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Optical observations of the birefringence and the domains of $\text{La}_x\text{Pr}_{1-x}\text{P}_5\text{O}_{14}$ near the ferroelastic phase transitions

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Abstract. The changes in the optical properties of five samples $\text{La}_x\text{Pr}_{1-x}\text{P}_5\text{O}_{14}$ with different La contents were measured for spontaneous birefringence and rotation angle of the ellipsoid indicatrix axes induced by the ferroelastic phase transitions. Two types of domain and their movement and reproduction were observed in temperature range from T_c to $T_c - 100^\circ\text{C}$. The transition temperature is found to vary linearly with La content. The experimental data are explained and fitted to an approximation considering high-order terms relating to the order parameter.

1. Introduction

The rare-earth pentaphosphate MP_5O_{14} ($M = \text{La} \sim \text{Tb}$) undergoes a ferroelastic phase transition at $130\text{--}150^\circ\text{C}$ (Tadashi *et al* 1976) from the monoclinic to the orthorhombic phase. This ferroelastic transition is a normal type with no modification of the number of molecules in the unit cell. Since the 1970s, various experimental results on the ferroelastic transition were obtained by means of methods which involve x-ray techniques (Albrand *et al* 1974, Schulz *et al* 1974, Liu Xiling *et al* 1986), EPR (Barthou *et al* 1981, Larlos *et al* 1981), DSC (Loiacono *et al* 1978, Qu *et al* 1990) and light scattering (Fox *et al* 1976, Scott 1979, Chen Ting and Hong Guangyan 1986, Toledano *et al* 1976, Errandonea and Sapiel 1979). These results can be interpreted with the phenomenological model of the Landau free energy (Errandonea 1980). The order parameter of the transition of MP_5O_{14} is the soft optic mode q with symmetry B_{2g} , the same as that of the spontaneous strain tensor component e_5 in the monoclinic phase where they couple with each other, making the optic mode and an acoustic mode soften up to the temperature T_c and triggering the ferroelastic phase transition.

What is the influence of the structural phase transitions (SPTs) on the physical properties of the crystals? The changes in the frequency and the infrared and Raman strength of lattice modes due to SPTs of Landau type have been investigated (Petzelt and Dvorak 1976) with the group theoretical method. The changes in the refractive indices of crystals induced by SPTs were considered with different types of phase transition (Fousek 1978,

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Fousek and Petzelt 1979). For the ferroelastic phase transition of the crystal $\text{La}_x\text{Pr}_{1-x}\text{P}_5\text{O}_{14}$, its spontaneous changes in optical properties are related to the order parameter q and the spontaneous strain tensor component e_5 .

Optical measurements can be employed to observe the spontaneous birefringence and the rotation of the indicatrix axes. Microscopically, the SPTs are characterised by shifts in the average positions of ionic nuclei and changes in the electronic structure which will result in optical changes. Macroscopically, because of the spontaneous deformation the optical index ellipsoid will vary with temperature but, in previous years, sufficient attention has not been paid to experimental measurements of the optical properties of ferroelastic materials. In this paper we present experimental data on the spontaneous birefringence and the rotation angle of the ellipsoid axes with respect to temperature of the crystal $\text{La}_x\text{Pr}_{1-x}\text{P}_5\text{O}_{14}$ with different x . A detailed analysis of these data and explanations are also given.

2. Experimental details

2.1. Sample preparation

High quality single crystals of $\text{La}_x\text{Pr}_{1-x}\text{P}_5\text{O}_{14}$ with $x = 0.1, 0.3, 0.5, 0.7$ and 0.9 were grown from phosphoric acid solution using the detailed procedures described by Tofield *et al* (1974). The samples for the optical experiments were thin plates cut along the b -plane with a width of about 0.1 mm and prepared for optical observations.

