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Birefringence measurements of the uniaxial-stress dependence of the incommensurate phase transition in K$_2$SeO$_4$

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The uniaxial-stress dependence of the incommensurate-phase-transition temperature (at 130 K) in K$_2$SeO$_4$ was measured along all three crystal axes by observation of the anomalies in the birefringence caused by the structure change. The results for the c-axis-stress dependence (-17.0 ± 0.2 K/kbar) agree with previous studies of other workers. This experiment has also provided the first direct measurements of the a-axis- and b-axis-stress dependences ($+3.1\pm0.2$ K/kbar and $+7.7\pm0.2$ K/kbar, respectively). Also, a value of -6.2 ± 0.3 K/kbar was calculated from these data for the dependence of the transition temperature on hydrostatic pressure. This is in agreement with hydrostatic-pressure measurements and thus confirms the reliability of the uniaxial-stress results.

INTRODUCTION

Potassium selenate at room temperature is an isomorph of the β-phase potassium sulfate structure. This crystal undergoes a series of interesting phase transitions and hence has been the subject of many studies.[1] Between the temperatures $T_2=129.5$ K and $T_3=93$ K, K$_2$SeO$_4$ exists in a structurally incommensurate phase.[2] Above T_2, and up to $T_1=745$ K, where it transforms to a hexagonal, disordered phase, it is a paraelectric substance of orthorhombic symmetry with space group *Pnam*. At T_2, the a-axis lattice constant ($a=7.66$ Å, $b=10.47$ Å, and $c=6.00$ Å at 20 °C) almost triples and a superlattice develops whose periodicity is related to the paraelectric a-axis lattice constant by $a'=3(1-\delta)a$ where δ is a small, temperature-dependent quantity that describes the incommensuration.[3] The parameter δ decreases with temperature until finally, at T_3, it goes to zero discontinuously and the structure again becomes commensurate with $a''=3a$. Also at T_3 the crystal develops a spontaneous polarization along the c axis. This ferroelectric phase is also of orthorhombic symmetry with space group *Pna*2. Recently another phase transition has been identified at $T_4=56$ K.[4]

To understand fully the driving mechanisms of these structural transitions, it is necessary to know the binding forces in detail. Toward this end, much work has been done on the dependence of the transition temperatures on external agents, most notably, hydrostatic pressure.[5–7] The hydrostatic-pressure dependences of the transition temperatures should yield information about the bulk compressibility of the crystal. More complete information, however, will be obtained by measuring the uniaxial-stress dependences of the transition temperatures.[8–10] This type of measurement separates the compressibility into three unique components along the three crystal axes and can also yield information about the stress dependence of the elastic constants. Also, from the uniaxial-stress values, one should be able to calculate the

hydrostatic-pressure dependence of the transition temperature. In this work, we look only at the stress dependence of the incommensurate transition temperature T_2 since birefringence changes are not observed at T_3.[11]

The most extensive work in this area has been done under hydrostatic pressure. As can be seen from Table I, most of the values for the hydrostatic-pressure dependence of T_2 fall between -6.5 and -7 K/kbar. Since there is reasonable consistency between the different methods used, we may assume that these values are reliable. When considering the reported uniaxial-stress work, it is notable that all direct experimental values are for stress along the c axis. The major reason for this is that all of these studies have determined the transition-temperature shift from Raman measurements of the shift in the soft-mode-peak frequency. The only values for the stress dependences along the a and b axes are cited in two articles[12,13] that calculate them thermodynamically.

The experiment described here was designed to address

TABLE I. Brief summary of uniaxial-stress and hydrostatic-pressure data for K$_2$SeO$_4$.

