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

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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.

## INTRODUCTION

$K_2SeO_4$ is the most studied member of the family of compounds with the $\beta$-$K_2SO_4$ structure, exhibiting incommensurate-ferroelectric phase transitions. $K_2SeO_4$ undergoes structural phase transitions at 745, 129.5, and 93 K, going from hexagonal to paraelectric-orthorhombic, to incommensurate, and finally to ferroelectric-orthorhombic, respectively. Our chief interest lies in the paraelectric-incommensurate ($T_i = 129$ K) and the incommensurate-ferroelectric ($T_c = 93$ K) transitions. Above $T_i$, $K_2SeO_4$ belongs to the *Pnam* ($D_{2h}^{16}$) space group, while below $T_c$ it has $Pna2_1$ ($C_{2v}^{9}$) symmetry. Between these temperatures, $K_2SeO_4$ exists in a structurally incommensurate state. The transition at $T_i$ is driven by the softening of an optical phonon along the $a$ direction with wave vector

$$q = \tfrac{1}{3}(1-\delta)a^* \ . \tag{1}$$

At $T_c$, this near tripling becomes exact; i.e., $\delta = 0$. Measurements of the optical birefringence of $K_2SeO_4$ have been previously reported by this laboratory[1] and others.[2,3] All of these reports were on studies of the anomalous birefringence at $T_i$, the paraelectric-incommensurate transition temperature.

The spontaneous birefringence at $T_i$ has been shown to be a continuous function of the order parameter, which is indicative of the second-order character of $T_i$. The structural phase transition (SPT) at $T_c$ is a discontinuous structure change which indicates a first-order SPT. At a first-order transition, we expect to observe step changes in quantities related to powers of the order parameter.[4] This should be the case with birefringence. We note however, that the data of Ref. 2 show no such anomaly, and while there appears to be a small feature in the data of Ref. 3, the authors make no mention of it; in fact, in a later publication,[4] these authors specifically state that there is no anomalous birefringence at $T_c$. The evidence in the current literature, therefore, suggests that the expected birefringence anomaly at $T_c$ is not observable.[5]

Measurements of the low-frequency (or static) dielectric constant, on the other hand, show anomalies at both $T_i$ and $T_c$ (although the anomaly at $T_i$ is much smaller than the one at $T_c$).[6] This is as expected and leads us to believe that there should be anomalous birefringence at $T_c$.

To investigate this, we used the rotating-analyzer method[7,8] to observe the relative birefringence of $K_2SeO_4$ for temperatures from 80 to 140 K, a range which includes both $T_i$ and $T_c$. This technique does not give the absolute birefringence. Instead it measures the relative birefringence up to an undetermined constant.

## EXPERIMENT

The experimental setup is shown schematically in Fig. 1, 632.8-nm light from a polarized He-Ne laser (Uni-Phase model 1105P) is passed through a Babinet-Soleil compensator to produce an elliptically polarized beam with a selectable ellipticity. The plane of polarization of the laser is directed approximately parallel to one of the crystal axes (although this could not be accurately set due to the construction of our cryostat). The compensator axis is positioned at 45° relative to the polarization direc-

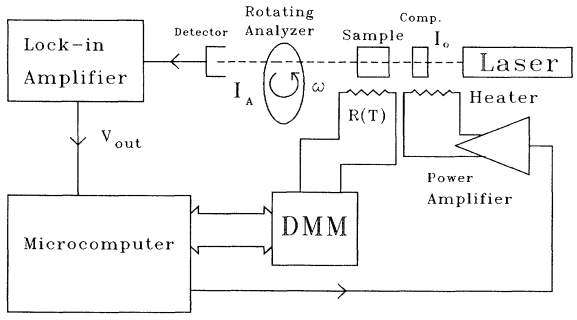


FIG. 1. Experimental setup.

