4{}^{2-}$ radicals, as we shall demonstrate, are very loosely attached to the orthorhombic "backbone" of the lattice. For the energy to remain nearly stationary as both types of displacements build up, the secondary displacements must be periodic around the hexagonal spiral. Hence, we obtain a tripled cell. However, if we decompose these displacements into plane waves, only two basic modulations are present, since all component wave vectors $\mathbf{Q}_n$ must satisfy the requirements, $\mathbf{Q}_n \parallel \mathbf{a}$ and

$$Q_n(3a) = 2\pi n,$$

or

$$Q_n = 2\pi n/3a. \tag{1}$$

Thus, when $n = 3$ (or some multiple of 3), we have a $\mathbf{q}_s = \mathbf{0}$ modulation (where $\mathbf{q}_s$ is restricted to the first zone); otherwise we have a $\mathbf{q}_s = \mathbf{a}^*/3$ component, i.e., a threefold modulation.

However, Eq. (1) can be expressed in another form:

$$q_s(x_k - x_{k'}) = 2\pi/6 \tag{2}$$

(where x_k and $x_{k'}$ are the **a** components of the basis vectors of the nearest-neighbor ion pairs around the hexagonal spirals).

In this form, it is apparent that this condition, because of the *latency of the symmetry,* cannot be *identically* satisfied for all pairs of ions. As a consequence, the near-sixfold helices tend to pucker and rotate. This implies intrahelical torques which would, were $\mathbf{q}_s$ free to vary, favor a slight unwinding. The result would be an *incommensurately modulated structure.* The proviso that the unwinding be small in this case arises from the strongly *commensurate* nature of the rotational motion—indeed, as the amplitude of the modulation increases, this forces the commensurate lockin.

Thus far, our discussion has been conducted in terms of the *ideal* lattices and *static* energies. However, we know that both lattices have strong instabilities, and we have already postulated[11,12] that the tetrahedra are disordered in some measure, in order to explain anomalies in the Raman spectra of the internal modes. We thus need to establish the basic validity of the foregoing arguments when the system is disordered and at finite temperature. We therefore carried out a molecular dynamics simulation which will be fully reported elsewhere.[13] The results essential to the present discussion are shown in Figs. 2(a) and 2(b).

In Fig. 2(a), we show the system at 335 K, above, but close to the transition. It can be seen that the trigonal layers are becoming correlated in precisely the manner we have predicted for the static structure. In Fig. 2(b), we show the same system at 255 K: The cell-tripling transition has clearly taken place since the correlation within the trigonal layers has been joined by the modulated interlayer correlation, again as predicted for the static system. The large Cl^- ellipsoids indicate rotational disorder of the $ZnCl_4{}^{2-}$ units. This partially decouples the spirals from the "backbone" of Rb^+ ions.

We have emphasized the structural aspect of latent symmetry since it seems likely that it can account for many, if not all, examples of incommensurate behavior in insulators. A completely different example is $ThBr_4$,[14] which does not contain ill-fitting molecular groups, but has eight bromide ions clustered above each thorium ion.