Hydrostatic pressure	
$\partial T_2/\partial P$ (K/kbar)	Method
-7.3	Dielectric constant (Ref. 5)
-6.7	Dielectric constant (Ref. 6)
-6.5	Neutron scattering (Ref. 7)
Uniaxial stress	
$\partial T_2/\partial\sigma_3$ (K/kbar)	Method
-25 ± 8	Raman scattering (Ref. 8)
-16	Raman scattering (Ref. 9)
-40 ± 10^a	Raman scattering (Ref. 10)

[a]The reported value of -40 K/kbar is now believed to be in error due to the inadvertent use of an incorrect piston area when calculating the stress on the crystal. The correct value should be -23 K/kbar.

the shortcomings of the previous uniaxial-stress work. In those Raman studies, the frequency shift of the soft amplitude mode was measured as a function of temperature for several different stresses. These data were plotted and the resulting curves were extrapolated to zero frequency shift to determine the transition temperature.[8] There are several drawbacks to this method. First, since the amplitude mode only exists in the low-temperature phases and decreases to zero amplitude at T_2, the transition temperature cannot be directly measured, it can only be estimated from an extrapolation. Second, the relationship between frequency shift and temperature is not linear, making the fit more uncertain, especially in the region very near the transition. Finally, the amplitude mode can only be observed in the aa scattering geometry. This limits the directions in which the uniaxial stress can conveniently be applied in a Raman experiment.

In contrast, birefringence measurements avoid these problems. The total birefringence of the crystal can be separated into two terms. The first term can be called the ordinary birefringence and is a continuous function of temperature through the phase transitions. This component is due to the ordinary thermal expansion of the crystal. The second term is called the spontaneous or anomalous birefringence and is due to the structure changes associated with the phase transition.[11] It is this second term which marks the transition. The anomalous component is a function of the square of the order parameter of the transition and thus has a value of zero above the transition temperature and some finite temperature-dependent value below the transition temperature. The major change in the structure and hence in the birefringence occurs at T_2; birefringence changes at T_3 have not yet been observed. We therefore associate an anomaly in the total birefringence of the crystal with the phase-transition temperature T_2 (see the analysis in the Appendix). By recording the total birefringence as a semi-continuous function of temperature, we then have a direct measure of the transition temperature.

EXPERIMENT

To measure the birefringence, a rotating-analyzer method was used in this work.[14,15] In this method, circularly polarized light is incident normal to the crystal. The exit beam is passed through an analyzer that rotates at a frequency ω. It can be shown that the intensity of the light exiting the rotating analyzer is

$$I_A \propto I_0[1 - \sin(2\omega t)\sin\delta] , \qquad (1)$$

where I_0 is the intensity of the light incident upon the crystal and δ is the phase shift between the two optical-field components vibrating along the crystal axes which are arranged in the plane perpendicular to the propagation direction. The beam exiting the analyzer is detected and a resultant signal is measured using a lock-in technique. This signal is directly proportional to the sine of the phase shift δ (as shown in Fig. 4). By measuring this signal as a function of temperature, a quasicontinuous (because of the digital instrumentation) reading of the total birefringence is obtained and therefore a direct measure of the transi-
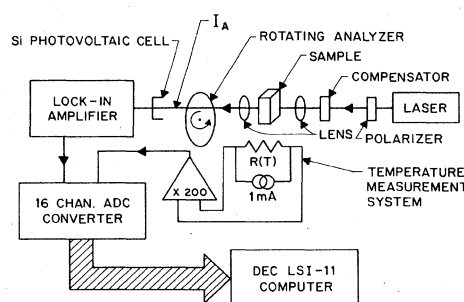

FIG. 1. Experimental setup.

tion temperature is made.

