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13. ABSTRACT *(Maximum 200 words)*

Work over a three year period on the optical and dielectric properties of a sequence of ionic molecular solids such as K_2SeO_4, KNO_3 and $NaNO_2$ is described. This work had both experimental and theoretical components. Principally the experiments used light scattering and birefringence to monitor structural and optical changes associated with solid-solid phase transitions. Theoretical studies concentrated on developing a unified theory of the ionic interactions in these systems which resulted in parameter free molecular dynamics simulations which closely reproduced the observed transition and structural behavior of these increasingly complex systems.

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Experimental and Theoretical Studies of Ionic
Molecular Solids

Final Report

J.R. Hardy and F.G. Ullman

1 November 1993

Army Research Office

DAAL03-90-G-0112

Department of Physics and Center for Electro-Optics
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Introduction

During the past three years, we have continued to extend and develop our capability of studying ionic molecular solids. While this began with elucidating the origins of incommensurate behavior in the A_2BX_4 compounds, such as K_2SeO_4, it has now extended into a general capability to study potentially any ionic molecular solid in which the molecular ions are present as individual units, without any sharing of ions between them. Thus we have studied, in addition to A_2BX_4 systems showing incommensurate behavior, sulfates, nitrates and nitrites. Moreover, in studying the last two families, we have developed a collaborative program with Drs. Gauss and Cornelison at ARL (Aberdeen) which is examining the microwave dielectric properties of these systems.

In what follows, the histories of these various studies are laid out in sequences of abstracts from published work, which are self-explanatory both in terms of the specific natures of the individual studies, and in their sequential development.

Experimental Work at Nebraska

The studies described in what follows have employed Raman and Brillouin scattering and birefringence. The birefringence work has been particularly fruitful both in its ability to "pinpoint" actual transitions and its sensitivity to the presence of "weak" transitions whose presence is not clearly revealed by other techniques. Also, most recently, in work on thiourea, it appears that this technique can also cast light on the presence or absence of optical gyrotropy in incommensurate phases.

Ferroelectrics, 1991, Vol. 117, pp. 245–259
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LIGHT-SCATTERING STUDIES OF IMPROPER COMMENSURATE AND INCOMMENSURATE FERROELECTRICS

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(Received July 24, 1989; in final form October 16, 1989)

Abstract Previous Raman-scattering studies of the improper ferroelectrics, GMO and TMO, and a phase transition model that resulted partially from those experiments, are reviewed. Internal mode spectra of these and of the A_2BX_4 incommensurates are compared, with special emphasis on the presence or absence of anomalies. The effect of uniaxial stress on the elastic constants of K_2SeO_4 as measured by Brillouin-scattering is also discussed briefly.

PHYSICAL REVIEW B VOLUME 44, NUMBER 14 1 OCTOBER 1991-II

Raman scattering and lattice-dynamical calculations of alkali-metal sulfates

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(Received 26 December 1990)

Raman-scattering measurements on single crystals of K_2SO_4, Rb_2SO_4, and Cs_2SO_4 have been made at both room and liquid-nitrogen temperatures. Lattice-dynamical calculations, based on a rigid-ion model using the Gordon-Kim method to calculate the short-range potentials, were performed. The influence of the alkali-metal ions on the lattice-dynamical properties of the crystals is discussed.

PHYSICAL REVIEW B VOLUME 43, NUMBER 13 1 MAY 1991

Observation of a birefringence anomaly at the 93-K phase transition in K_2SeO_4

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(Received 14 May 1990; revised manuscript received 23 January 1991)

The relative birefringence of K_2SeO_4 was measured by the rotating-analyzer method, over a temperature range from 140 to 80 K. We report here clear observation of anomalous birefringence at the incommensurate-ferroelectric phase transition at 93 K. The observation of anomalous birefringence at both the paraelectric-incommensurate and the incommensurate-ferroelectric phase transitions is consistent with low-frequency dielectric measurements and illustrates the complementary nature of these two measurements.

JOURNAL OF RAMAN SPECTROSCOPY, VOL. 22, 525–528 (1991)

Raman Spectrum of $CuSO_4 \cdot 5H_2O$ Single Crystal

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The Raman spectrum of a $CuSO_4 \cdot 5H_2O$ single crystal was measured at 95 K. The assignment of the internal modes of the molecular complex $Cu^{2+}(H_2O)_4$ and of differently bonded water molecules is discussed.

