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Ferroelastic Phase Transition in $BiVO_4$. I. Birefringence Measurements using the Rotating-Analyser Method

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Abstract

A brief review of methods of measuring birefringence is given. Apparatus for the accurate measurement of optical birefringence at high temperatures using a modulation (rotating-analyser) method is described in detail, together with suggestions for further applications of the equipment. The technique is applied to the particular case of the ferroelastic monoclinic–tetragonal phase transition in $BiVO_4$. The birefringence was found to show mean-field behaviour over a wide temperature range with a mean-field transition temperature of 519·9 (3) K.

Introduction

The optical properties of crystals have long been of interest to crystallographers, although it is unfortunately true that this traditional subject is now often unjustly neglected. When undertaking studies of solid-state phase transitions generally involving strongly pseudo-symmetric structures, birefringence information is especially valuable, since it provides a rapid and extremely sensitive technique for observing structural changes. A simple polarizer–compensator method, for example, may have a sensitivity orders of magnitude greater than that obtainable by X-ray crystallographic methods.

In spite of their experimental simplicity, birefringence measurements are often considered to be of qualitative rather than quantitative value. An exact microscopic theory of the refractive indices of solids does not exist and theoretical treatments of this problem are more often concerned with the derivation of ionic polarizabilities from observed refractive index data (Lo, 1973; Pohl, 1978) than with the exact calculation of the optical anisotropy of the material. However, in materials undergoing phase transitions it is found that there is often a simple relationship between the birefringence and the order parameter for the transition – for example, in ferroelectric materials the birefringence and the spontaneous polarization will be coupled *via* the electro-optical coefficients. Thus observations of birefringence can give useful information on the critical exponent for the transition (Courtens, 1972, 1973; Gehring, 1976; Becker & Gehring, 1975; Harley & Macfarlane, 1975; Iio, Sakatani & Nagata, 1978). An advantage of birefringence measurements in such studies is their high sensitivity; changes of less than 1×10^{-6} can be detected in a 1 mm thick crystal. Disadvantages include the need for a transparent sample, which generally must have single-domain regions large enough to be observed, though techniques using multidomain specimens have been reported (Germann, 1976).

In the first section of this paper we describe equipment for the accurate measurement of optical birefringence as a function of temperature using a rotating-analyser method. The second part presents data collected from the ferroelastic material $BiVO_4$, in which the birefringence is shown to have a mean-field behaviour. In part II (Wood, Welber, David & Glazer, 1980), apparatus for simultaneous high-pressure/high-temperature birefringence measurements will be described and the results of a further study of $BiVO_4$ at a hydrostatic pressure of about 7×10^8 Pa will be presented.

Experimental details

(i) *General survey*

Before discussing in detail the rotating-analyser apparatus, a brief survey of some available methods for measuring birefringence will be given. Traditionally, birefringence has been measured by using compensators, *i.e.* the effects of the specimen under investigation are cancelled by introducing into the light path a second crystal of variable optical retardation. Such devices, which range in accuracy from the simple quartz wedge to the more elaborate instruments devised by Berek, Erhinghaus and Sénarmont (see *e.g.* Hartshorne & Stuart, 1970), suffer from a number of disadvantages:

(*a*) Manual point-by-point measurements are needed.

(*b*) The inherent accuracy of the measurements is limited. The Berek device used in this laboratory has a sensitivity to changes in optical retardation of about 10 nm. With a good Sénarmont compensator changes in retardation of approximately 1 nm can just be resolved (Toledano, 1979), though the absolute accuracy claimed for the method is generally lower than this (see *e.g.* Toledano & Schneck, 1975).

(*c*) When measuring dispersive crystals with large optical retardations it is often difficult to establish the true compensation position, since observation in white light can then produce a zero-order band which is not black (see *e.g.* Hartshorne & Stuart, 1970, p. 582).

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The accuracy of compensator measurements can be increased by the use of arrangements such as that of Courtens (1973), who obtained the compensation position by measurement of the compensation curve with a photomultiplier, followed by curve fitting to find the position of the minimum. Whilst this method increases the sensitivity by about ten times, it is a tedious procedure unless on-line computing facilities are available for immediate processing of the data.