2.2. Experimental procedures

The optical experiments were carried out in a perpendicular polarisation system which involves monochromatic light (546 nm) propagating along the direction of the twofold axes of the sample. The angle α characterising the orientation of the indicatrix axes (in the x - z plane) in the monoclinic phase with respect to that in the orthorhombic phase was measured using a polarimeter with Faraday-cell modulation. The birefringence n_{13} was measured by means of a compensator which made the intensity of the light emitted from it minimum. The spontaneous birefringence $\delta_s n_{13}$ induced by the ferroelastic phase transition in the monoclinic phase is compared with that in the orthorhombic phase near T_c . No detectable temperature hysteresis was observed when the temperature was increased and decreased. This means that the difference between the temperatures measured and the temperature of the sample in the oven is less than 1 °C. The accuracy of measurement of the angles is better than 6'. The light from the Hg lamp was focused to a small beam to ensure illumination on a single domain. However, because the domain density at a temperature near T_c is very high, the experimental data in this temperature range (which is no more than 1 °C below T_c) became relatively unreliable. Also, one edge of the sample was cut parallel to the domain wall [001] and glued to the crystal holder, which ensures that the contribution from thermal expansion to the rotation angle is nearly zero (Fousek *et al* 1979). The contribution of the thermal expansion to the birefringence can be neglected from the experimental point of view: in the paraelastic phase no detectable difference of the birefringence with respect to temperature was measured (Fousek *et al* 1979). The domains and their movement and reproduction were also observed in the experiments.

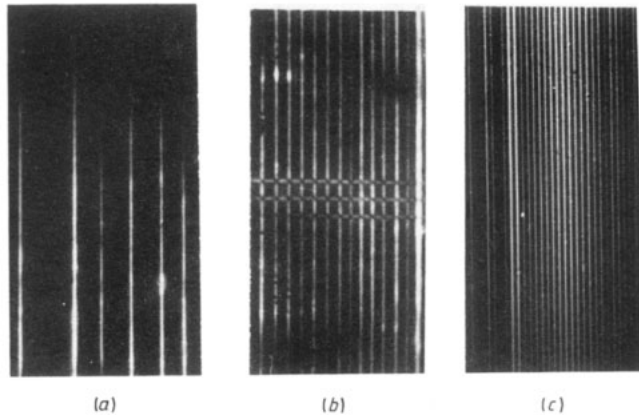


Figure 1. (a) Needle-shaped domains; (b) type a and type b domains; (c) domains near transition temperature (less bright domains are those just reproduced at increasing temperature).

3. Experimental results and analysis

3.1. Observation of the domains

It is well known that the monoclinic phase $2/m$ is ferroelastic which involves spontaneous strain and existence of the domains (Weber *et al* 1975, Budin *et al* 1975). Group theoretical analysis (Sapriel 1975) predicts that two types of domain may occur with their orientations parallel to $[001]$ and $[100]$; these are called type a and type b, respectively. The former may be easily induced by a small external strain and exists in the crystal more commonly as observed in figure 1. It can be seen that some of the a-type domains, which are needle shaped, did not penetrate to the opposite edge of the sample. When the temperature was increased to transition point T_c , the density ρ of the domains became large with the relation $\rho \sim (T_c - T)^{-1}$ (Wang YeNing *et al* 1989). This increase can be attributed to two factors: on the one hand the needle-shaped domains are extended along their length and penetrate gradually to the opposite edge of the sample; on the other hand, within some domains which are wide enough, new domains can be produced suddenly with the reverse direction of spontaneous strain. This means that the sample tends to have the same domain density homogeneously. In some samples a different situation was observed: the distribution of the domains remained the same on increase in temperature but of course would disappear at the transition. We assumed that this was associated with the existence of an internal stress or defects in the sample, so that the domains cannot move or reproduce, namely, domains are pinned.

In this experiment we also measured the angle φ between the orientations of the indicatrix axes in the x - z plane of adjacent domains at different temperatures below T_c . It was found that this angle was always 2α , where α is the angle between the corresponding axis and the orthorhombic (x) axis. This implies that the adjacent domains are twinned with respect to the domain wall. Therefore, φ is relatively large (about 16° at 20°C) in spite of the fact that the spontaneous deformation angle β is no more than 1° in the temperature range from T_c to $T_c - 100^\circ\text{C}$. The above features are demonstrated in figure 2.

