A Priori Predictions of Phase Transitions in $KCaF_3$ and $RbCaF_3$: Existence of a New Ground State

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We have made an *a priori* theoretical study of the potential-energy surfaces for $KCaF_3$ and $RbCaF_3$, and have examined the relative stability of the various lower-symmetry structures generated from the cubic perovskite phase by "rotations" of the CaF_6 octahedra. A completely new ground state was discovered which, when included in the sequence of energy levels, allows us to give a full account both qualitatively and, in the case of $RbCaF_3$, quantitatively of the phase transition sequences in both systems.

Theoretical predictions of the relative stability of different phases of a given system are currently quite rare and are confined to simple structures. For more complex systems such calculations are essentially nonexistent. In this Letter we wish to report what we believe to be the first ever *a prior* prediction of the relative stability of structures containing as many as forty ions per unit cell. The specific systems with which we are concerned are the halide-based perovskites $RbCaF_3$ and $KCaF_3$. As a result of these calculations we are able to predict the transition sequences in systems which have only in recent years been measured experimentally.[1-7] While the oxygen-based perovskites have been studied over a much longer period,[8] they are theoretically less tractable because of the presence of large field effects on the charge density of the O^{-2} ion, which is unstable in the free state.

Intuitively, one would expect the behavior of $RbCaF_3$ and $KCaF_3$ to be qualitatively similar, with the principal difference being higher transition temperatures for the potassium compound due to its smaller cell size and tighter binding.

Experiment apparently confounds this intuition in every respect. The only thing common to the two systems is that the observed superstructures are apparently generated by combinations of "pseudorotations" of the fluorine octahedra about their three (100) axes [the term "pseudorotation" is here used to indicate that the actual displacements are not "pure" rotations, since the F^- ions are constrained to remain in the (100) cube faces]. Thus the rubidium compound shows a single pseudorotation of the octahedra at 195 K followed by what appears to be a final condensation

of two further pseudorotations at 50 K into a phase where all three are equally present (effectively a [111] rotation). However, one group[1] reported a third transition at about 9 K of unknown origin. Since all possible pseudorotations have been exhausted, the tendency is to attribute this result to the large thermal hysteresis of the 50-K transition.

The potassium compound behaves quite differently; the structure apparently goes directly from the perovskite phase above 560 K to a state where there are two approximately equal pseudorotations (effectively a [110] rotation), followed almost immediately by the condensation at 551 K of the third pseudorotation to produce a structure which is evidently, at least down to 300 K, evolving into the same final state as that adopted by the rubidium compound below 50 K.

We have previously examined theoretically the 193-K transition of the rubidium compound[9] and, more recently, reported a systematic survey of halide-based perovskites in which we concentrated on finding the stable ground state as determined by the static energy surfaces.[10] The same approach predicts that $CsCaF_3$ is stable in the perovskite structure down to absolute zero.[11]

In extending our investigation to $KCaF_3$ and $RbCaF_3$ we have broadened the scope of our calculations to attempt to find all possible stable or metastable states for both compounds and determine the relative static energies for each sequence of states. The key feature of our findings is the theoretical prediction that there exists a state of both systems of *lower* symmetry than the [111] rotated state which is the *absolute* ground state. By invoking this ground

TABLE I. Well depths and estimated transition temperatures for $RbCaF_3$ and $KCaF_3$. Perovskite E/cell = -36.77577 eV for $RbCaF_3$ and -36.89295 eV for $KCaF_3$.

	RbCaF₃		KCaF₃	
	Well depth (eV)	Transition temp. (K)[a]	Well depth (eV)	Transition temp. (K)[a]
1,0,0 rotation	0.009 94	42.9	0.101 184	847
1,1,1 rotation	0.011 034	30.11	0.140 656	389
1,1,0 rotation	0.011 711	22.26	0.148 385	299
Ground state	0.013 629		0.174 158	

[a]Transition temperatures estimated under the assumption that the ground state is at 0 K.

state we can predict the transition sequences in both systems, both qualitatively and semiquantitatively, by comparing calculated energy differences with observed transition temperatures. While one should certainly compare free energies rather than static energies, this is a much more laborious undertaking which we reserve for the future. We believe that, at least for $RbCaF_3$, the present results should be definitive since the temperature regime involved is so close to absolute zero (below 50 K).