A second method of measuring birefringence is to observe the light intensity transmitted through the sample when viewed between crossed polars (as used by, for example, Harley & Macfarlane, 1975). Under these conditions a signal of the form

$$I = I_0 \sin^2 2\varphi \sin^2 \delta/2$$

is obtained (Born & Wolf, 1975, p. 696), where I_0 is the incident light intensity, φ is the angle between the polarizer and an allowed vibration direction in the crystal and δ is the phase shift introduced by the optical retardation [$\delta = (2\pi/\lambda)\Delta nt$ for wavelength λ, birefringence Δn and thickness t]. When used in conjunction with a 'fringe-counting' method, such as that to be described for $BiVO_4$, this technique can give extremely accurate results. It does however have the disadvantages that

(i) It is sensitive to fluctuations in the incident light intensity and to noise from stray-light detection.

(ii) For small δ the dependence of the signal is nonlinear. An advantage of this method over the modulation technique described below is that in some circumstances it appears to be less sensitive to the effects of domain reorientation in the specimen (see paper II).

The most sensitive techniques for measuring birefringence are the modulation methods, such as used in the rotating-analyser system described here. Possibly the most sensitive is that of Benard & Walker (1975) who used a photoelastic polarization modulator. This method has advantages over the rotating-analyser device in that, as no moving parts are required, higher and more stable modulation frequencies may be obtained, though it appears in other respects to be rather less versatile.

Finally, mention must be made of two traditional methods which are both capable of very high accuracy but which suffer from the disadvantage that large and carefully prepared specimens are needed. The first of these is the method of minimum deviation for the determination of refractive indices (see *e.g.* Bond, 1965) which requires accurately oriented prisms to be cut from crystals of the specimen. The second is the use of interferometric methods such as the construction of Fabry–Perot etalons from polished plates of the crystal (Miller & Savage, 1966), a technique which allows both the variation of refractive indices and of birefringence to be measured directly.

(ii) *The rotating-analyser apparatus*

Various rotating-analyser techniques have been described by a number of previous workers (Suits, 1971; Chudakov, Grechushnikov & Prave, 1972). However, while these techniques have been used to measure effects such as magneto-optical rotation (Suits, 1971), they do not seem to have been applied to studies of structural phase transitions. It should perhaps be pointed out at this stage that these methods are best suited to observing relative changes in birefringence as a function of some continuous variable (temperature, specimen position, *etc.*) rather than to determination of the birefringence at a particular point. Particular advantages are their high sensitivity, their experimental convenience and their ability to make continuous, rather than point-by-point measurements. The apparatus may therefore be used either in a qualitative or semi-quantitative way to examine a material for possible phase transitions (see *e.g.* Hidaka, Wood, Wanklyn & Garrard, 1979) or for precise quantitative measurements of birefringence.

The optical components in the present device are:

(*a*) an initial polarizer;

(*b*) a $\lambda/4$ plate set at 45° to the polarizer, producing circularly polarized light incident on the sample;

(*c*) the specimen, with orientation φ and phase lag δ (symbols as defined previously);

(*d*) an analyser, rotating at angular frequency ω.

Under these conditions the light intensity passing the analyser takes the form

$$I = (I_0/2)\,[1 + \sin 2(\omega t - \varphi) \sin \delta]\,,$$

which thus gives an AC signal of frequency 2ω, phase 2φ and amplitude proportional to $\sin \delta$.

The experimental arrangement used is shown in Figs. 1 and 2. To allow examination of small specimens the apparatus is assembled around a Reichert Zetopan polarizing microscope, with the rotating-analyser equipment attached to the microscope's camera port. No structural modifications to the microscope are required and the microscope optics may be removed or inserted at will. The light source used is a 1 mW He/Ne laser (6328 Å), though examination in white or filtered light may also be made, using the microscope's tungsten lamp. The rotating analyser consists of a Polaroid disc rotated by a belt and pulley drive at about 3000 rev/min to give a 2ω signal of approximately 100 Hz. The AC amplitude of the light-intensity signal, detected by a photomultiplier, is measured by a phase-sensitive detector locked to the analyser frequency by an optical chopper. In order to eliminate the effects of incident light variation, the amplitude of the AC signal is finally divided by the DC component giving a final output proportional to $\sin \delta$. The phase of the AC signal (2φ) gives a measure of the rotation of the optical indicatrix of the specimen.