The experimental setup is shown in Fig. 1. The light source was a C.W. Radiation, Model No. LS-2R, He-Ne laser which provided a beam power of 1 mW after the polarizing optics. The first polarizer was a Polaroid sheet, oriented to produce the most intense output from the laser. The compensator (made by B. Halle of Berlin and purchased from Special Optics Co.) was of the Babinet-Soleil type and was adjusted to act as a $\lambda/4$ plate. The resulting circularly polarized beam was focused into the sample which was mounted in a stress cell, as shown in Fig. 2. The stress cell was then mounted in a standard optical cryostat. The beam exiting the crystal was collimated by a second lens and passed through the rotating analyzer. The rotating analyzer was made by replacing the main blade of a Princeton Applied Research (PAR) Model No. BZ-1 chopper with a sheet polarizer and using a two-slot reference blade. The modulated signal coming from the analyzer was detected by a silicon photovoltaic cell that was connected to the input of a PAR Model No. HR-21 lock-in amplifier.

The sample was cooled by conduction with about one atmosphere of helium gas. This, in turn, was conduction cooled through the stainless-steel wall of the inner cryostat chamber by either liqiud N_2 or by cold N_2 gas. The temperature was measured with a standard four-wire platinum resistor and a constant current source of 1 mA.

The stress cell, like the cryostat, was of our own design and construction. The body of the stress cell, which is shown in Fig. 2, was made of stainless steel. The sample
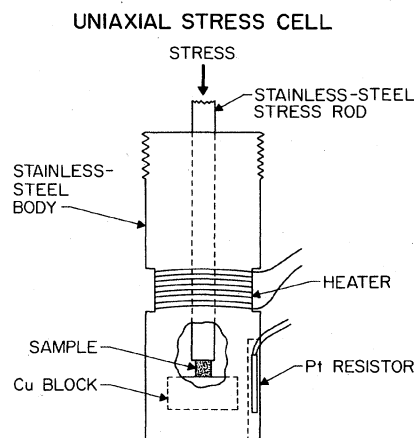

FIG. 2. Sample probe tip.

was mounted between two thin pads of indium to distribute the stress evenly. This "sandwich" rested on a copper anvil with a thin, flat piece of stainless steel between the top of the sample and the stress rod. Two coils of Wilbur B. Driver Co. Nichrome resistance wire, one above and one below the sample, were used to heat it to the desired temperature. Stress was applied to the sample by carefully placing lead weights on a pan attached to the top of the stress rod.

The birefringence signal and the temperature signal were read and recorded on floppy disks by a Digital Equipment Corporation LSI-11 microcomputer through an Analog Devices RTI 1251, 12-bit analog-to-digital converter (ADC). To remove high-frequency noise on both of the signals, the temperature and birefringence were read and averaged over the time interval that it took the instantaneous temperature to drift outside a preset interval (usually about 0.05 K). The limits of the integration interval were controlled by the computer, as were the heating and cooling rates. This effectively averaged out any noise on the inputs and extended the resolution of the ADC. When taking data, the heating and cooling rates were set to 0.5 K/min to reduce thermal gradients between the platinum resistor and the sample.

The samples used were cut from a single-crystal specimen which was grown by slow evaporation of an aqueous solution of K_2SeO_4 and supplied to us by The Institute of Physics, Czechoslovak Academy of Sciences, Prague. Three different samples were used to obtain the data. All were cut as plates about 0.8 mm thick, about 2.5 mm long, and about 2.5 mm tall. The plates were polished and their orientations were determined from their known Raman spectra.[16]