 

tion and the retardation is adjusted to produce circularly polarized light leaving the empty, room-temperature cryostat. This beam is incident on a crystal that is mounted in a liquid-nitrogen-cooled, exchange-gas cryostat of our own design and construction. The beam exiting from the crystal passes through the "rotating analyzer" which is a sheet of linear polaroid mounted in place of the blade in a chopper (Princeton Applied Research model BZ-1) rotating at angular frequency $\omega$. The intensity of the beam of wavelength $\lambda$, after passing through the analyzer for a sample of thickness $d$ and birefringence $n_1-n_2$ is given by

$$I_A = I_0[1+\sin(2\omega t)\cos(\phi+\Delta)] , \tag{2}$$

where

$$\Delta = \frac{2\pi(n_1-n_2)d}{\lambda} \tag{3}$$

and $\phi$ is a constant phase shift produced by all other elements in the optical train. This beam is detected by a silicon photocell and the resulting signal is lock-in detected at a frequency reference provided by the chopper. The voltage output of the lock-in amplifier is thus proportional to $\cos(\phi+\Delta)$. This signal is digitized and recorded together with the temperature by a microcomputer. The temperature is measured with a four-wire platinum resistor read by a Keithley model 197 digital multimeter (DMM). The DMM is interfaced to the microcomputer over an IEEE-488 bus. Through a digital-to-analog converter and a small dc power amplifier, the computer controls the temperature drift (up or down) by sending a current through a coil of nichrome wire wrapped around the cryostat probe tip.

The data obtained with the above procedure are first normalized to lie between $+1$ and $-1$. The relative phase shift is then calculated by taking the arccosine of this normalized signal (inverting and adding $\pi$ where appropriate to reconstruct a continuous function of $T$). Finally, using the measured crystal thickness $d$ and the incident wavelength $\lambda$, the relative birefringence is calculated from Eq. (3).

The crystal used for this study was grown by evaporation of an aqueous solution of $K_2SeO_4$ and was provided to us by the Institute of Physics, Czechoslovak Academy of Sciences, Prague. The sample was cut and polished into a rectangular prism with sides of lengths 3, 0.81, and 2.2 mm along the $a$, $b$, and $c$ axis, respectively (where $b>a>c$). The orientation was determined by observation of the Raman spectrum. The sample was mounted in the cryostat to allow the incident beam to propagate along the $b$ axis, thus allowing the $n_a-n_c$ birefringence component to be observed.

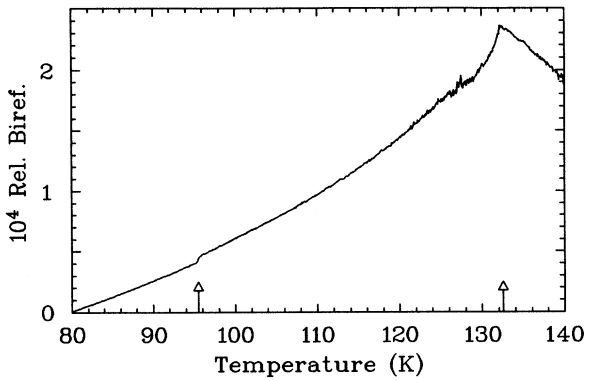


FIG. 2. Relative birefringence of $K_2SeO_4$ vs temperature. The arrows mark phase transition anomalies at $T_i=132$ K and $T_c=96$ K (the feature at 127 K is an artifact of the data reduction).

## RESULTS AND CONCLUSIONS

Figure 2 shows the results of a typical birefringence scan after the data were reduced to relative birefringence (there is an undetermined constant in the data which represents the contribution of $\phi$ and the zero of the birefringence). It is estimated from test runs on an empty cryostat that the cryostat windows contribute less than $1\times10^{-7}$ K$^{-1}$ to the data of Fig. 2, justifying our earlier assumption of constant $\phi$. Both $T_i$ and $T_c$ are clearly visible in the figure. Comparing the two anomalies, it is clear that the two have different behavior. As expected, $T_c$ appears to be a steplike function consistent with the first-order nature of the transition, and $T_i$ exhibits a continuous onset and a nonlinear temperature dependence below $T_i$. We also observe that the size of the anomaly at $T_i$ is larger than the one at $T_c$.

These results are consistent with previous dielectric studies.[6] As expected, both anomalies show up in high-frequency dielectric measurements (i.e., birefringence) as well as in low-frequency dielectric measurements. We also observe that in the low-frequency measurements, the anomaly at $T_c$ is much larger than the one at $T_i$, just the opposite of the observed relative size in birefringence reported here. Clearly, the low-frequency dielectric measurements and the birefringence measurements provide complementary information about these phase transitions.

## ACKNOWLEDGMENTS

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