The equipment has two main modes of operation. If $\delta \to 0$ or $n\pi$ the signal will be essentially linear and the system then gives a very sensitive direct measure of optical retardation. Using a Berek compensator as a test crystal, it was found that the noise level of the instrument corresponded to approximately ±0·14 nm in retardation, and so was roughly 100 times more sensitive than the manually operated Berek device. This method is useful in cases where the change in birefringence is small. To satisfy the requirement that $\delta \simeq n\pi$ a fixed compensator may be introduced into the optical path or, alternatively, for uniaxial specimens, a section cut nearly perpendicular to the optic axis may be examined. A disadvantage of this technique is that it does depend directly on measurement of light intensity and so must be calibrated to obtain an absolute scale – a possible method for eliminating this problem, using a modified Sénarmont technique, will be described later.

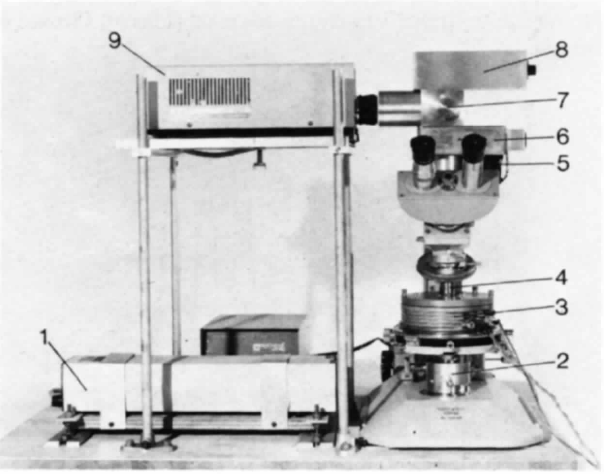

Fig. 1. Photograph of rotating-analyser apparatus. 1. He/Ne laser; 2. 45° mirror and $\lambda/4$ plate; 3. hot stage; 4. objective; 5. motor; 6. rotating analyser, frequency $\simeq 50$ Hz; 7. camera port; 8. photomultiplier tube; 9. TV camera.

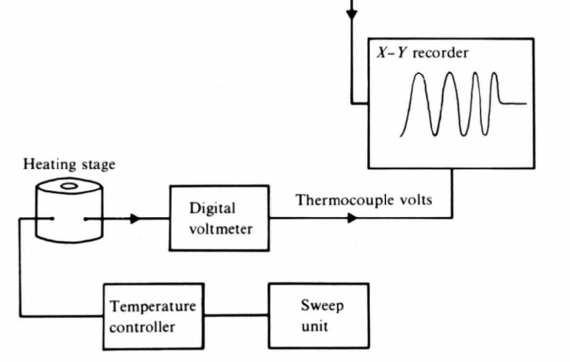

Fig. 2. Block diagram of signal-analysis equipment.

If the change in optical retardation is large ($\gg \lambda$), the output from the instrument will be periodic (see Fig. 4) and the change in retardation may then be obtained simply by noting the positions of the maxima and minima of the signal. This method can produce very accurate results and in particular it should be noted that the only source of error lies in the accuracy to which the peak position can be estimated, since the change in retardation between maxima and minima must be equal to $\lambda/2$. It is also important to note that changes in indicatrix orientation (φ) have no effect on the estimates of peak maxima and minima (and hence birefringence), unless the change in φ is rapid compared with the change in optical retardation, δ – a remote possibility.

Use of a highly monochromatic light source is essential in this mode if the higher-order peaks are to be well resolved. Comparable results may be obtained by examining the light intensity transmitted between crossed polars (see paper II) but the modulation method offers advantages in clarity of signal and normalization of the light intensity.