DATA AND ANALYSIS

A sample of the raw data is shown in Fig. 3. The phase transition is evident as the discontinuity in the curve, indicated by an arrow. These data can be normalized and then the arcsine function, which gives the phase shift directly, can be calculated to show the phase transition more clearly. This has been done in Fig. 4, which also shows clearly the two components of the birefringence. Since the spontaneous component of the birefringence below the transition is directly proportional to the square of the order parameter,[11] a Landau expression to the sixth
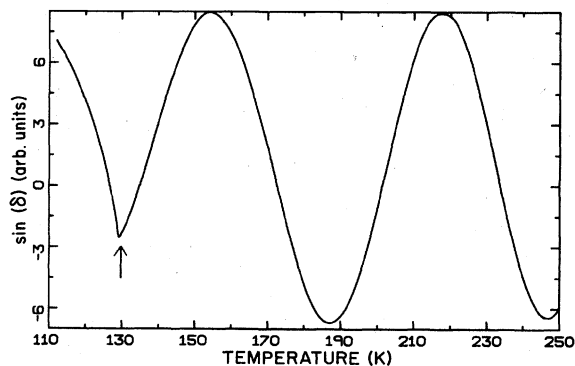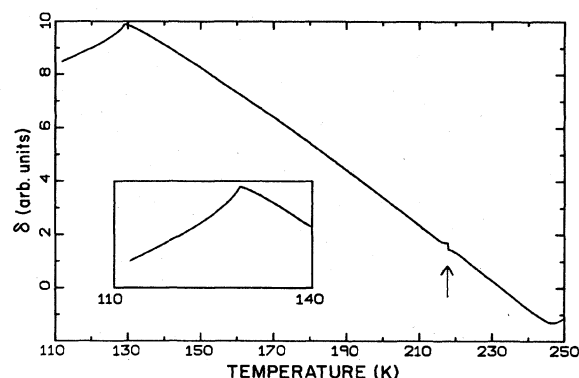

FIG. 4. Arcsine of the unstressed data showing the anomaly in the phase shift δ. The inset shows the nonlinearity of the spontaneous component of the birefringence below T_2. (The anomaly at the arrow is an artifact of the instrumentation).

order can be solved for the spontaneous birefringence which is then found to be a nonlinear function of temperature. In Fig. 4 this departure from linearity is clearly seen.

The final results of this experiment are summarized in Fig. 5 and in Table II. The transition temperatures were taken directly from the recorded data for different stresses and since the absolute calibration of the thermometer was only accurate to ±0.5 K, the temperature shift from the unstressed transition was calculated. The uniaxial-stress dependences listed in Table II are the results of a linear least-squares fit of the transition-temperature shift versus stress data. Several measurements were made (for both heating and cooling runs) with stress along the a and b axes and found to show good reproducibility (to about ±10%). Measurements with stress along the c axis, however, seemed to exhibit a stress memory. Because of this,

FIG. 3. Unstressed data showing the anomaly in the sine of the phase shift δ at $T_2 = 129$ K.
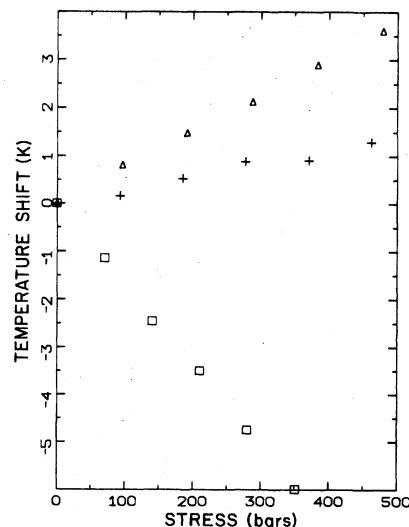

FIG. 5. Shift of the transition temperature T_2 as a function of the applied stress for all three crystal axes. (For clarity, note that not all of the data used in the line fits have been plotted.) Open squares represent the stress along c; open triangles, stress along b; crosses, stress along a.

TABLE II. Results of this work compared to the calculated results of Refs. 12 and 13.

Stress direction	$\partial T_2/\partial\sigma$ (K/kbar)		
	This work	Ref. 12	Ref. 13
a	$+3.1\pm0.2$	$+3.1$	$+3$
b	$+7.7\pm0.2$	$+7.4$	$+8$
c	-17.0 ± 0.2	-17.3	-18
Hydrostatic	-6.2 ± 0.3	-6.8	-7

only one trial (from a previously unstressed crystal) is plotted for stress along the c direction. (Additional comments on this effect are given in the conclusions.)