Our calculations are based on the use of *ab initio* interionic potentials obtained by the Gordon-Kim[12] approach. Details of the method and potentials have been presented previously.[13]

Initially calculations were carried out which allowed the ions in the lattice to relax in such a way as to simulate pseudorotations of fluorine octahedra about [001], [110], and [111] axes. Lattice constants as well as ion-

ic displacements were adjusted until the normal stress components and force components on each ion were zeroed. (Shear stresses were also zeroed but the shear angles required were so small that they had negligible effect on the static energies.) The static energy and eigenfrequencies of this equilibrium configuration were then computed and the frequency spectrum examined to determine whether a given configuration was stable or metastable as well as the nature of any instabilities present.

In Table I and Figs. 1 and 2 we list the energies and well depths associated with the perovskite structure and the various rotated configurations of $KCaF_3$ and $RbCaF_3$. In both cases the [110] rotated phase is lower in energy than the [111] rotated phase, in apparent
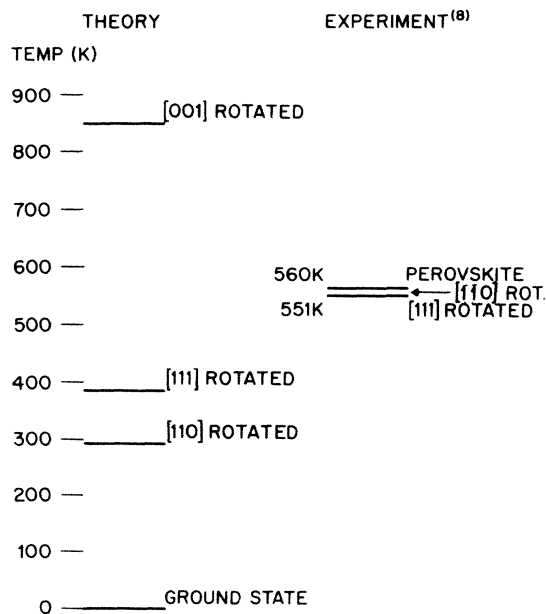

FIG. 1. Theoretical and experimental energy-level diagrams for $KCaF_3$ showing transition temperatures.
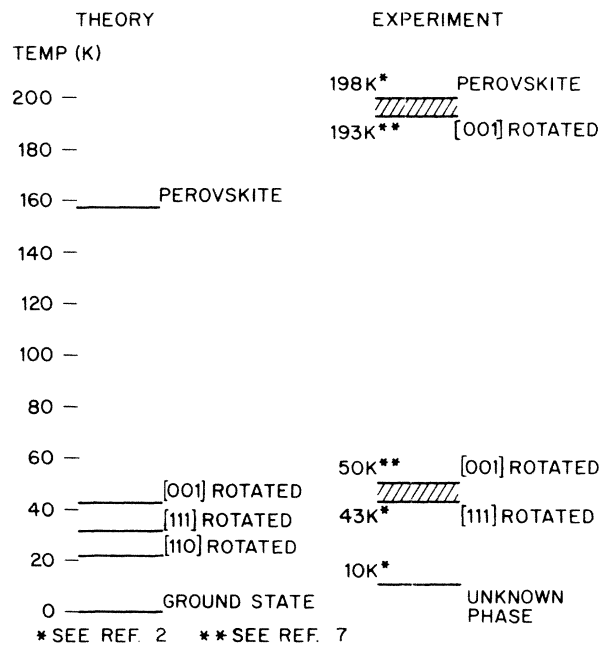

FIG. 2. Theoretical and experimental energy levels for $RbCaF_3$ showing transition temperatures. The hatched-in regions reflect variations in results between different experimental groups.

disagreement with experiment. However, we found both of these configurations to be metastable with instabilities at the zone center. Using the eigenvectors associated with these instabilities, we searched for and found a totally new phase which cannot be described in terms of pure rotations of the fluorine octahedra but includes translational displacements of the fluorine ions and the alkali-metal ions also. This is displayed in detail in Fig. 3 and Table II. We wish to point out that the displacements and lattice constants listed were obtained with no symmetry constraints imposed. The spectrum of this structure contains no imaginary frequencies; hence the configuration must be at least locally stable and is likely to be the state of absolute lowest energy. Note that in spite of its somewhat lower symmetry this state still exhibits no net dipole moment.