(iii) *The high-temperature stage*

A schematic diagram of the stage used for our high-temperature experiments is shown in Fig. 3. This device, constructed in the Clarendon Laboratory, currently has a temperature range from room temperature to about 1270 K, though higher temperatures may be achieved by small modifications to the heater and sample holder. Temperature control (to ±0·05 K) is provided by a two-term (proportional and derivative) controller which can be combined with a sweep unit to give continuously varying temperatures (sweep range 300–1270 K, sweep time 0–1000 min, separately variable). For qualitative work rapid sweep rates may be used and it is often possible to obtain useful information in a matter of minutes. For accurate measurements, however, a slower scan rate ($\lesssim 1$ K/min) is needed to ensure thermal equilibrium of the sample and thermocouple.

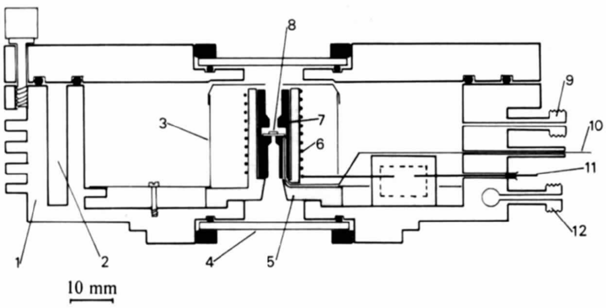

Fig. 3. Cross section of heating stage. 1. Outer casing; 2. cooling-water channel; 3. steel heat shield; 4. silica window; 5. pyrophyllite former; 6. nichrome furnace windings; 7. metal or pyrophyllite specimen holder; 8. sapphire plate plus specimen; 9. gas inlet; 10. thermocouple; 11. heater input; 12. cooling-water inlet.

The specimen under examination rests on a polished sapphire plate accurately oriented perpendicular to its optic axis, thereby giving an optically isotropic section of high thermal conductivity. The specimen temperature is measured with a chromel/alumel (type *K*) thermocouple mounted within the sample holder close to the crystal. For accurate work the specimen is placed well within the furnace windings (Fig. 3) using an enclosed metal or (for very-high-temperature work) pyrophyllite specimen mount. In this configuration the absolute and relative values of the specimen temperature are well defined (to better than 1 and 0·1 K respectively, in the range 300–670 K) and vertical and horizontal temperature gradients across the specimen are minimal. Alternatively, when visually examining very small crystals, the specimen may be positioned near the top of the furnace windings. This allows shorter working-distance objectives to be used but does lead to problems in accurately determining the true specimen temperature. Facilities also exist for water cooling of the cell body and for filling the sample volume with an inert gas to prevent sample oxidation.

The ferroelastic phase transition in BiVO$_4$

The presence of a second-order purely ferroelastic phase transition in BiVO$_4$ at about 520 K was first discovered by Bierlein & Sleight (1975). The transition is from a tetragonal scheelite structure (space group $I4_1/a$) to a low-temperature monoclinic distortion (space group $I2/a$). Using Aizu's (1969) terminology, it may be classified as $4/mF2/m$. Raman scattering experiments (Pinczuk, Burns & Dacol, 1977; Pinczuk, Welber & Dacol, 1979) have shown that the transition involves strong coupling between a zone-centre optic mode and the ferroelastic strain of B_g symmetry (in the paraelastic phase) and have suggested that the transition is driven by the soft optic phonon. It was also found that the order parameter had a mean-field (Landau) behaviour over a wide temperature range. Recently, David, Glazer & Hewat (1979) have examined the structural distortions associated with the transition using powder neutron diffraction. The results indicated that the displacements of the Bi^{3+} ions play the dominant role in the transition and suggested a structural mechanism for the strong optic–acoustic mode coupling.

In this paper we present a study of the transition using optical birefringence at atmospheric pressure. The change in birefringence from room temperature to the transition is very large ($\sim$0·11) and the material is very pressure sensitive (see paper II) which suggests a possible application in photoelastic modulation devices.

BiVO$_4$: results and discussion

The crystal boule used in our experiments was supplied by the Royal Signals and Radar Establishment (Malvern). A single-domain, polished plate of BiVO$_4$ was cut from the boule and accurately oriented perpendicular to the twofold axis of the low-temperature phase. The specimen size was 3 × 2 × 0·238 mm. The experimental trace from the rotating analyser apparatus is shown in Fig. 4 and the derived birefringence curve in Fig. 5. The heating rate used was approximately 1 K/min; experiments carried out at slower rates indicated that the temperatures were reliably determined at this rate of scan. In deriving the birefringence curve the thermal expansion of the crystal was neglected since the change in the length of the *c* axis is very small, amounting to approximately 0·2% over the whole temperature range covered (David, Glazer & Hewat, 1979).

