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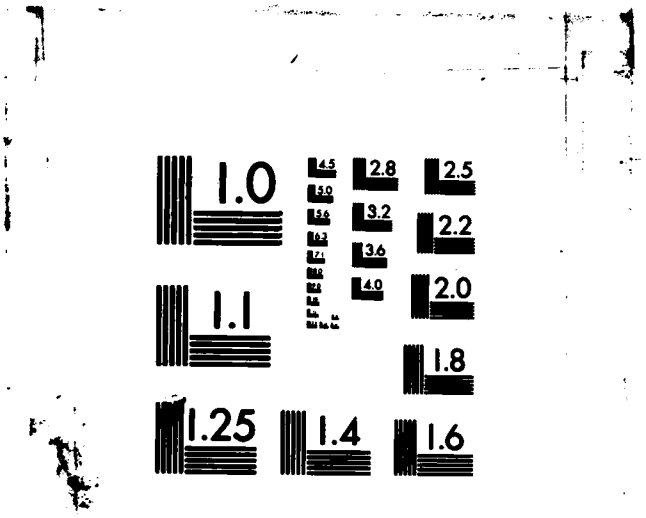

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Improper Ferroelectricity: A Theoretical and Experimental Investigation

Final Report #1

J. R. Hardy and F. G. Ullman

3 February 1984

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Department of Physics and Astronomy
University of Nebraska-Lincoln
Lincoln, NE 68588-0111

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

A combined theoretical and experimental study has been made of the origins and properties of the improper ferroelectricity associated with structural modulations of non-zero wavelengths. Two classes of materials have been studied: rare earth molybdates (specifically, gadolinium molybdate: GMO), and potassium selenate and its isomorphs. In the former, the modulation is produced by a zone boundary phonon instability, and in the latter by the instability of a phonon of wave vector approximately two-thirds of the way—>
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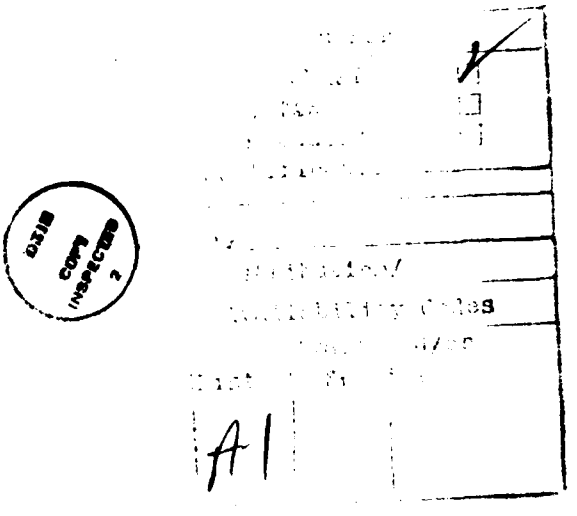
to the zone-boundary. In the second case the initial result is a modulated structure whose repeat distance is not a rational multiple of the basic lattice repeat distance. This results in a modulated polarization which, when the basic modulation "locks in" to a rational multiple of the lattice spacing, becomes uniform, and improper ferroelectricity results. The origins of these effects have been elucidated by theoretical studies, initially semi-empirical, but subsequently from first-principles. These complemented the experimental work, which primarily used inelastic light scattering, uniaxial stress, and hydrostatic pressure, to probe the balance between the interionic forces through the effects on the phonons and dielectric properties.



1. Introduction

This program was initiated in October 1976 when ARO commenced funding of our studies on the improper ferroelectric gadolinium molybdate $Gd_2(MoO_4)_3$ (or GMO). The work carried out on GMO under the present program can be regarded as the "winding up" of a major study previously funded by AFOSR.

Subsequently, we moved into studies of incommensurate phase transitions in insulators, which produce improper ferroelectricity when the associated sinusoidal modulation "locks in" by adjusting its wavelength to become commensurate with the underlying lattice, i.e., the wavelength becomes a simple multiple of the basic lattice constant.

We began by studying potassium selenate, K_2SeO_4, which, at that time, was the only system known to exhibit this behavior. As other isomorphous compounds were reported to exhibit similar behavior, we made preliminary studies of these systems, but the bulk of our effort was absorbed by extensive studies on K_2SeO_4 as it was found to have increasingly rich and complex behavior. Valuable insight into this was provided by a theoretical study on rubidium calcium trifluoride, $RbCaF_3$, which provided a first-principles understanding of the structural instability in this simpler system. From this, certain general principles emerged regarding instabilities in systems containing molecular groups which we were able to apply to K_2SeO_4.