While the new phase cannot be described in terms of a mixing of single pseudorotations about (100) axes, the fluorine displacements reflect a strong contribution from the [111] rotated phase. In the case of $KCaF_3$ the lowest temperature for which experimental results were reported was 300 K. Thermal vibrations at that temperature would be expected to mask the true static equilibrium displacements sufficiently that the configuration might appear to be the [111] rotation. The apparent transition from the mixed state to the [110] rotated configuration (the next lowest energy) appears to take place at too low a temperature. However, as mentioned previously, one must remember that the energies used in the estimation of the transition temperatures are static, not free, energies.

At this point, the subsequent evolution of the actual system appears totally inconsistent with our predicted energies. According to these the next transition is to the [111] rotated state at about 90 K above the [110] rotated state; experiment indeed gives a transition at about 10 K higher, but apparently to the perfect perovskite structure. We can resolve this paradox by reexamining what these transitions imply. In reality, the new ground-state energy is far below that of the perovskite phase, while both [110] and [111] rotated states are locally unstable with respect to the ground state. Consequently, the actual transition sequence is not from one state to the next as the appropriate temperatures are reached, but through a sequence of increased freedoms of the ground state. Thus above the lower transition temperature, the basic ground-state
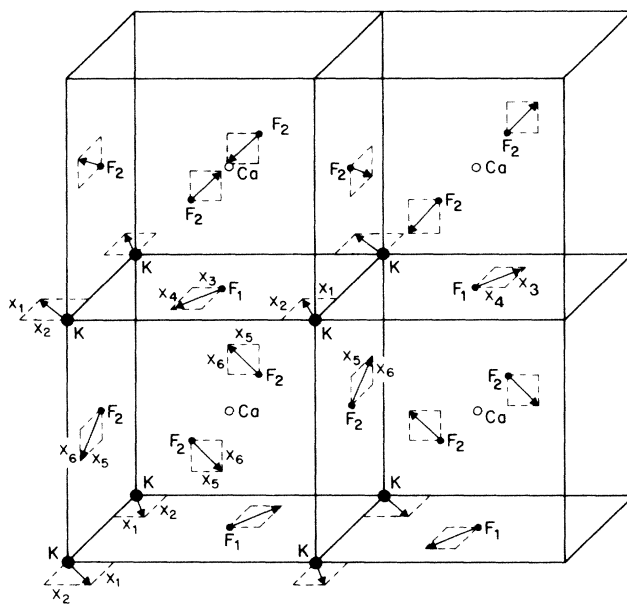

FIG. 3. Ionic displacements in the ground-state configuration of $KCaF_3$. The configuration is identical for $RbCaF_3$ if the K ions are replaced by Rb ions. Displacements are shown only for half of the unit cell. The calcium ion in the lower left cube is at the origin of the cell coordinates.

configuration can jump through the [110] local maximum and reverse the signs of its displacement components orthogonal to the [110] plane. Consequently the symmetry *appears* to be [110]—the other components average out to zero. However, the [110] sense is retained since the first two directions cannot reverse sign. This only becomes possible at the higher transition when the [111] rotated state becomes accessible. At the higher transition temperature the [111] state becomes accessible and *complete reorientation becomes possible* leading to a structure which *appears* to be perfect perovskite; in reality it is only so on an average.

Thus we have a consistent picture—the only remaining discrepancy is the disparity between observed and predicted transition temperatures (300 and 390 K, theory; 55 and 560 K, experiment). In view of our results for the rubidium compound, we think it is likely that most of this arises from the comparison of static energies rather than free energies at these elevated temperatures. We have examined the variation in stat-

TABLE II. Ionic displacements for the mixed state (units of $2a$ except as noted). See Fig. 3 for identification of displacements.

	X_1	X_2	X_3	X_4	X_5	X_6 $(2c)$	$a = b$ (Bohr)	c (Bohr)
$KCaF_3$	0.014 07	0.021 13	0.027 14	0.056 29	0.042 08	0.043 87	8.102	8.087
$RbCaF_3$	0.005 136	0.006 601	0.016 95	0.023 19	0.024 36	0.020 56	8.250	8.260

ic well depths as a function of increasing cell size, however, and find them to be essentially constant.