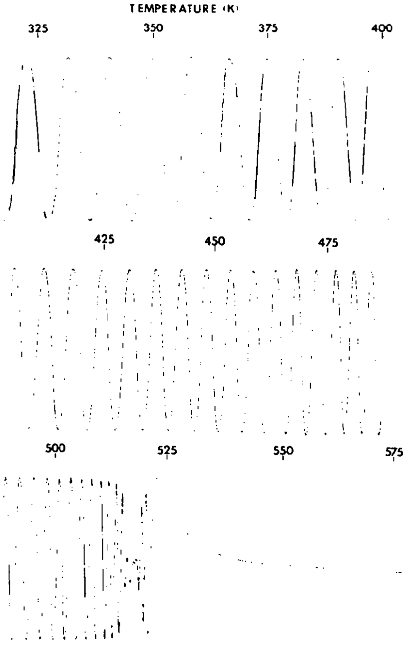

Fig. 4. Signal output for a crystal of BiVO$_4$.

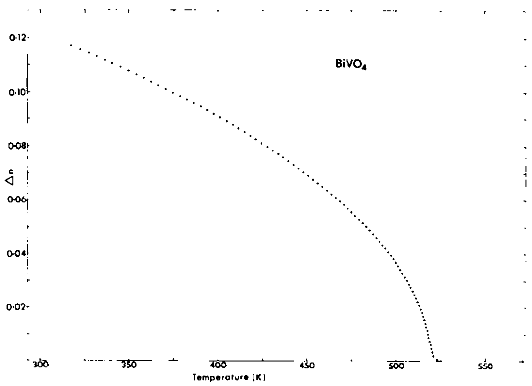

Fig. 5. Birefringence *versus* temperature from the data in Fig. 4. The points are at intervals of $\lambda/2t$ in the vertical direction. The first data point above zero is at $\lambda/4t$.

The disruption of the signal at about 518 K is caused by the appearance and reorientation of ferroelastic domains just below the phase transition. The presence of these domains becomes very noticeable as the transition is approached. Measurements made without normalization of the light intensity show a considerable decrease in the signal in this region caused by light scattering from the domains. A plot of Δn^2 against temperature is shown in Fig. 6. The behaviour is linear over a wide temperature range; a straight line fitted by least squares between 333 and 517 K has a slope of $-6{\cdot}765\,(7)\times 10^{-5}\ \mathrm{K}^{-1}$, and an intercept of 519·9 (3) K, which corresponds to the mean-field transition temperature. The departure of Δn^2 from linearity in the region above 518 K results from the birefringence tail shown in Fig. 5, which persists for some 50 K above the transition. The origin of this tail is at present unknown but may involve regions of short-range order persisting into the high-temperature phase, suggesting that an X-ray diffuse scattering study in this region might be of interest. Similar effects have been observed in $TbVO_4$ and $DyVO_4$ by Harley & Macfarlane (1975) who attributed their origin to internal strains within the specimen.

Below the phase transition the elastic strain is given by the symmetric tensor

$$\begin{pmatrix} \varepsilon_1 & \frac{1}{2}\varepsilon_6 & 0 \\ \frac{1}{2}\varepsilon_6 & \varepsilon_2 & 0 \\ 0 & 0 & \varepsilon_3 \end{pmatrix},$$

taking the unique axis as [001] and using the matrix notation given by Nye (1969). The reference axes used correspond to those of a hypothetical paraelastic phase existing below T_c and are chosen so as to make equal angles with the **a** and **b** axes of the monoclinic ferroelastic phase (a necessary condition if the strain tensor is to be symmetric). The spontaneous strain, arising at the transition, is, for a particular orientation state of the crystal, given by (Aizu, 1970)

$$\begin{pmatrix} [(\varepsilon_1-\varepsilon_2)/2 & \frac{1}{2}\varepsilon_6 & 0 \\ \frac{1}{2}\varepsilon_6 & [(\varepsilon_2-\varepsilon_1)/2] & 0 \\ 0 & 0 & 0 \end{pmatrix}.$$