Our final major piece of work during this funding period was the development of a new model for the behavior of GMO which appears to provide a unified explanation for a wide range of puzzling anomalies, some reported

by others and some by ourselves, which hitherto have defied explanation. In a very direct sense, this is the true conclusion of our work on GMO, since it follows very directly from our earlier work on this system where we reported the first observation of a second soft mode, apparently associated with the transition from the low-temperature (improper ferroelectric) phase to the high-temperature (paraelectric) phase.

2. Nature of the Studies

Our program is a combined experimental and theoretical effort, the former employing principally inelastic light-scattering techniques, and the latter principally involving detailed lattice-dynamical calculations for complex structures.

In order to provide a brief but adequate overall description of our work, each major aspect of the work will be described separately by an introductory summary followed by the abstract(s) of our major papers in that area.

2.1 Studies on GMO

These consist of our earliest ARO-sponsored work on the Raman scattering from this system, in which we identified the presence of two apparent soft modes associated with the phase transition from the ferroelectric to the paraelectric phase, and our most recent work in collaboration with Dr. Jan Petzelt of the Czechoslovak Academy of Sciences, which advances a unified theory of the structural instability in this system. They are described more fully in the following two abstracts:

...AL REVIEW B VOLUME 18, NUMBER 7 (p.3579) 1 OCTOBER 1978

Anomalous damping of phonons in ferroelectric $Gd_2(MoO_4)_3$

Q. Kim* and F. G. Ullman
Behlen Laboratory of Physics, University of Nebraska, Lincoln, Nebraska 68588
(Received 21 April 1978)

Measurements of the A_1 Raman spectrum of ferroelectric $Gd_2(MoO_4)_3$ as a function of uniaxial stress up to about 1.5 kbar at temperatures near the 433-K transition T_0 and as a function of temperature from 20 to 523 K, have provided new information about the anomalously damped lines peaking at about 50 and 75 cm^{-1} at 300 K. The force-constant parameter ω_0 of the 75-cm^{-1} line is independent of stress whereas its damping constant Γ decreases with increasing stress as found previously for the 50-cm^{-1} line. No other lines are observed to be stress dependent in this stress range. The stress dependences of the 50- and 75-cm^{-1} lines are identical. An analysis of the integrated intensities at zero stress from 80 to 523 K showed all lines except the two at 50 and 75 cm^{-1} to approximate the expected Bose-Einstein temperature dependence. The 50- and 75-cm^{-1} lines damp anomalously on heating; their integrated intensities go through maxima near 320 K. At 15 K, the 75-cm^{-1} line splits into a doublet with 81- and 83-cm^{-1} peaks, similar to the known splitting of the 50-cm^{-1} line below 300 K into 44.5- and 51.5-cm^{-1} peaks. Only two lines below T_0 are allowed by symmetry to correlate with the "soft" doubly degenerate zone-boundary phonons of the paraelectric phase. Since in these measurements none of the lines "soften" significantly with increasing temperature or "harden" with increasing stress, the identities of the "soft" phonons in the ferroelectric phase remain undetermined.

CENTRAL PEAK-SOFT MODE COUPLING IN FERROELECTRIC $Gd_2(MoO_4)_3$

J. Petzelt and F. Smutný

Institute of Physics, Czech. Acad. Sci.

I8200 Prague 8, Na Slovance 2, Czechoslovakia

V. Katkanant, F. G. Ullman and J. R. Hardy

Department of Physics, University of Nebraska

Lincoln, Nebraska 68588-0111

and

A. A. Volkov, G. V. Kozlov and S. P. Lebedev

Institute of General Physics, Acad. Sci. U. S. S. R.

117 942 Moscow, Ul. Vavilova 38, U..S. S. R.