PHYSICAL REVIEW B VOLUME 46, NUMBER 9 1 SEPTEMBER 1992-I

Optical study of Cs_2ZnI_4

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(Received 2 December 1991; revised manuscript received 23 March 1992)

The relative linear birefringence of Cs_2ZnI_4 was measured along all orthorhombic *Pnam* axes with use of the rotating-analyzer method. These measurements showed three distinct phase transitions at 120, 109, and 94 K and another possible phase transition near 101 K. The transition at 94 K showed definite hysteresis (≈ 1 K), which indicates that it was a first-order transition. No hysteresis was observed at either of the transitions at 109 and 120 K. The shapes of these transitions, however, indicate that the one at 120 K was second order, and the one at 109 K was first order in nature. Rough Brewster's-angle measurements were made which yielded a crude estimate of the average index of refraction of between 1.77 and 1.80. X-ray-diffraction measurements were also made to confirm our identification of the crystals grown and to identify the crystal orientation. These measurements yielded accurate values for the axial lengths of the room-temperature structure that are in very good agreement with previous measurements.

Ferroelectrics, 1992, Vol. 137, pp. 357–371
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UNIAXIAL STRESS STUDIES OF FERROELECTRIC AND FERROELASTIC PHASE TRANSITIONS†

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(Received May 1, 1992)

Measurements of the behavior of ferroelectric and ferroelastic phase transitions under uniaxial stress are relatively sparse. Reviewed here are several studies of the uniaxial stress dependence of commensurate and incommensurate transitions observed in measurements of dielectric properties, inelastic light scattering, and birefringence.

PHYSICAL REVIEW B VOLUME 45, NUMBER 5 1 FEBRUARY 1992-I

Raman scattering and lattice-dynamical calculations of crystalline KNO_3

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(Received 19 August 1991)

The Raman spectrum of a KNO_3 single crystal was measured at both room and liquid-nitrogen temperatures. Lattice-dynamical calculations, based on the rigid-ion approximation and empirical potentials, were performed. The possibility of a phase transition at 217 K was investigated by measuring the temperature dependence of the Raman spectrum.

Ferroelectrics, 1993, Vol. 143, pp. 27–37
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RAMAN SCATTERING AND BIREFRINGENCE STUDIES OF THE PHASE TRANSITIONS IN CESIUM ZINC TETRAIODIDE*

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(Received December 14, 1992)

Measurements of the linear birefringence of Cs_2ZnI_4 along all three crystal axes and of temperature-dependent, polarized Raman scattering have been made. The results are described and used to interpret the structural phase transition sequence exhibited by Cs_2ZnI_4.

Keywords: phase transitions, incommensurate, ferrelastic, ferroelectric, Raman scattering, birefringence, Cs_2ZnI_4

Ferroelectrics (in press)

OPTICAL ACTIVITY AND BIREFRINGENCE IN THE INCOMMENSURATE PHASE OF THIOUREA

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Abstract Thiourea $\{SC(NH_2)_2\}$ is an optically transparent insulator which undergoes several structural phase transitions. We report here the results of a polarization study over the incommensurate temperature range. The results are interpreted in terms of a model in which thiourea is both birefringent and optically active.

Theoretical Work

Again, this is sequentially described by the following abstracts. The most notable achievements are definitive studies of the phase sequences in both K_2SeO_4 and Rb_2ZnCl_4, the latter is further enhanced by corollary work on K_2ZnCl_4. From these entirely parameter-free studies has emerged what we believe to be a definitive understanding of incommensurate behavior in complex insulators as a purely structural phenomenon. When "stiff" ionic units, having their own inherent shape and size, are packed together in a periodic array, they are often locally unstable due to the relatively small size of the positive ions which bind the overall structure. In this situation, where there is no relationship between ion sizes and lattice constants, what would otherwise be an exact symmetry of the lattice is disrupted and the modulation of the basic rotational instability, produced by coupling between molecular units, which shows maximum instability will most probably be incommensurate with the basic lattice.

Ferroelectrics, 1990, Vol. 111, pp. 43–47
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AB INITIO SIMULATIONS OF PHASE TRANSITIONS IN KNO_3

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(Received February 4, 1990)

We report a first-principles simulational study of phase transitions in KNO_3, using our recently developed method to treat ionic molecular solids. With the inter- and intra-molecular potentials calculated from *ab initio* electron charge densities of the ions, our structural static relaxation gave good fits to both the normal room temperature (α-phase) and the ferroelectric (γ-phase) structures. Our molecular dynamics simulations with a supercell containing 540 ions closely reproduced the transition from the α-phase to the high temperature disordered β-phase.