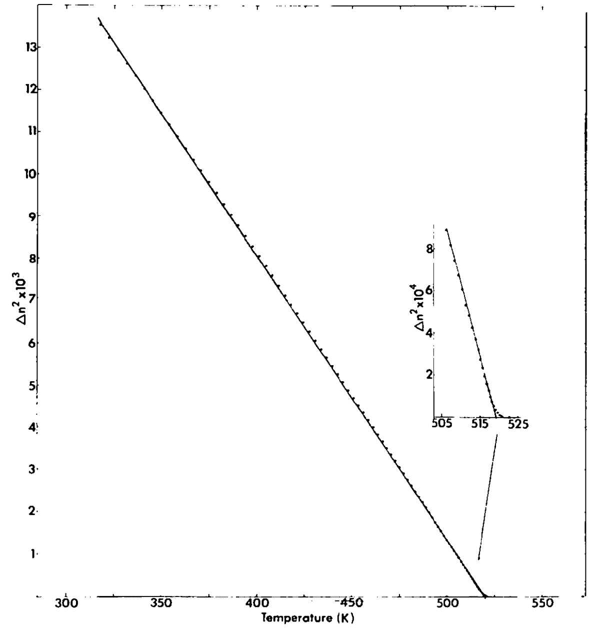

Fig. 6. Plot of Δn^2 against temperature for $BiVO_4$. The inset shows the region near the phase transition in detail.

The free energy of the crystal may be written as

$$F=F_0+\Delta W_1+\Delta W_2+\Delta W_3,$$

where

$$\Delta W_1=\tfrac{1}{2}\alpha Q^2+\tfrac{1}{4}\beta Q^4,$$

$$\begin{aligned}\Delta W_2=\tfrac{1}{2}[&C_{11}(\varepsilon_1^2+\varepsilon_2^2)+C_{33}\varepsilon_3^2+C_{66}\varepsilon_6^2+2C_{12}\varepsilon_1\varepsilon_2\\&+2C_{13}(\varepsilon_1\varepsilon_3+\varepsilon_2\varepsilon_3)+2C_{16}(\varepsilon_1\varepsilon_6-\varepsilon_2\varepsilon_6)],\end{aligned}$$

$$\begin{aligned}\Delta W_3=&A_1Q[m(\varepsilon_1-\varepsilon_2)+n\varepsilon_6]\\&+A_2Q^2[m'(\varepsilon_1+\varepsilon_2)+n'\varepsilon_3],\end{aligned}$$

α, β, A_1, A_2, m, m', n and n' being constants. Higher-order terms in ΔW_1, ΔW_2 and ΔW_3 are omitted in this approximation. Q is an order parameter having the same symmetry properties as the normal coordinate of the soft optic phonon and is therefore of B_g symmetry in the paraelastic phase (Aubry & Pick, 1971). ΔW_2 is the elastic energy of the crystal (Nye, 1969). ΔW_3 describes the interaction energy of the soft optic mode and the elastic strains; the term $\{A_2Q^2[m'(\varepsilon_1+\varepsilon_2)+n'\varepsilon_3]\}$ is included here for consistency with the analysis of Pinczuk, Welber & Dacol (1979). Either Q or η [$=m(\varepsilon_1-\varepsilon_2)+n\varepsilon_6$ (Boccara, 1968)] can be regarded as a primary order parameter for the transition, since structurally they are closely linked (David, Glazer & Hewat, 1979).