ABSTRACT

Transmission measurements on $Gd_2(MoO_4)_3$ in the 5-50 cm^{-1} region were performed using tuneable backward-wave oscillator sources (5-30 cm^{-1}) and a Fourier spectrometer (30-50 cm^{-1}). The resulting dielectric spectra show an additional low-frequency dispersion which was fitted to a standard central peak model. Its characteristic relaxation frequency is $\sim$20 cm^{-1} and the coupling between the soft mode and central mode increases near the transition temperature. This model also accounts very well for the weak anomaly in the clamped permittivity ε_c measured at 63 MHz. The same central mode was used to fit earlier Raman soft-mode spectra. All of these data were fitted to a three coupled-mode model which revealed that the soft mode spectrum consists of two strongly coupled bare modes: a higher frequency mode which softens and carries the entire Raman strength and a lower frequency mode which is hard (59 cm^{-1}) and Raman-inactive. Both these modes are also coupled to the central mode and this coupling increases sharply near the transition. This model is consistent with all existing experiments. The relatively large width of the central mode indicates its intrinsic nature and suggests partial disorder near the transition.

2.2 Theoretical Work on K_2SeO_4

The initial object of this work was to develop a lattice-dynamical model for this complex structure which would trace the origins of the incommensurate (modulation) instability to a balance between the interionic forces. This was successful as is described in more detail in the following abstract:

PHYSICAL REVIEW B VOLUME 21, NUMBER 1 (p.245) 1 JANUARY 1980

Theoretical lattice-dynamical studies of the incommensurate phase transformation in K_2SeO_4

M. S. Haque* and J. R. Hardy†
Behlen Laboratory of Physics, University of Nebraska, Lincoln, Nebraska 68588
(Received 7 May 1979)

We have made detailed lattice-dynamical studies of the origin of the incommensurate phase transition in potassium selenate. These were based on a rigid-ion model with Coulomb interactions, and also short-range interactions between restricted numbers of close neighbors. The associated short-range force constants were determined using the static equilibrium conditions for the crystal and the observed Raman frequencies. The calculations were made for the room-temperature structure using the quasiharmonic approximation in which the effects of varying temperature were simulated by varying the short-range force constants. In this way we were able to show that the crystal has a low-frequency optic branch of Σ_2 symmetry which displays softening and instability for wave vectors $\vec{q}$ in the vicinity of $\vec{q}=0.3\vec{\tau}^*$ where $\vec{\tau}^*$ is the first reciprocal-lattice vector along the [100] direction. This is in agreement with experimental neutron scattering results and implies a transition to an incommensurate phase. Full sets of dispersion curves at 130 K for the [100] direction are presented. We also present comparisons of the calculated and experimental low-frequency Σ_2 and Σ_3 branches at 130, 145, and 250 K. We show, by decomposition of the squares of the normal-mode frequencies into a sum of Coulomb and short-range components, that the balance between these two kinds of interatomic forces is very delicate. This decomposition also shows that a transition to an incommensurate phase is very likely for both the selenate and isomorphous structures. Our model also enables us to predict that uniaxial stress will rapidly depress the transition temperature; a result also in accord with experiment.

2.3. Studies of Stress and Pressure Effects

As the last abstract explains, we found that the balance between the interionic forces was very delicate, suggesting (as preliminary experimental work had demonstrated) that the transition temperature could be markedly

altered by the application of both uniaxial stress and hydrostatic pressure. This led to a series of experiments designed to examine the stress and pressure dependence of both the incommensurate and commensurate transition temperatures. In the course of this work, two collaborations were developed, one with Dr. J. D. Axe, at Brookhaven National Laboratory, in which neutron scattering measurements were used to probe the effects on the transition temperature of relatively low hydrostatic pressures, and one with Dr. G. Samara at Sandia Laboratories, in which dielectric measurements were used, to extend the range of pressures to much higher levels. The highest pressure used was sufficient to suppress the commensurate transition entirely.

This work is described in the following abstracts, along with our own most recent studies in which Raman scattering measurements of the peak frequency of the soft mode were used to monitor the effect of uniaxial stress on the incommensurate transition temperature.

PHYSICAL REVIEW B VOLUME 22, NUMBER 1 (p.332) 1 JULY 1980

Effect of hydrostatic pressure on the incommensurate phase of K_2SeO_4

W. Press
Brookhaven National Laboratory, Upton, New York 11973
and Institut für Festkörperforschung der Kernforschungsanlage, Jülich, West Germany

C. F. Majkrzak and J. D. Axe
Brookhaven National Laboratory, Upton, New York 11973

J. R. Hardy, N. E. Massa, and F. G. Ullman
University of Nebraska-Lincoln, Lincoln, Nebraska 68588
(Received 12 February 1980)

A neutron scattering study of the effect of hydrostatic pressure on the incommensurate phase transformation in K_2SeO_4 was performed in order to obtain information concerning the nature of the competing forces that give rise to a structural instability at a general wave vector. It was found that an increase in pressure lowers the transition temperature ($dT_i/dP_i = -6.5$ K/kbar) and results in a smaller value of the initial incommensurate wave vector. The pressure dependence of the incommensurate to ferroelectric phase transition was also investigated ($dT_c/dP_c = -9$ K/kbar). The latter transition displays a distinct pressure hysteresis.