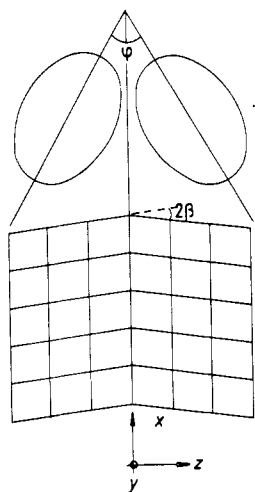


Figure 2. Adjacent domains and the corresponding indicatrix with respect to their lattice. φ and β are defined in the paper.

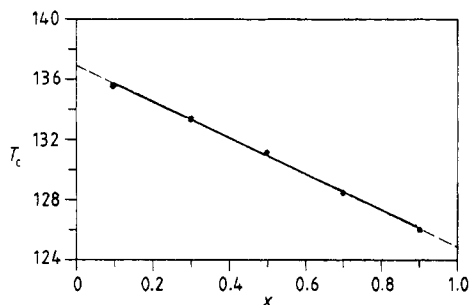


Figure 3. Phase transition temperature of $\text{La}_x\text{Pr}_{1-x}\text{P}_5\text{O}_{14}$.

Table 1. Optical properties of $\text{La}_x\text{Pr}_{1-x}\text{P}_5\text{O}_{14}$ at 20 °C.

	Rotation angle (deg)	Birefringence n_{13}
$\text{La}_{0.1}\text{Pr}_{0.9}\text{P}_5\text{O}_{14}$	9.0	1.57×10^{-2}
$\text{La}_{0.3}\text{Pr}_{0.7}\text{P}_5\text{O}_{14}$	8.8	1.58×10^{-2}
$\text{La}_{0.5}\text{Pr}_{0.5}\text{P}_5\text{O}_{14}$	8.5	1.53×10^{-2}
$\text{La}_{0.7}\text{Pr}_{0.3}\text{P}_5\text{O}_{14}$	8.3	1.50×10^{-2}
$\text{La}_{0.9}\text{Pr}_{0.1}\text{P}_5\text{O}_{14}$	7.9	1.45×10^{-2}

The occurrence of domains will decrease the spontaneous deformation-induced elastic energy until a balance is achieved. Minimising the Landau free energy which has accounted for the energy of the domain wall, the density of the domains can be obtained theoretically. In other experimental measurements the effect of the domains on the physical properties was detected (Loiacono *et al* 1978, Qu *et al* 1990).

3.2. Relation between T_c and x

Previous work has shown that the ferroelastic transition temperature T_c of the rare-earth pentaphosphate MP_5O_{14} is related directly to the rare-earth ion (Tadashi *et al* 1976); increasing its radius corresponds to decreasing T_c . In ferroelastic materials, the ions are arranged along the bands as M–O–P–O–M, having the twofold symmetry. Two types of ions La^{3+} and Pr^{3+} in the five samples can be convincingly assumed to be located in the same band. The transition temperature should in principle be the same with respect to the effective radius of the ions of different x . Figure 3 gives the experimental results from which a linear relationship between T_c for $\text{La}_x\text{Pr}_{1-x}\text{P}_5\text{O}_{14}$ and x can be obtained.

Extrapolating the line to different x such as $x = 0$ and $x = 1$, one can obtain T_c for $\text{PrP}_5\text{O}_{14}$ and $\text{LaP}_5\text{O}_{14}$, respectively. Because of the experimental accuracy ($\pm 1^\circ\text{C}$) it is convenient to compare the present results with those obtained in previous work as shown in table 1. The dependence of T_c on the radius of the ion implies that the corresponding band M–O–P–O–M is a principal factor in triggering the ferroelastic phase transition.

3.3. Results on $\delta_s n_{13}$ and α versus temperature

If the monochromatic light penetrates along the b -axis, the experimental data are related to the two axes of the ellipsoid indicatrix on the x - z plane of the sample. With the change in temperature the birefringence will vary slightly in the two phases; the two axes will rotate in the monoclinic crystals, which can be characterised by the angle as defined above. These data with respect to temperature are shown in figures 4 and 5. The optical properties of these samples at room temperature are listed in table 2. Analogous to the former conclusion on T_c versus x , we can see that the spontaneous birefringence $\delta_s n_{13}$ and rotation angle α increase with increasing x . In figure 4(a) and 5(a) it is clear that $\delta_s n_{13}$ and α decrease with increase in temperature until the transition occurs. In the paraelastic phase (group mmm), n_1 or n_3 and α can be expected to vary much less but linearly with temperature. From the results obtained by Errandonea (1980) we know that the thermal expansion coefficients in the para-elastic phase are much smaller than in the ferroelastic phase. For our experimental arrangement, we should note that n_{13} and α were independent of the contribution of the thermal expansion in the para-elastic phase. The temperature range above T_c is not our major interest in this paper.