PHYSICAL REVIEW B VOLUME 42, NUMBER 13 1 NOVEMBER 1990

Ab initio studies of the phase transitions in K_2SeO_4

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(Received 18 June 1990)

An *ab initio* model is developed for the potentials in ionic molecular solids in which the electron covalency within the molecular ions substantially affects the interionic interactions. By treating the intermolecular and intramolecular interactions on the basis of the true electron charge densities of the molecular ions, this new model leads to an accurate parameter-free description of the potential-energy surfaces for such crystals. We performed first-principles static structural relaxation, supercell molecular-dynamics simulation, and lattice-dynamics studies for the room-temperature paraelectric phase and the lower-temperature ferroelectric superstructure of K_2SeO_4 and predicted with good accuracy the transition from the former to the latter. Given the excellent agreement between theory and experiment, we then explored the delicately balanced potential-energy surfaces for K_2SeO_4 and found that they contain a double-well type of structure which is the essential origin of the incommensurate and the subsequent commensurate transitions in K_2SeO_4.

Ferroelectrics, 1991, Vol. 117, pp. 53–61
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THE PRINCIPLE OF LATENT SYMMETRY - BASIC ORIGIN OF INCOMMENSURATE PHASE TRANSITIONS IN INSULATORS

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(Received July 24, 1989; in final form November 1, 1989)

Abstract A general exposition of the principle of latent (hidden) symmetry as the origin of incommensurate phases in insulators is presented. It is demonstrated that such a symmetry can cause transitions to an incommensurate and imperfect helical structure. It is also shown how such general consideration of the lattice potential function can elicit the possibility of long-period superlattices due to a higher symmetry being broken locally by the point groups of molecular ions.

PHYSICAL REVIEW B VOLUME 43, NUMBER 7 1 MARCH 1991

First-principles study of the lattice dynamics of K_2SO_4

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(Received 20 July 1990)

Using a newly developed first-principles approach to simulations of ionic molecular crystals, we performed static relaxation, molecular-dynamics simulation, and lattice-dynamics calculations, and measurements of the Raman spectrum, for the *Pnam* structure of K_2SO_4. It was found that the structure does not have the zone-center instability present in isomorphous K_2SeO_4 found in an earlier study. This difference between the two systems is attributed to the different charge distributions in the molecular ions. The calculated Raman-active zone-center frequencies for the *Pnam* structure of K_2SO_4 were found to be in general agreement with the experimental Raman frequencies.

PHYSICAL REVIEW B VOLUME 44, NUMBER 14 1 OCTOBER 1991-II

First-principles study of phase transitions in KNO_3

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(Received 21 December 1990; revised manuscript received 20 May 1991)

We report a first-principles simulation study of phase transitions in KNO_3, using our recently developed method for treating ionic molecular solids. With the interionic potentials calculated from *ab initio* electron charge densities of the ions, our structural static relaxation gave close fits to both the normal room-temperature (α-phase) and the ferroelectric (γ-phase) structures. Our supercell molecular-dynamics calculations closely simulated the transitions from the α phase and γ phase to the high-temperature disordered β phase, and successfully reproduced the abnormally large c-axis thermal expansion observed in experiment. Both transitions were found to be initiated by the rotations of the nitrate ions about their triad axes parallel to the c axis. Our lattice-dynamics calculations in the spirit of the quasiharmonic approximation revealed that these rotations are intimately connected to the large c-axis thermal expansion, and both of them derive from the strong anharmonicity in the system.

PHYSICAL REVIEW B
CONDENSED MATTER

THIRD SERIES, VOLUME 45, NUMBER 14 1 APRIL 1992-II

Simulations of phase transitions in Rb_2ZnCl_4

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(Received 30 August 1991)

Structural relaxations, molecular-dynamics simulations, and lattice-dynamics calculations were performed to study the phase transitions in Rb_2ZnCl_4, using intermolecular and intramolecular potentials generated from *ab initio* quantum-chemistry calculations for the whole molecular ion $ZnCl_4^{2-}$. Compared with an earlier treatment of the system by a polarizable-ion model, the present approach emphasizes the static effect of the electron covalency within the molecular ions that affects strongly both the intermolecular and intramolecular interactions. The calculations gave a close agreement with experiment on the static structures of the *Pnam* and the $Pna2_1$ phases and the transition temperature from the former to the latter. For the lower-temperature, monoclinic phase of Rb_2ZnCl_4, the detailed structure of which is unknown, our simulations predict a structure with *C*1*c*1 space-group symmetry, which doubles the $Pna2_1$ structure along both the b and c axes and thus has 48 formula units per unit cell. The lattice-dynamics calculations for the $Pna2_1$ structure clearly revealed the lattice instability responsible for the $Pna2_1$-monoclinic transition and provided a more convincing explanation of a previous Raman measurement. We have shown that the potential-energy surface in Rb_2ZnCl_4 pertinent to the phase transitions contains a double-well structure, very similar to that of K_2SeO_4, except that the double well is much deeper, causing the much more severe disordering in the *Pnam* structure of Rb_2ZnCl_4 observed experimentally.