In the case of $RbCaF_3$ the static energy differences between the various phases are much smaller. Once again on the assumption that the new state is the ground state of the system, theory predicts a transition to the apparent [110] rotated phase at about 22 K with a subsequent transition to the [111] rotated state at 30 K and the [100] state at about 43 K with the final transition to the apparent perovskite phase at 158 K. Again, these energies should be interpreted as transitions which occur as a result of new "channels" opening up for motion of our new minimum energy state. Thus at about 22 K the [110] "wagging" becomes possible and an apparent [110] symmetry structure should result. Above 30 K the [111] "wagging" should commence giving an apparent perovskite structure. Since vibrational contributions to the free energy should be very much smaller than for the potassium compound, one can directly compare energies with transition temperatures.

There is some disagreement between various experimental groups as to the behavior of this compound below the 50-K transition. Modine et al.[1] report a further transition from a tetragonal state at about 10 K to a cubic state at about 20 K. However, Bulou et al.,[7] using neutron powder profile refinement to examine the structure at 4.5 K and again at 20 K, report a cubic phase at both temperatures. It should also be noted that while these authors appear to be saying that the ground state is the [111] rotated structure, they also quote displacements for the Rb ions, which are on the same order of magnitude as ours but with a very dissimilar displacement pattern. We feel that our present results provide a simple explanation of this discrepancy: The ground state which we have found is, in essence, cubic, as can be seen from Table II, as is the [111] rotated state. The [110] rotated state, however, is distinctly tetragonal. Hence if one looks above and below the very small temperature range (about 8 K) separating the transition to the [110] state and the subsequent transition to the [111] state as temperature is increased, one would believe the crystal structure to be cubic over this entire range.

The one major inconsistency is that the [111] "wagging" is apparently absent since the structure appears cubic ([111] rotated but frozen) up to 50 K. However, one must remember that this sort of "unfreezing" would be driven by R-point phonons and at the low temperatures involved these should not be present in

significant numbers. It is important to note that the only other equilibrium configuration, other than the ground state, for which the cations are displaced from the cube corners is the [110] rotated state, which is the next state above the ground state, and it would appear that these locked-in cation displacements are responsible for giving the [110] direction a "preferred" sense and with it a preferred direction of the [111] axis in the ground state. Consequently, above 30 K, while the octahedra can rotate their axes from [110] to [111], they cannot reorient and the overall average structure appears to be purely [111] rotated. These arguments become invalid at elevated temperatures since ample thermal fluctuations are present to destroy "memory effects," while at 10-30 K there is large thermal hysteresis.

On the basis of these findings we believe that we have a unified understanding of the phase transitions in both $KCaF_3$ and $RbCaF_3$ based on the use of a priori potentials with no disposable parameters.

[1]F. A. Modine, E. Sonder, W. P. Unruh, C. B. Finch, and R. D. Westbrook, Phys. Rev. B 10, 1623 (1974).

[2]R. Almairac, M. Rousseau, J. Y. Gesland, and B. Hennion, J. Phys. 38, 1429 (1977).

[3]C. Ridou, M. Rousseau, and A. Treund, J. Phys. (Paris), Lett. 38, L359 (1977).

[4]M. Rousseau, J. Nouet, and R. Almairac, J. Phys. 38, 1423 (1977).

[5]M. Sakata, M. Hidaka, and J. S. Storey, Solid State Commun. 32, 813 (1979).

[6]A. Bulou, C. Ridou, M. Rousseau, J. Nouet, and A. W. Hewat, J. Phys. (Paris) 41, 87 (1980).

[7]A. Bulou, J. Nouet, A. W. Hewat, and F. J. Schafer, Ferroelectrics 25, 375 (1980).

[8]M. E. Lines and A. M. Glass, Principles and Applications of Ferroelectrics and Related Materials (Oxford Univ. Press, Oxford, 1977), Chap. 8.

[9]L. L. Boyer and J. R. Hardy, Phys. Rev. B 24, 2577 (1981).

[10]J. W. Flocken, R. A. Guenther, J. R. Hardy, and L. L. Boyer, Phys. Rev. B 31, 7252 (1985).

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

[12]R. G. Gordon and Y. S. Kim, J. Chem. Phys. 56, 3122 (1972).

[13]J. W. Flocken, R. A. Guenther, J. R. Hardy, and L. L. Boyer, to be published.