Figure 4(b) and 5(b) show the relations of $\log[\tan(2\alpha)]$ and $\log(\delta_s n_{13})$ against $\log(T_c - T)$. The experimental data can be fitted using the following equations:

$$\tan(2\alpha) = a(T_c - T)^m \quad \delta_s n_{13} = b(T_c - T)^n. \quad (1)$$

The constants a , b , m and n are obtained and listed in table 3. It is found that the temperature range from T_c to $T_c - 100^\circ\text{C}$ can be divided into two parts with different exponents. The temperature at which the relationship changes is about 5°C below T_c , indicating that the experimental data obtained from T_c to $T_c - 5^\circ\text{C}$ can be explained approximately. In the temperature range from $T_c - 5^\circ\text{C}$ to $T_c - 100^\circ\text{C}$, the experimental data, on the other hand, cannot be explained without considering higher-order terms relating to the order parameter.

The temperature at which the relationship change, which is about 5°C below T_c should be compared with the previous result of about $T_c - 13^\circ\text{C}$ obtained by measurement of the strain (Errandonea 1978). This means that the optical properties of $\text{La}_x\text{Pr}_{1-x}\text{P}_5\text{O}_{14}$ are more sensitive to the ferroelastic phase transitions. This phenomenon can be assumed to correspond to the softening of the optical mode B_{2g} . Because the optical mode represents the relative motion of the ionic nuclei, the softening of this normal mode will accordingly perturb the interaction of the adjacent nuclei and their electron structure. As the condensation of the soft mode which will eventually induce the ferroelastic phase transition is a macroscopic effect, the change in optical properties can be measured in optical experiments.

4. Discussion

In order to analyse the change in the optical properties of the ferroelastic material, we first obtain the Landau free energy, which involves the deformation elastic energy and