The relationship between the elastic strains, ε_i, and the order parameter, Q, may be found from the equations

$$\partial F/\partial\varepsilon_{ij}=\sigma_{ij}=0$$

(since for the free crystal all stresses are zero). These give a series of equations relating ε_i and Q, whose solutions may be written in the form

$$\varepsilon_1-\varepsilon_2=K_1Q;\quad \varepsilon_6=K_2Q;$$
$$\varepsilon_1+\varepsilon_2=K_3Q^2;\quad \varepsilon_3=K_4Q^2,$$

where the K_i's are constants determined by the values of A_1, A_2, m, m', n, n' and C_{ij}. Thus, providing the coupling between Q and η is linear, there is a linear relationship between the order parameter Q and each component of the spontaneous strain in the crystal. The free-energy expansion may then be written in terms of Q alone as

$$F=F_0+\tfrac{1}{2}\alpha'Q^2+\tfrac{1}{4}\beta'Q^4+\ldots,$$

where α' and β' include terms from ΔW_2 and ΔW_3. Assuming that the temperature dependence of the coefficient α' takes the form

$$\alpha' = \alpha_0(T - T_c),$$

with all other coefficients temperature independent, and applying the equilibrium condition that $\partial F/\partial Q = 0$, we obtain the result

$$Q^2 \propto (T_c - T) \propto (\varepsilon_1 - \varepsilon_2)^2 \propto \varepsilon_6^2$$

for $T < T_c$ which is the usual mean-field behaviour of the order parameter. An alternative derivation of this result may be obtained by expanding the free energy in terms of η (Boccara, 1968), from which we obtain $\eta^2 \propto (T_c - T)$. Since m and n are constants it follows that $(\varepsilon_1 - \varepsilon_2)$ and ε_6 may be expected to show the same temperature dependence.

A simple relationship between the order parameter and the birefringence may now be derived in terms of the photoelastic moduli of the paraelastic phase. The changes in the relative dielectric impermeability tensor are given by

$$\delta B_m = p_{mn}\varepsilon_n$$

(Nye, 1969, p. 249). Introducing the photoelastic moduli appropriate to the point group of the paraelastic phase ($4/m$), we obtain for the crystal below the phase transition:

$$\begin{aligned}
B'_1 &= B_1 + \delta B_1 = B_1 + p_{11}\varepsilon_1 + p_{12}\varepsilon_2 + p_{16}\varepsilon_6\,;\\
B'_2 &= B_1 + \delta B_2 = B_1 + p_{12}\varepsilon_1 + p_{11}\varepsilon_2 - p_{16}\varepsilon_6\,;\\
B'_3 &= B_3 + \delta B_3 = B_3 + p_{31}\varepsilon_1 + p_{32}\varepsilon_2\,;\\
B'_4 &= 0\,;\\
B'_5 &= 0\,;\\
B'_6 &= p_{61}\varepsilon_1 - p_{61}\varepsilon_2 + p_{66}\varepsilon_6\,.
\end{aligned}$$

Terms in ε_3 have been omitted as they do not appear in the spontaneous strain tensor. Diagonalization of the impermeability tensor gives eigenvalues

$$\begin{aligned}
\lambda_1, \lambda_2 = \tfrac{1}{2}(2B_1 &+ (p_{11} + p_{12})(\varepsilon_1 + \varepsilon_2)\\
&\pm \{[p_{11} - p_{12})(\varepsilon_1 - \varepsilon_2) + 2p_{16}\varepsilon_6]^2\\
&+ 4[p_{61}(\varepsilon_1 - \varepsilon_2) + p_{66}\varepsilon_6]^2\}^{1/2}),\\
\lambda_3 = B_3 &+ p_{31}(\varepsilon_1 + \varepsilon_2)\,.
\end{aligned}$$

The relationship between the dielectric impermeability and the refractive indices is of the form

$$B = 1/n^2$$

and hence

$$\delta n_i = -(n_i^3/2)\delta B_i\,.$$

To a sufficient approximation we may replace n_i by n_o and n_e, the refractive indices of the paraelastic phase. The birefringence perpendicular to the **c** axis is therefore given by

$$\begin{aligned}
\Delta n &= \delta n_1 - \delta n_2\\
&= -(n_o^3/2)\,\{[(p_{11} - p_{12})(\varepsilon_1 - \varepsilon_2) + 2p_{16}\varepsilon_6]^2\\
&\quad + 4[p_{61}(\varepsilon_1 - \varepsilon_2) + p_{66}\varepsilon_6]^2\}^{1/2}.
\end{aligned}$$