Ferroelectrics, 1981, Vol. 36, pp. 335-338
0015-0193/81/3601-0335/$06.50/0

VANISHING OF THE PHASE TRANSITIONS AND QUANTUM EFFECTS IN K_2SeO_4 AT HIGH PRESSURE

G. A. SAMARA*
Sandia National Laboratories†, Albuquerque, New Mexico 87185, U.S.A.
N. E. MASSA and F. G. ULLMAN**
University of Nebraska, Lincoln, Nebraska 68588, U.S.A.

Abstract-The effects of pressure on the dielectric properties and phase transition in K_2SeO_4 were investigated. The incommensurate-to-commensurate ferroelectric transition vanishes at 0.73 GPa, and the paraelectric-to-incommensurate transition is expected to vanish at $\sim$ 1.13 GPa. These large pressure effects can be understood in terms of the delicate balance between Coulomb and short-range interactions. The results show the increased influence of quantum effects on approaching the displacive limit (i.e. T_c = 0 K), and they confirm the existence of a γ = 2 regime in the temperature dependence of the susceptibility, as predicted by recent theories.

Solid State Communications, Vol.42, No.3, pp.175-178, 1982.
Printed in Great Britain.

0038-1098/82/150175-04$03.00/0
Pergamon Press Ltd.

UNIAXIAL STRESS DEPENDENCE OF THE INCOMMENSURATE PHASE TRANSITION IN K_2SeO_4*

N. E. Massa, F. G. Ullman**, and J. R. Hardy

Behlen Laboratory of Physics, University of Nebraska, Lincoln, Nebraska 68588-0111

(Received 16 November 1981 by A. A. Maradudin)

The effect of uniaxial stress along the orthorhombic "c" axis of K_2SeO_4 crystals (c<a<b) on the peak frequency of the soft "amplitude" mode has been measured by Raman scattering at 82, 93, 97 and 105 degK. (The ferroelectric transition is at T_c = 93K and the incommensurate transition is in the range T_i = 125-130K, at zero stress.) The change in T_i with stress is estimated by extrapolation of isobaric Curie-Weiss plots of the square of the amplitude mode peak frequency, ω_b^2, vs. T. T_i is found to decrease with stress along the "c" axis at a rate of about -40 ± 10 degK/kbar, a value that is much larger than the -6.5 degK/kbar found with hydrostatic pressure. The Curie-Weiss plots show significant sub-linear deviations at their low temperature ends. The stress range was limited to below 300 bars; above 300 bars, the crystals yielded.

2.4 Raman Scattering Studies

Our major achievement in this area was a definitive determination of all the Raman spectra of K_2SeO_4. In particular, our examination of the high frequen. regi. of these spectra led us to postulate that the selenate

groups are orientationally disordered above the incommensurate transition (and possibly below). Recent Japanese work on the structure of isomorphous Rb_2ZnCl_4 has demonstrated such disorder to exist in this system where it is quite large, and thus easier to detect.

The following abstract describes our K_2SeO_4 work:

PHYSICAL REVIEW B VOLUME 27, NUMBER 3 (p.1523) 1 FEBRUARY 1983

Interpretation of anomalies in the Raman spectrum of K_2SeO_4 in terms of oxygen sublattice disorder

Nestor E. Massa
Behlen Laboratory of Physics, University of Nebraska, Lincoln, Nebraska 68588

Frank G. Ullman
Behlen Laboratory of Physics and Department of Electrical Engineering, University of Nebraska, Lincoln, Nebraska 68588

J. R. Hardy
Behlen Laboratory of Physics, University of Nebraska, Lincoln, Nebraska 68588
(Received 29 December 1981; revised manuscript received 25 May 1982)