If we write the hydrostatic pressure as a function of the uniaxial stress σ as

$$P = \sum_j \sigma_j , \qquad (2)$$

where $j = a$, b, or c, respectively, then

$$\partial T_2/\partial P = \sum_j (\partial T_2/\partial\sigma_j)(\partial\sigma_j/\partial P) , \qquad (3)$$

where $\partial\sigma_j/\partial P = \partial\sigma_j/\partial\sum_i\sigma_i$. For a given j, we know that in the case of uniaxial stress

$$\sigma_{i\neq j} = 0 ,$$

therefore,

$$\partial\sigma_j/\partial\sum_i\sigma_i = 1 .$$

Thus, we have

$$\partial T_2/\partial P = \sum_j (\partial T_2/\partial\sigma_j) . \qquad (4)$$

From our uniaxial-stress data, we then calculate a hydrostatic-pressure dependence of

$$\partial T_2/\partial P = -6.2\pm0.3 \text{ K/kbar} ,$$

which compares favorably with the hydrostatic-pressure data reported in the literature (see Table I). The error bars for the individual data points in the graphs are too small to be plotted and the errors in the calculated slopes are therefore assumed to be due primarily to the scatter of the data points.

CONCLUSIONS

The c-axis data that were obtained in this experiment are not in disagreement with the other values reported in the literature. The birefringence data in principle should give more reliable results than the Raman measurements of the soft-mode frequency shifts since the birefringence is (1) directly proportional to the square of the order parameter, (2) measurable on both sides of the transition, and (3) does not have to be extrapolated or fitted to an assumed functional dependence to determine the transition temperature.

There are no other direct experimental measurements of the dependence of T_2 on stress along the a and b axes. The only values available for comparison with our results are the thermodynamically calculated ones[12,13] listed in

Table II. For stress along the a axis, Flerov et al. report a value of $+3.1$ K/kbar and Sannikov and Golovko state a value of $+3$ K/kbar. Both of these are in excellent agreement with our value of $+3.1\pm0.2$ K/kbar. For stress along the b axis, Flerov et al. calculate two values, $+7.4$ K/kbar from the Ehrenfest relationship and $+6.8$ K/kbar from the Pippard-Janovec relation, while Sannikov and Golovko report $+8$ K/kbar. Again these values are in very good agreement with our value of $+7.7\pm0.2$ K/kbar. It would seem that in Ref. 12, the values calculated from the Ehrenfest relationship are in better agreement with the experimental results than the ones calculated from the Pippard-Janovec relation.

Using the Ehrenfest relationship[12] for stress along the c axis, a stress dependence of -17.3 K/kbar is calculated in Ref. 12 and in Ref. 13, a value of -18 K/kbar is found. These results are also in good agreement with our experimental value of -17.0 ± 0.2 K/kbar as well as the value of -16 K/kbar found by Wada et al.[9] There is less agreement between our c-axis value and those reported by Haque et al.[8] and Massa et al.[10] Since those values would result in a hydrostatic-pressure dependence that is too large, the value reported here and in Ref. 9 is believed to be more reliable.

As stated, our calculated hydrostatic-pressure dependence of -6.2 ± 0.3 K/kbar is in good agreement with the calculated values, -6.8 K/kbar (Ref. 12) and -7 K/kbar (Ref. 13). More significant, perhaps, is the agreement between our calculated value and the directly measured values of Kudo and Ikeda,[5] -7.3 K/kbar, Samara et al.,[6] -6.7 K/kbar, and Iizumi et al.,[2] -6.5 K/kbar. It should be noted, however, that in all cases this experiment used lower stress than any of the other reported work. This is significant if, as Samara et al.[6] report, the quantity $\partial T_2/\partial P$ becomes nonlinear at high stress. This would tend to give a larger value of $\partial T_2/\partial P$ in a linear fit to the data than would our lower-stress measurements.