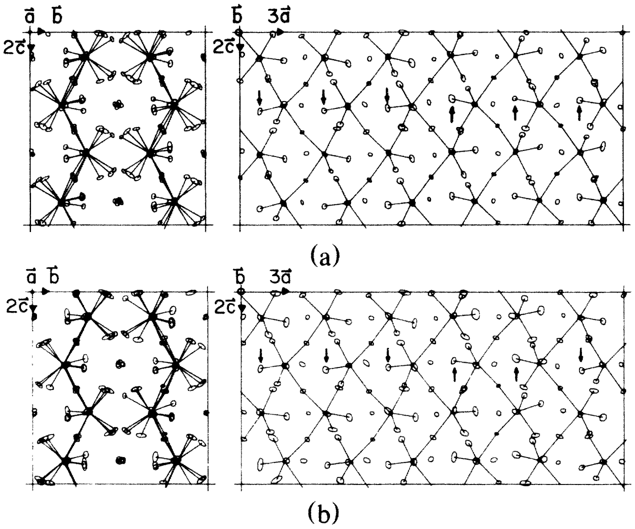

FIG. 2. (a) **a**-**c** and **b**-**c** cross sections of the molecular-dynamics simulation of Rb_2ZnCl_4 at 335 K. The ellipsoids are drawn about the *average* positions of the ions, and have principal axes equal to the appropriate root-mean-square deviations. Note the correlations parallel to **c**. The arrows indicate the senses of rotation about **a** of their associated tetrahedra. These clearly show mixed periodicity, i.e., disorder, along **a**. (b) **a**-**c** and **b**-**c** cross sections of the molecular-dynamics simulation of Rb_2ZnCl_4 at 255 K. Again the arrows show the senses of the tetrahedra rotations. This now has a single periodicity: Three positive followed by three negative, i.e., the unit cell has tripled. (Note that in both figures half the rubidium ions in the **a**-**c** projection are almost concealed by zinc ions lying above them.)

In this case, from Fig. 1 of Ref. 14, the latent symmetry along the **z** (**c**) axis appears to be that of an approximate fourfold screw axis. Thus, for this case, we have, for the ionic z coordinates z_k,

$$q_z(z_k - z_{k'}) = \pi n/2, \tag{3}$$

where $\mathbf{q}_s = (0,0,q_z)$. Since

$$z_k - z_{k'} \sim 0.75c, \tag{4}$$

if $n = 1$, it follows that

$$\mathbf{q}_s = (0,0,q_z) \sim \mathbf{c}^*/3 \text{ (the observed value).}$$

Again, the symmetry is not exact, since there are other basis-vector differences; hence an incommensurate phase appears. Its wide range of stability may be due to the absence of associated large molecular motions which favor commensurateness.

Thus we feel that we have isolated the mechanism which produces incommensurate behavior in Rb_2ZnCl_4 and its isomorphs. Briefly: *Incommensurate behavior arises from the presence in the parent (high-temperature) structure of imperfect and mechanically unstable helices of atoms or groups. The imperfection causes intrahelical torques and an incommensurate structure results, when the helices open to relieve these particular stresses during the transition.*

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[1] M. Iizumi, J. D. Axe, G. Shirane, and K. Shimaoka, Phys. Rev. B **15**, 4392 (1977).

[2] J. A. Wilson, F. J. DiSalvo, and S. Mahajan, Adv. Phys. **24**, 117 (1975), and Phys. Rev. Lett. **32**, 882 (1974).

[3] K. Gesi and M. Iizumi, J. Phys. Soc. Jpn. **45**, 1777 (1978).

[4] K. Gesi and M. Iizumi, J. Phys. Soc. Jpn. **46**, 697 (1979).

[5] C. J. de Pater and C. van Dijk, Phys. Rev. B **18**, 1281 (1978).

[6] L. L. Boyer, Phys. Rev. Lett. **42**, 584 (1979). A fuller account is given in Phys. Rev. B **23**, 3673 (1981).

[7] L. L. Boyer, Phys. Rev. Lett. **45**, 1858 (1980), and **46**, 1172 (1981).

[8] L. L. Boyer and J. R. Hardy, Phys. Rev. B **24**, 2527 (1981).

[9] L. L. Boyer, J. Phys. C **17**, 1825 (1984).

[10] R. G. Gordon and Y. S. Kim, J. Chem. Phys. **56**, 3122 (1971).

[11] N. E. Massa, F. G. Ullman, and J. R. Hardy, Phys. Rev. B **27**, 1523 (1980).

[12] V. Katkanant, F. G. Ullman, and J. R. Hardy, Jpn. J. Appl. Phys., Suppl. Pt. 2 **24**, 790 (1985).

[13] P. J. Edwardson, V. Katkanant, J. R. Hardy, and L. L. Boyer, to be published.

[14] L. Bernard, R. Currat, P. Delamoye, C. M. E. Zeyen, S. Hubert, and R. De Kouchovsky, J. Phys. C **16**, 433 (1983).