Raman scattering from K_2SeO_4 crystals has been studied in the (20—800)-K temperature range. Three portions of the spectrum are discussed: defect-induced scattering, primarily below 100 cm^{-1}, the external mode spectrum below 200 cm^{-1}, and the internal mode spectra in two regions, 300—500 and 800—950 cm^{-1}. The temperature dependence of the low-frequency, defect-induced scattering has been correlated (in previous studies) with the temperature dependence of certain nonzero-wave-vector phonons that have been observed by others using inelastic neutron scattering. Close to the incommensurate transition temperature, $T_i = 129$ K, a large enhancement and line narrowing develops below 10 cm^{-1}; no satisfactory interpretation of this effect has yet emerged. Above 129 K, in the paraelectric phase, the multiplicity of the external modes agrees with the predictions of the Raman-scattering selection rules. The internal mode spectra, however, consistently contain more lines than prescribed by the selection rules. These observed internal mode spectra would have the correct multiplicity if the crystal did not possess the center of symmetry of the presumed *Pnam* space group, thus suggesting a distortion of the selenate sublattice. Small frequency shifts above 375 K in the external mode spectra are similar to those observed in the incommensurate phase and, also, differential thermal analyses of powders and crystals show small, diffuse, reproducible peaks in the (373—473)-K range. Both effects may be associated with glasslike phase changes in the selenate sublattice. A qualitative model of orientational disorder in the selenate sublattice is offered to account for all these observations.

2.5 Theoretical work on $RbCaF_3$

This work, whose results markedly influenced our understanding of the Raman spectra of K_2SeO_4, was a collaborative effort with Dr. L. L. Boyer

of the Naval Research Laboratory which built on his success in developing parameter-free equations of state for the alkali halides. It represented a major extension of the formalism to handle the more complex lattice distortions associated with the cooperative rotations of the CaF_6 octahedra which are responsible for the structural phase transition in this system. $RbCaF_3$ was chosen as the trial system for two reasons: it was the system about which most was known experimentally, and, more importantly, good free ion wave functions existed for all the constituents, thus making possible accurate interionic potential calculations for all pairs of ions.

The following abstract describes the salient conclusions:

PHYSICAL REVIEW B VOLUME 24, NUMBER 5 (A2527) 1 SEPTEMBER 1981

Theoretical study of the structural phase transition in $RbCaF_3$

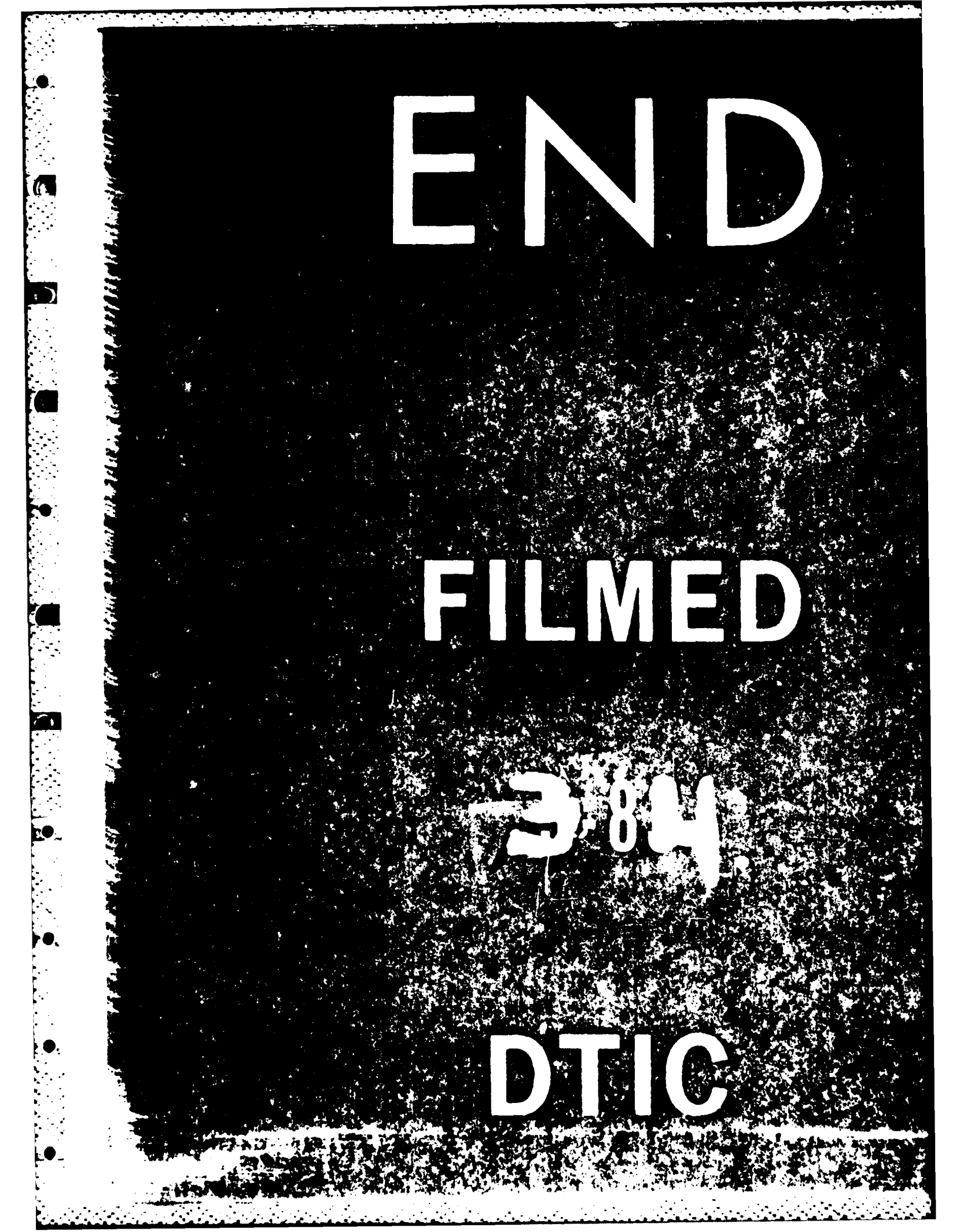
L. L. Boyer
Naval Research Laboratory, Washington, D. C. 20375