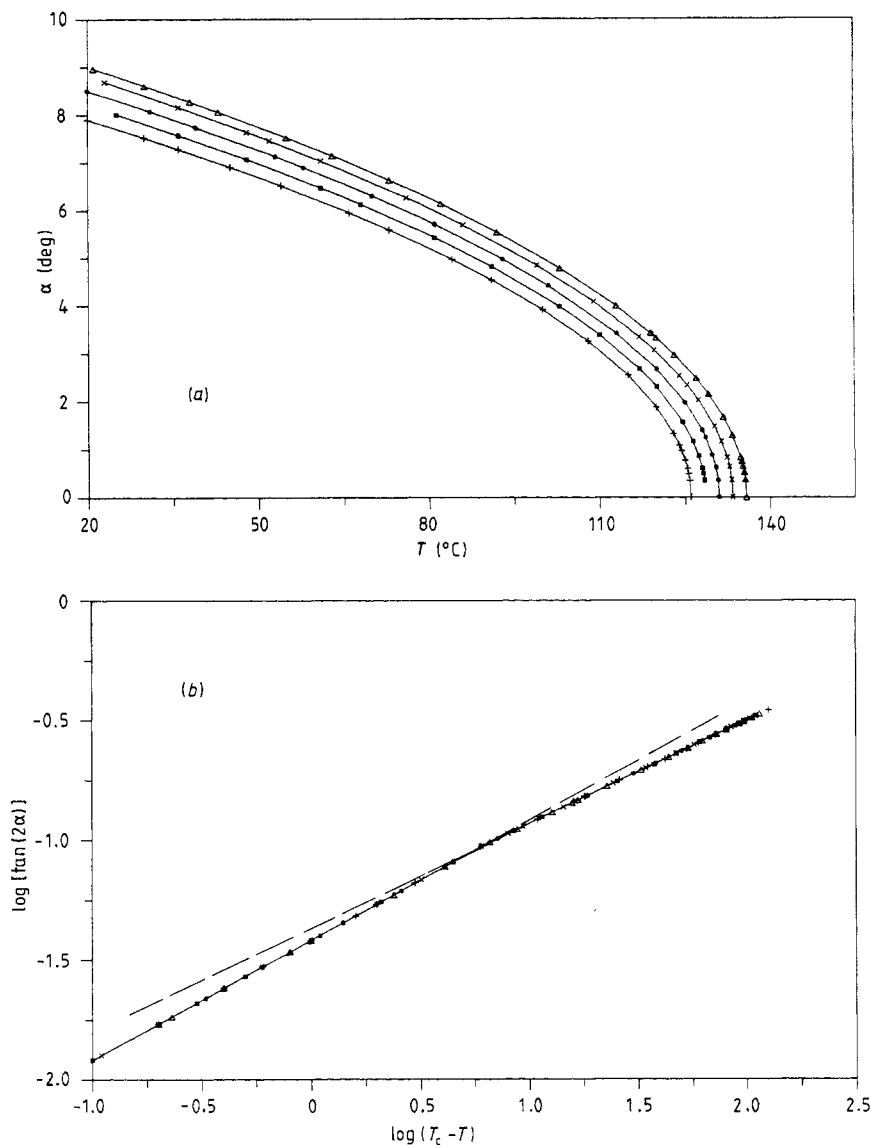


Figure 4. Temperature dependence of the rotation angle α of the indicatrix axis for $\text{La}_x\text{Pr}_{1-x}\text{P}_5\text{O}_{14}$: \triangle , $x = 0.1$; \times , $x = 0.3$; \bullet , $x = 0.5$; \blacksquare , $x = 0.7$; $+$, $x = 0.9$.

coupling terms between the order parameter and the spontaneous strain component e_s , which can be written as follows:

$$\Phi = \Phi_0 + \frac{1}{2}\alpha_0(T - T_0)q^2 + \frac{1}{4}\beta q^4 + \frac{1}{2}ce_s^2 + Fe_s q. \quad (2)$$

The constants α_0 , β , c and F are independent of temperature. Minimising Φ , one can obtain the following equations:

$$T_c = T_0 + F^2/\alpha_0 c \quad (3a)$$

$$q_s = -(c/F)e_{5s} \quad q_s \sim e_{5s} \sim (T_c - T)^{0.5} \quad (3b)$$

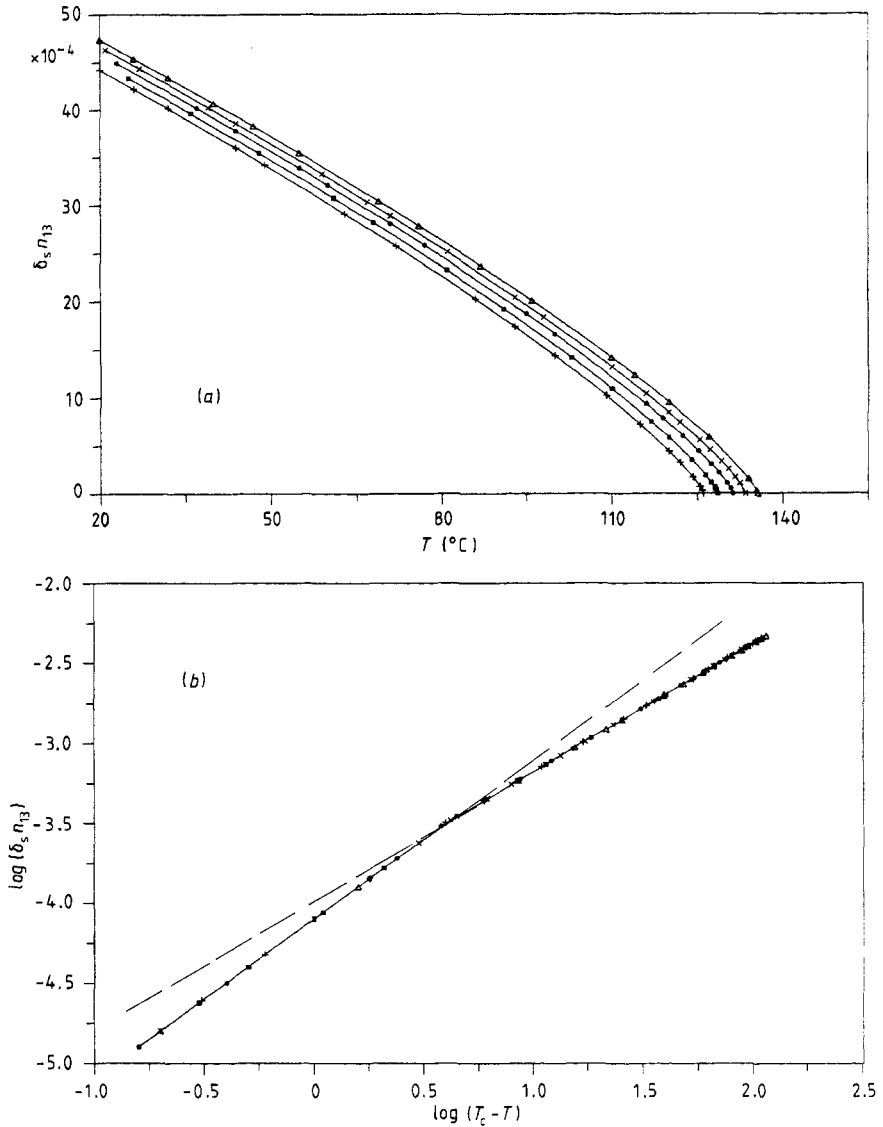


Figure 5. Temperature dependence of the spontaneous birefringence $\delta_s n_{13}$ for $\text{La}_x\text{Pr}_{1-x}\text{P}_5\text{O}_{14}$: Δ , $x = 0.1$; \times , $x = 0.3$; \bullet , $x = 0.5$; \blacksquare , $x = 0.7$; $+$, $x = 0.9$.

$$e_{55}^2 = \alpha_0 F^2 (T - T_0) / \beta (c^q)^2. \quad (3c)$$

The optical properties are defined by the indicatrix involving α and birefringence n_{13} , which is related to B_i (B_i is the abbreviated symbol of $B_{ij} = \partial E_i / \partial D_j$ (Fousek and Petzelt 1979)). As far as the ferroelastic material is concerned, the change in optical properties can be attributed to the order parameter q and the strain which is not necessarily spontaneous in the common case. After considering the restrictions resulting from the group theory, these terms can be listed as follows:

$$\delta B_5 = P_{35}^q e_5 + m^* q + R e_3^3 + S q^3 + T e_3^2 q + V e_5 q^2 + \dots \quad (4a)$$

$$\delta B_4 = \delta B_6 = 0 \quad (4b)$$

Table 2. Transition temperature T_c of $\text{La}_x\text{Pr}_{1-x}\text{P}_5\text{O}_{14}$.

Sample	T_c (°C)	Reference
$\text{LaP}_5\text{O}_{14}$	124.9	This work
	125.0	Errandonea (1980)
	123.0	Tadashi <i>et al</i> (1976)
	118.0	Weber <i>et al</i> (1975)
$\text{PrP}_5\text{O}_{14}$	137.0	This work
	140.0	Weber <i>et al</i> (1975)
	138.0	Tadashi <i>et al</i> (1976)
$\text{La}_{0.1}\text{Pr}_{0.9}\text{P}_5\text{O}_{14}$	135.6	This work
$\text{La}_{0.3}\text{Pr}_{0.7}\text{P}_5\text{O}_{14}$	133.4	This work
$\text{La}_{0.5}\text{Pr}_{0.5}\text{P}_5\text{O}_{14}$	131.2	This work
$\text{La}_{0.7}\text{Pr}_{0.3}\text{P}_5\text{O}_{14}$	128.5	This work
$\text{La}_{0.9}\text{Pr}_{0.1}\text{P}_5\text{O}_{14}$	126.0	This work

Table 3. Value of the coefficients using the best-fit method.