Two other observations should be mentioned. First, the transition point tended to broaden with increasing stress. This effect is greater for thicker samples. This phenomenon was observed along all three axes but was most prominent along the c axis and might have been caused by domain instability near the transition point. This effect can be seen in some typical results on a thick sample shown in Fig. 6. This hypothesis is supported by the observation that thinner crystals showed less broadening than thicker ones. To minimize the errors in determining transition temperatures, the thinner samples were used for the data shown in Fig. 5. This reduced the size of the broadening errors to less than the scatter of the data points.

The other effect was the apparent stress-memory effect for stress along the c axis. Following the first stress series along the c axis on a new crystal, a later stress series would show a shallower slope (for $\partial T_2/\partial\sigma_3$). We did not try to quantify this effect and do not have an explanation for it, but it was consistent in behavior for several samples tested and we are confident that it is a real crystal effect and not an artifact of the measurement system. In Raman measurements on K_2SeO_4 and Rb_2ZnCl_4 under c-axis stress,[17] we have seen time-dependent frequency shifts at
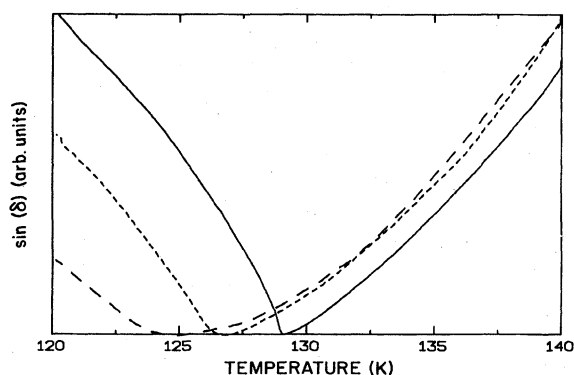
FIG. 6. c-axis-stress data on a thick sample showing the broadening of the transition with increased applied stress. (Note that these data were not used in the calculation of the stress dependence.) Solid line, zero stress, $T_2 = 129.14$ K; short-dashed line, 152 bars, $T_2 = 126.86$ K; long-dashed line, 304 bars, $T_2 = 125.99$ K.

stresses greater than a few hundred bars that suggest stress relief (i.e., plasticity). These effects were not observed for stress along a and b up to stress values greater than 1.0 kbar. In the present work, we have not studied this instability but rather have tried only to minimize it.

ACKNOWLEDGMENTS

APPENDIX

The optical phase shift can be expressed as the sum of three temperature- and stress-dependent parts: (1) The temperature-dependent birefringence, (2) the zero-stress thermal expansion of the crystal, and (3) the elastic response of the crystal to the applied stress. Thus, the phase shift at temperature $T_0 + dT$ and uniaxial stress σ to order dT is

$$\delta(T_0 + dT, \sigma_i) = (2\pi/\lambda)L_0[(\Delta n_0)_{ik}(1 + \sigma_i/C_{ij})$$
$$+ (d\Delta n_{ik}/dT)(1 + \sigma_i/C_{ij})$$
$$+ \alpha_j \Delta n_{ik} dT] , \qquad (1)$$

where L_0 and T_0 are the length and temperature at T_0, Δn_0 is the birefringence at T_0, α_j is a component of the thermal expansion, C_{ij} is a component of the elastic-constant tensor, and σ_i is the applied uniaxial stress. The subscripts i, j, and k, respectively, refer to the crystal direction parallel to the applied stress, the direction parallel to the propagation direction, and the third perpendicular direction.

Using data from Refs. 18 and 19 for the stresses applied in this work the elastic response can be seen to contribute at most only 0.3% to the phase shift. Similarly, at approximately 10 K from the transition, the thermal-expansion term is only about 10% of the birefringence term. Although very near the transition, it is unclear which term dominates; however, both will be anomalous at T_2 so only the magnitude of the phase shift will be affected by the thermal expansion. Thus, the measured anomaly in the phase shift does give a reliable measurement of the transition temperature.

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