Since $(\varepsilon_1 - \varepsilon_2)$ and ε_6 are both separately proportional to Q it follows that there is a linear relationship between the birefringence in the (001) plane and the order parameter. The data presented in Fig. 6 therefore show that $\mathrm{BiVO_4}$ has a mean-field behaviour over a very wide temperature range. This conclusion is in agreement with the previous Raman scattering results of Pinczuk, Burns & Dacol (1977), although it is apparent that the birefringence method is of considerably higher accuracy. A further test of the validity of the theory is provided by the orientation of the optical indicatrix. Defining θ as the angle between the principal axes of the impermeability tensor and the hypothetical paraelastic reference axes we obtain the relation

$$\tan 2\theta = \frac{[2p_{61}(\varepsilon_1 - \varepsilon_2) + p_{66}\varepsilon_6]}{[(p_{11} - p_{12})(\varepsilon_1 - \varepsilon_2) + 2p_{16}\varepsilon_6]}\,,$$

an expression which, on the basis of the theory presented above, is temperature independent. Approximate measurements over the range from room temperature to the phase transition, made by visual estimation of the extinction angle, indicate that, despite the enormous change in birefringence, the rotation of the indicatrix is indeed small (<2°), which strongly supports our interpretation. In future work, it is hoped to measure this more exactly using the phase-measuring method described below. Other projected experiments include the direct measurement of the spontaneous strain by high-temperature single-crystal X-ray diffraction, which should then enable several of the photoelastic coefficients of the material to be calculated.

Further applications

The system described above, for high-temperature birefringence studies, represents just one application of the rotating-analyser apparatus. The equipment has, however, considerable versatility and may be used in a number of other modes, some of which are outlined briefly below.

(*a*) *Phase measuring*

In the previous discussion it was shown that the phase of the AC signal (2φ) from the rotating-analyser system gives a measure of the orientation of the optical indicatrix of the crystal. Phase-measuring equipment is currently being constructed for use with the apparatus, which will therefore allow a continuous read-out of the rotation of the indicatrix during the experiment. By removing the $\lambda/4$ plate, this system may, additionally, be used to measure Faraday rotation in magnetic materials and optical activity. Previous work by Suits (1971) indicates that very precise results (to ~0·01°) can be obtained in this way. Alternatively, by repositioning the $\lambda/4$ plate above the specimen, a modified Sénarmont compensator is produced. In this configuration the phase of the AC signal is proportional to the phase lag introduced by the crystal (δ) and so it is possible to obtain a continuous measurement of optical retardation by monitoring the phase. An advantage of this method is that no measurement of intensity is involved. A linear change in birefringence appears as a linear change in the phase signal thus making it an excellent method for measuring moderate changes ($\sim\lambda$) in optical retardation.

(*b*) *Data logging*

Currently, the birefringence data are plotted on an X–Y recorder with manual logging of the temperatures. The system is now being interfaced to a Research Machines 380Z microcomputer, which will then act as a data logger. As well as offering an increase in reliability and operator convenience, this should produce great improvements in data analysis, as, for example, curve fitting to find the maxima and minima of the signal can then be carried out.

(*c*) *Measurements on small areas*

By introducing the microscope optics together with an extension tube and small aperture below the rotating analyser, it is possible to make measurements on extremely small regions of the specimens ($<2\ \mu$m). Since the technique measures relative changes, translation of the specimen across the field of view determined by the small aperture gives a birefringence signal related to position. Preliminary work on diamond and on ferrimagnetic garnets suggests that this is a potentially valuable technique for the study of multidomain specimens and also possibly for examining the structure of domain walls in ferromagnetic and ferroelastic crystals.

(*d*) *Simultaneous observation of the specimen*

By introducing a partially reflecting mirror below the analyser it is possible to view the crystal, using a television camera and video monitor, whilst measurements are being made. Because of the variation of reflectivity with polarization, this modification currently produces some perturbation in the measurements, though when used with a 'fringe-counting' method this should not present any serious difficulty. We believe this to be a useful facility since it allows, for example, the motion of domain walls in the specimen to be observed during the course of a birefringence measurement.

In addition to the modifications described above facilities are also being developed for work at low temperatures and at variable wavelengths, using interference filters or monochromators. Measurements made at simultaneous high pressures and temperatures are described in paper II.

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