Temperature range	Rotation angle	
	T_c to $T_c - 5^\circ\text{C}$	$T_c - 5^\circ\text{C}$ to $T_c - 100^\circ\text{C}$
m	0.50	0.43
a	0.0382	0.0435
Temperature range	Spontaneous birefringence	
	T_c to $T_c - 4^\circ\text{C}$	$T_c - 4^\circ\text{C}$ to $T_c - 100^\circ\text{C}$
n	1.0	0.8
b	7.96×10^{-5}	1.05×10^{-4}

$$\delta B_i = P_{i5}e_5^2 + m_i^*q^2 + W_i e_5 q + \dots \quad (i = 1, 2, 3). \quad (4c)$$

Here P_{55}^q and m_i^* are first-order elasto-optic coefficients; $R, S, T, V, P_{i5}, m_i^*$ and W_i are second-order elasto-optic coefficients; etc.

The rotation angle α is given by

$$\begin{aligned} \tan(2\alpha) &= 2\delta B_5 / (B_1'^2 - B_3'^2) = 2\delta B_5 / [(B_1 + \delta B_1)^2 - (B_3 + \delta B_3)^2] \\ &= [2\delta B_5 / (B_1^2 - B_3^2)] - [4\delta B_5 (B_1 \delta B_1 - B_3 \delta B_3) / (B_1^2 - B_3^2)^2]. \end{aligned} \quad (5)$$

B_i ($i = 1, 2, 3, 5$) are the optical polarisation coefficients in the orthorhombic phase; δB_i is the slight change which can be induced by, for example, the external strain or the order parameter in the monoclinic phase. If we call Q and u_5 the conjugate force of the order parameter q and the strain component e_5 , respectively, we have from equation (2)

$$Q = (\partial\Phi/\partial q) = \alpha_0(T - T_0)q + Fe_5 \quad (6a)$$

$$u_5 = (\partial\Phi/\partial e_5) = ce_5 + Fq. \quad (6b)$$

As a first approximation we consider only the linear terms in equation (4a) and the first

term in equation (5) in order to give a quantitative explanation of α with respect to temperature. This means that

$$B_5 = P^q e_5 + m^* q = P_{55}(T) e_5 + vQ. \quad (7)$$

In the para-elastic phase above T_c it is clear that $Q = 0$ and $u_5 = 0$ or the order parameter $q = 0$ where no external strain exists. If external strain is applied, the change in optical properties can be obtained by equation (7):

$$\delta B_5 = [P^q - M^* F / \alpha_0 (T - T_0)] e_5 = P_{55}(T) e_5 \quad (8a)$$

$$P_{55}(T) = P^q - m^* F / [\alpha_0 (T - T_0)] \quad P_{55}(T_c) = P^q - m^* c / F. \quad (8b)$$

In the ferroelastic phase below T_c the spontaneous strain exists and results in a change in optical properties which can be measured in optical experiments. In this situation we have

$$q/e_5 = -c/F. \quad (9)$$

Then equation (8a) becomes

$$\delta_s B_5 = (P^q - m^* c / F) e_5 = P_{55}(T_c) e_5 \quad (10a)$$

$$\tan(2\alpha) = 2\delta B_5 / (B_1^2 - B_3^2) \sim e_5 \sim (T_c - T)^{1/2}. \quad (10b)$$

This means that the change in the optical polarisation coefficient B_5 is related linearly to e_5 . Consequently, as far as the rotation angle of the optical indicatrix axes and the spontaneous birefringence are concerned, the classical critical exponent m and n in equation (1) should be $m = 0.5$ and $n = 1$ in agreement with the Landau mean-field theory. Therefore the experimental data in the temperature range from T_c to $T_c - 5^\circ\text{C}$ can be explained in this approximation.

