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Brillouin scattering and birefringence in K_2SeO_4 under uniaxial stress and a molecular dynamics simulation of K_2NiF_4 structure compounds

Billesbach, David Paul, Ph.D.

The University of Nebraska - Lincoln, 1987

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PREVIEW

BRILLOUIN SCATTERING AND BIREFRINGENCE IN K_2SeO_4

UNDER UNIAXIAL STRESS

AND

A MOLECULAR DYNAMICS SIMULATION OF K_2NiF_4

STRUCTURE COMPOUNDS

by

David P. Billesbach, Ph.D.

A DISSERTATION

Presented to the Faculty of

The Graduate College in the University of Nebraska

In Partial Fulfillment of Requirements

For the Degree of Doctor of Philosophy

Major: Physics and Astronomy

Under the Supervision of Professor Frank G. Ullman

Lincoln, Nebraska

December, 1987

TITLE

Brillouin Scattering and Birefringence in K_2SeO_4 Under
Uniaxial Stress and A Molecular Dynamics Simulation of
 K_2NiF_4 Structure Compounds

BY

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BRILLOUIN SCATTERING AND BIREFRINGENCE IN K_2SeO_4
UNDER UNIAXIAL STRESS

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David Paul Billesbach Ph.D.

University of Nebraska, 1987

Advisor: Frank G. Ullman

This dissertation contains two sections. The first deals with uniaxial stress effects on K_2SeO_4 . This material is known to undergo a structural phase change at 129K to an incommensurately modulated structure. We have studied this transition with the techniques of optical birefringence and Brillouin scattering under uniaxial stress. In the birefringence experiment we have measured the dependence of the transition temperature on stress for all three unique axes. In the Brillouin scattering experiment, we have demonstrated that at the phase transition, certain of the third-order elastic constants show anomalous behavior which is possibly related to the anharmonic properties of the lattice.

In the second part is a theoretical simulation of the A_2BX_4 layered perovskite-like compounds. In particular Rb_2CaCl_4 was examined. This family of compounds may be thought of as being constructed from normal perovskite unit cells only with a different stacking arrangement. In recent months, this structural family has become extremely important since it is the parent structure from which the new class of high temperature superconductors comes from. The simulation was done using ab initio potentials with no adjustable parameters. Our calculations show a specific heat anomaly at 400K which corresponds to an observed pseudo-rotation of the $CaCl_6$ octahedral group. This rotation is similar to the structural phase transitions observed in the perovskite structure family. We also postulate a dynamically disordered high temperature structure for this compound. Finally, we compare our results for Rb_2CaCl_4 to similar structural studies on La_2CuO_4 .

ACKNOWLEDGEMENTS

In the course of my studies, there have been many people who either through their help, friendship, or (in many cases) both have contributed to this dissertation.

I wish to first express my thanks and love to my parents, Matt and Jean Billesbach and my sister Ann for their support, love, and understanding. It was partly their encouragement that helped get me to where I am today.

Within the Physics Department, there have been so many people who are deserving of my gratitude that I can hardly hope to mention everyone. I would like to express my deepest appreciation and thanks to my advisor Prof. Frank G. Ullman who encouraged me, supported me (both financially and morally), and occasionally gave me a much needed kick in the pants. Practically all of my work came from his original ideas. Also I would like to thank Prof. John R. Hardy. He helped me immensely in understanding the theory

behind much of the experimental work as well as providing critical support. My thanks also to Prof. Roger D. Kirby. He is one of the most insightfull and knowledgeable experimentalists that I have ever met. I also thank Prof. Toshiro Yagi without whose help, I may never have completed the construction of the scattering system. I am proud to call you all my friends.

There have also been many graduate students who have been my friends and co-workers throughout these many years, Mike and Cathy Engelhardt, Paul Edwardson, Randy Fagerquist, Kevin Aylesworth, Van Katkanant, Tom Stephen, Ken Stricklett, Don Galliardt, George Freund, and the list could go on. If I have forgotten anyone, please forgive me and accept my thanks. The whole crowd has made these the most enjoyable years of my life (so far!!)

I also thank the Physics Department as a whole for supporting me and providing me with my education. The teaching staff has been excellent. To the support and management staff, (Judy, Bev, John-Bob (or is it Bob-John?), Don F., Jean, Jo, Mary, Al, and the all of rest) many of whom I am privileged to call my friends,

thank you all for having made my life run so smoothly.
Also thanks to Paul, LeAnn, and Suzie for keeping
everything clean and nice!

I would like to thank a very special person who,
when I first came to this department, took me under his
wing and gave me his friendship and guidance. Though
he is now retired and no longer living in Lincoln, I
will never forget him or the many things that he taught
me. Thank you Mr. Menno Fast.

Lastly and most importantly, I must express my
deepest thanks and love to a very special friend,
Jennifer Bauman. She suffered through the many long
nights of studying and data taking when I could not be
home. Her love, friendship, and understanding have
been my inspiration. I could never have gotten here
without you.