PHYSICAL REVIEW B VOLUME 46, NUMBER 10 1 SEPTEMBER 1992-II

Lattice- and molecular-dynamics studies of phase transitions in $CsLiSO_4$

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(Received 28 February 1992)

We report results of a simulation of the phase transitions in $CsLiSO_4$. These are based on our previously developed method for calculating parameter-free potential-energy surface for ionic molecular crystals. Our lattice-dynamical and molecular-dynamics studies show that the room-temperature (*Pncm*) phase is unstable and transforms to the observed low-temperature ($P112_1/n$) phase over approximately 200–280 K. The unstable modes of the *Pncm* phase have maximum instability at the zone center, which indicates a possible phase transformation without a cell multiplication. The rotational ordering of tetrahedral SO_4^{2-} was found to be the driving mechanism of these phase transitions. The quality of the agreement between theoretical and experimental structural parameters and transition temperatures confirms that our potentials for Li^+ containing sulfates are of comparable accuracy to those for other alkali sulfates.

PHYSICAL REVIEW B VOLUME 46, NUMBER 13 1 OCTOBER 1992-I

Brief Reports

Brief Reports are accounts of completed research which, while meeting the usual **Physical Review** *standards of scientific quality, do not warrant regular articles. A Brief Report may be no longer than four printed pages and must be accompanied by an abstract. The same publication schedule as for regular articles is followed, and page proofs are sent to authors.*

Phase transitions in K_2ZnCl_4

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(Received 16 March 1992)

It is shown that the potential-energy surface in K_2ZnCl_4 contains a double-well structure, very similar to some of the other A_2BX_4 compounds (e.g., K_2SeO_4, Rb_2ZnCl_4), except that the double well is much deeper and broader, giving rise to a highly disordered high-temperature phase as observed experimentally. A lattice-dynamics study of the $Pnc2_1$ structure shows an instability with the wave vector $q=0.5b^*+(0.5\pm\delta)c^*$, providing an explanation to the incommensurate phase transition reported recently.

Ferroelectrics
(in press)

DOUBLE-WELL POTENTIAL ENERGY SURFACES IN Cs_2CdBr_4 and Cs_2ZnI_4

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W.M. Mei, Department of Physics, University of Nebraska-Omaha, Omaha, NE 68182

Abstract. We discuss the apparently anomalous behavior of the Pnam structure A_2BX_4 compounds Cs_2CdBr_4 and Cs_2ZnI_4. At least for the former, it appears that while its first structural transformation is to an incommensurate phase, modulated along $\vec{a}$, it subsequently "locks in" to a $\vec{q}=0$ modulation leaving the periodicity along $\vec{a}$ *unchanged*. We address this problem using lattice dynamics, and computer molecular dynamics (CMD) employing parameter-free Gordon-Kim potentials. These appear to reproduce the transition temperatures in Cs_2CdBr_4, although the lowest temperature transformation remains ambiguous. We argue that the failure to form a tripled superlattice along $\vec{a}$ reflects the fact that the incommensurate modulation is almost midway between $\vec{q} = 0$ and $\vec{q} = \frac{\vec{a}^*}{3}$. Thus, given the substantially lower static energy of the $\vec{q} = 0$ modulation, the system favors the latter.

Ferroelectrics
(in press)

FIRST-PRINCIPLES STUDY OF PHASE TRANSITIONS IN THE $ALiSO_4$ (A = K, Rb, Cs)

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Abstract The lithium alkali metal double sulfates display a rich variety of structural instabilities.[1] We have recently reported the results of a first-principles (parameter free) study of $CsLiSO_4$, which has the simplest phase diagram.[2] We were able to reproduce the basic instability in this system by our Gordon-Kim Quantum-Chemistry approach.[3] Further, we identified its origin as rotational double-well in the lattice potential energy for the sulfate rotations. The present study extends that work to cover the basic instabilities and more complex behavior of $RbLiSO_4$ and $KLiSO_4$.

FIRST PRINCIPLES THEORY OF PHASE TRANSITIONS AND INCOMMENSURATE BEHAVIOR IN A_2BX_4 COMPOUNDS

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Abstract We present a general discussion of the origins of incommensurate behavior in the compound K_2SeO_4 and its isomorphs. We present the results of lattice dynamical and computer molecular dynamics (CMD) based on *a priori* potentials derived by the Gordon-Kim technique employing molecular ion charge densities derived from a full quantum chemistry calculations. We argue, based on these results, that the tendency for these compounds to form incommensurate superlattices has an intrinsic *structural* origin and reflects an imperfect 6-fold screw axis along the Pnam $\vec{a}$ axis which produces a maximum instability for a certain modulation of the local BX_4^{2-} rotational instabilities. However, because the symmetry is not perfect, the periodicity of this maximum instability is not commensurate with the Pnam lattice. Other consequences of this "latent" symmetry are also addressed.