J. R. Hardy
Department of Physics, University of Nebraska, Lincoln, Nebraska 68588
(Received 18 May 1981)

We have made a first-principles study of the structural phase transition at $T_c = 193$ K in $RbCaF_3$, using interionic potentials derived by the Gordon-Kim approach, and a new extension of the quasiharmonic approximation for the free energy. The transition is caused by instability of a triply degenerate R-point vibration which leads to a coordinated rotation of the CaF_6 octahedra. We find that, as the lattice contracts, the quasiharmonic frequency of the R-point vibrations becomes imaginary at approximately 1280 K: Below this temperature the *static* lattice energy, as a function of CaF_6 rotation, has a double minimum. However, the quasiharmonic *free energy* has no minimum for finite rotations until $T \lesssim 125$ K. Thus the present theory predicts that $T_c \cong 125$ K (cf $T_c = 193$ K, experimental). In the region between 125 and about 1280 K "nests" of modes about the zone edges have imaginary quasiharmonic frequencies. By a simple extension of the quasiharmonic theory their contribution to the free energy has also been included. We also predict that the melting temperature is approximately 1350 K, which agrees very well with the measured value of 1382 K. However, the predicted thermal expansion of the perovskite phase at room temperature is ~17% *lower* than the observed value. This leads us to argue that the good agreement between theoretical and experimental melting temperatures is, in part, due to a cancellation between neglected anharmonic effects and certain deficiencies in the interionic potentials. We also find that, for the tetragonal phase, the calculated c/a ratio and rotation angle for the CaF_6 octahedra which minimize the static energy are in good agreement with measured values at low temperature. We also discuss certain more general implications of the present work. Specifically, we suggest that our results indicate that it may be more natural to regard the structural phase transition as arising from the "unfreezing" of the distortion associated with the lower-symmetry phase. Our results also provide a natural explanation for the apparently universal tendency of transition temperatures for zone-boundary instabilities to be raised by hydrostatic stress.

3. Conclusions

During the present funding period we have, by means of our joint experimental and theoretical studies, proceeded from an initial situation where we had a limited understanding of the structural transition in one complex system (GMO), based on limited experimental data and semi-empirical theory, to the point where we are now predicting and explaining from first principles a much wider range of observations for a general class of systems. We now have the ability to study the whole range of structural instabilities which are possible when displacement patterns of non-zero wavelengths become unstable: of these, the transition in GMO is just one special case; incommensurate transitions, as typified by the behavior of K_2SeO_4, are of a much more general nature and offer the possibility of a rich diversity of new physical phenomena whose scientific and technological implications have yet to be explored.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