However, from the experimental data we see that $m < 0.5$ and $n < 1$ in the temperature range below $T_c - 5^\circ\text{C}$; this cannot be interpreted by the linear approximation in equation (7). Higher-order terms related to the order parameter should be considered. Substituting equation (3) for equation (4) we can obtain the spontaneous change in B_5 :

$$\delta_s B_5 = a' q + b' q^3 + c' q^5. \quad (11)$$

Obviously the first term represents the linear approximation. The other terms represent the higher-order coupling terms between the optical properties and the order parameter which should involve high elasto-optic effects. Therefore, equation (5) can be applied as below in the second-order approximation:

$$\tan(2\alpha) = a(T_c - T)^{0.5} - b(T_c - T) + c(T_c - T)^{1.5}. \quad (12)$$

The constants a , b and c can be obtained from the fitting method. The first term represents the mean-field theory which is in good agreement with experimental data in the temperature range from T_c to $T_c - 5^\circ\text{C}$. The constant a is clearly related to the first order elasto-optic coefficients. When considering the first two terms the appropriate temperature range for which the experimental results can be convincingly explained can be expanded to between T_c and $T_c - 20^\circ\text{C}$. The constant b is related to the first- and second-order elasto-optic coefficients. For our results in temperature range from T_c to $T_c - 100^\circ\text{C}$ it is necessary to account for the three terms in equation (11). The constant c can be related to the first-, second and third-order elasto-optic coefficients. The data

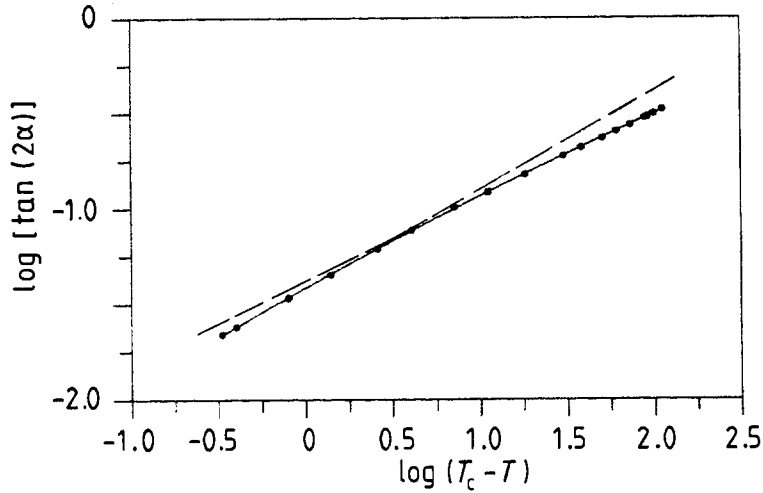


Figure 6. Theoretical line (broken line) with respect to experimental data (dots) on $\text{La}_{0.5}\text{Pr}_{0.5}\text{P}_5\text{O}_{14}$ using the best-fit method.

for one sample is given in figure 6: line 1 is for $0.5 \log(T_c - T) - 1.4175$ in the temperature range from T_c to $T_c - 5^\circ\text{C}$ while line 2 is for $0.42 \log(T_c - T) - 1.3615$ in the range from $T_c - 5^\circ\text{C}$ to $T_c - 100^\circ\text{C}$. Line 3 is our theoretical prediction where the least-squares fitting method is used in order to estimate the best values of the coefficients a , b and c . We obtain $a = 3.8 \times 10^{-2}$, $b = 2.4 \times 10^{-4}$ and $c = 1.8 \times 10^{-6}$ when the experimental and theoretical lines overlap very well as shown in figure 6. Furthermore, the second term should be negative to explain the classical critical exponent $m < 0.5$ and $n < 1$. For our estimated values of these coefficients, if some theoretical value such as P_{55} is available, we could check whether it is suitable to explain the experimental data in the temperature range from T_c to $T_c - 100^\circ\text{C}$. However, although little information could be obtained, it is clear that it is necessary to consider the third-order elasto-optic effect in this approximation.

The spontaneous birefringence can be explained by a similar procedure and the same conclusion obtained.

5. Conclusion

The changes in optical properties (spontaneous birefringence and rotation angle of the indicatrix axes) of the ferroelastic material $\text{La}_x\text{Pr}_{1-x}\text{P}_5\text{O}_{14}$ were reported in the near- T_c temperature region. Domains of two types and, their movement and reproduction, were observed in temperature-increasing steps. The transition temperature, which was found to be the same within experimental accuracy in the various experimental procedures for one $\text{La}_x\text{Pr}_{1-x}\text{P}_5\text{O}_{14}$ sample, is related linearly to x . Finally the optical data are explained by an approximation considering higher-order terms relating to the order parameter according to the phenomenological model.

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