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PART II

Under the supervision of Prof. John R. Hardy

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CHAPTER 1

K_2SeO_4 is a member of a class of crystals which in some temperature range are isomorphous to $\beta-K_2SO_4$. This compound exhibits a rich and interesting variety of phases (see Fig. 1). The highest temperature phase, which exists between melting and $745K^1$ has hexagonal symmetry and belongs to the space group $P6_3/mmc^2$. Between the temperatures of $745K$ and $129K^3$ the crystal is in the orthorhombic $\beta-K_2SO_4$ structure with symmetry $Pnam^4$ ($c < a < b$). From $129K$ down to $93K$, K_2SeO_4 exhibits a structurally incommensurate phase⁵ where the lattice is modulated by the wave vector:

$$\vec{q} = (2\pi(1-\delta)/3a^*, 0, 0)$$

The modulation parameter δ decreases with temperature through this phase and goes to zero discontinuously at $93K$. At this temperature, the structure assumes the

Phases of K_2SeO_4

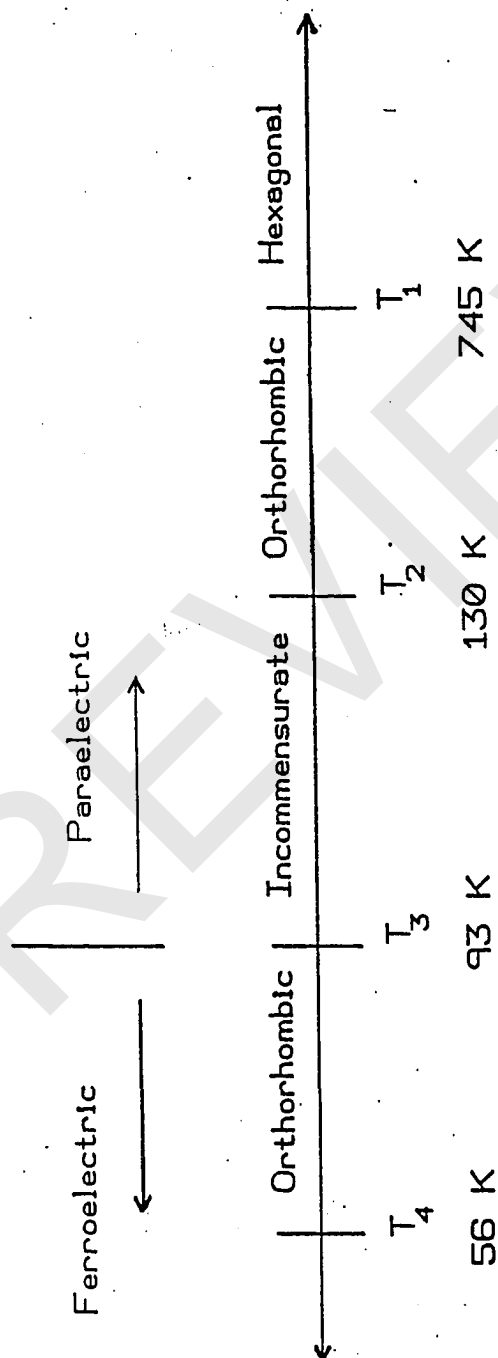


Fig. 1

$Pna2_1$ symmetry and becomes ferroelectric with the spontaneous electrical polarization along the c axis. There is specific heat evidence for another structural phase transition at $56K^6$, however no structural data for this phase is available.

The feature that makes K_2SeO_4 particularly interesting is its broad, relatively low temperature, incommensurate phase. The transition from the room temperature structure to this phase is driven by the softening or condensing of a Σ_2 symmetry optical phonon. Among the members of this group of crystals, K_2SeO_4 is particularly well suited for studies of the incommensurate phase and as such has received much attention^{7,8,9}. The reason for this is the relatively low incommensurate transition temperature of K_2SeO_4 (129K vs. 306K for Rb_2ZnCl_4 for example). The lower transition temperature means that there will be much less thermal broadening of the Raman and Brillouin lines and they can be observed with greater precision.

There has been some work done on K_2SeO_4 as a function of hydrostatic pressure^{10,11,12} and to a lesser extent, under uniaxial stress^{13,14,15}. One fact that emerges from this body of work is that the

transition temperatures (at least the normal to incommensurate and the incommensurate to ferroelectric) change with pressure or stress. In the case of hydrostatic pressure, this result can be viewed in the most elementary terms, by considering the change in internal energy at the transition temperature due to the structure change. If we call this energy change ΔU , we can write it as:

$$\Delta U = P\Delta V + T_1 \Delta S$$

The change in internal energy ΔU associated with the structural change is only a function of the ionic positions, it is therefore independent of P and T and will be the same regardless of what temperature and pressure the phase transition occurs at. Similar statements can be made about ΔV and ΔS . It is therefore obvious that as P increases, T_1 must decrease. The case of uniaxial stress is not as simple. Under uniaxial stress, the crystal has much more freedom to deform and dissipate energy in processes that are not associated with the phase transition. Unfortunately, there has been no complete uniaxial stress study of either phase transition. In the same vein this suggests that the elastic properties