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The effect of impurities on the phase transitions in the ferroelectric semiconductors $TlInS_2$ and $TlGaSe_2$

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Abstract

The temperature dependences of the dielectric constants of the ferroelectric semiconductors $TlInS_2$ and $TlGaSe_2$ have been studied following their annealing within the incommensurate phase. Unusual memory effects accompanied by both a remarkable inflection of the temperature dependence curves in the incommensurate phase and various shifts of the incommensurate (T_i) and commensurate (T_c) phase transition temperatures have been revealed in both crystals. The observed effects are explained on the basis of a defect density wave model taking into account the interaction of modulation waves with charge carriers localized at impurity states. The thermally activated population of these states during the heating or cooling processes is responsible for the changes of the phase transition temperatures.

1. Introduction

The ternary compounds $TlInS_2$ and $TlGaSe_2$ belong to the group of semiconductors having layered crystalline structure. According to structural investigations [1], the crystals possess monoclinic structure with the space symmetry group C_{2h}^6. It has been established that both of the crystals investigated exhibit a sequence of structural phase transitions to incommensurate (at $T_i \sim 214$ K in $TlInS_2$ and ~ 113 K in $TlGaSe_2$) and commensurate ferroelectric (at $T_c \sim 196$ K in $TlInS_2$ and ~ 105 K in $TlGaSe_2$) phases. According to existing data, the transition to the incommensurate phase is associated with condensation of a soft mode at point $\mathbf{q}(\delta, \delta, 0.25)$ of the Brillouin zone, where δ is the incommensuration parameter. On subsequent cooling

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both crystals exhibit a phase transition into the commensurate phase with quadrupling of the unit cell parameter along the direction perpendicular to the layers. In the polar phase the spontaneous polarization vector lies in the plane of the layers [2, 3].

As is known, the presence of incommensurately modulated structure in crystals leads to the occurrence of long lived metastable states in the temperature interval of the successive incommensurate and commensurate phase transitions, which brings about thermal hysteresis and so-called memory effects [4, 5], which were found to be observed after annealing of the crystals in the incommensurate phase. It is the case that on scanning the temperature after annealing, the crystals 'remembered' the annealing temperature in subsequent heating or cooling cycles. According to the widely accepted explanation from the literature [5], these effects are considered to be caused by mobile defects interacting with a modulated distortion. The mobile defects move to new positions during the long time annealing of the crystal within the incommensurate phase and create a so-called defect density wave (DDW). These defects still remain at their new positions on subsequent heating or cooling and, as a result, some changes in measuring parameters will be registered. Such 'classic' memory effects, which include the influence of annealing on the shape of the dielectric constant's temperature dependence, were observed in a number of crystals with incommensurate phases [6–8]. In these cases the temperature dependence of $\nabla\varepsilon/\varepsilon$ has an 'inflexion' point at the annealing temperatures ($\nabla\varepsilon$ is the difference between ε values measured after and before the annealing). Besides this, the low temperature shifts of the incommensurate–commensurate phase transition temperature can be observed after annealing the sample inside the incommensurate phase (a kind of memory effect) [9, 10].

The present paper reports the results of measurements of temperature behaviour of dielectric constants of $TlInS_2$ and $TlGaSe_2$ crystals on heating with different temperature scanning rates after annealing the crystals for some hours at some fixed temperatures within the incommensurate phase. Various shifts both to higher and lower temperatures for T_i and T_c, depending on the heating rate, were observed for the first time together with the 'classic' memory effect. The results obtained are discussed in the framework of the DDW model, which takes into account the role of charge carriers localized on the defects in commensurate–incommensurate and incommensurate–paraelectric phase transitions.

2. Experimental details

The crystals were grown by the Bridgman method and oriented along the polar axis, which lies in the cleavage plane. The samples had rectangular form and the surfaces perpendicular to the layer plane were polished and covered with silver paste. The dimensions of the electrodes were 6×2 mm^2 with an inter-electrode distance of 2 mm. Measurements of the real part of the dielectric susceptibility were performed using a capacitance bridge at the frequency of 1 kHz in the temperature range of 77–300 K. A cryostat and temperature controller allowed us to scan the temperature at a rate between $\sim$0.5 and $\sim$3 K min^{-1} and to stabilize the temperature with accuracy better than 0.05 K.

The measurements were performed according to the following procedure. Firstly the samples were cooled down to 77 K and the temperature dependence of the dielectric constant was measured on heating. After this measurement the samples were cooled down to 77 K and kept at this temperature for 20 min, then they were heated and annealed at some fixed temperature within the incommensurate phase for some hours. Then the samples were cooled again for 15–30 min and the temperature dependences of the dielectric constant were measured in a heating cycle. After each measurement the sample was heated up to the room temperature then cooled, and the next cycle of measurement was performed.

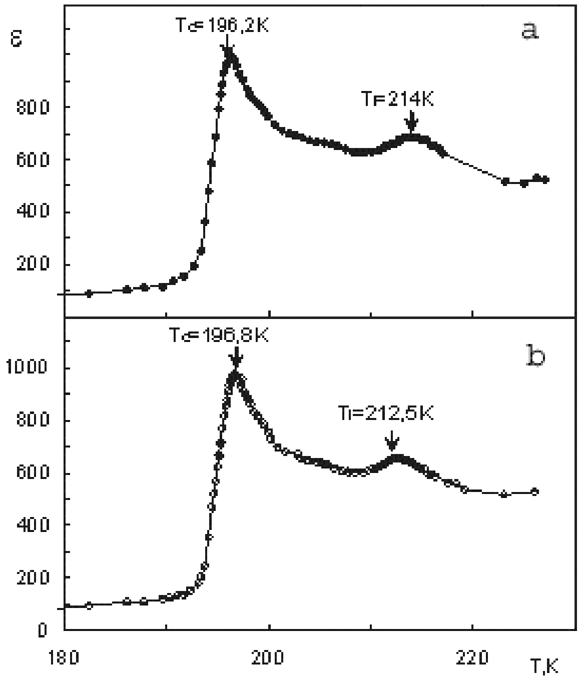

Figure 1. Temperature dependences of the real part of the dielectric constant of $TlInS_2$ crystal measured on heating at the rate 1.11 K min^{-1}: (a) without annealing, (b) after annealing for 3 h at 210 K.

3. Experimental results

The temperature dependences of the dielectric constants of $TlInS_2$ and $TlGaSe_2$ crystals without and after annealing the samples at 208 and 110 K respectively are shown in figures 1 and 2. All $\varepsilon(T)$ curves are characterized by peaks, which correspond to phase transition points T_i and T_c. Thermal annealing within the incommensurate phase leads to two main effects: the classic memory effect, characterized by the change of the $\varepsilon(T)$ curve within the incommensurate phase and the shifting of phase transition points, which are discussed in detail below. Figures 3 and 4 demonstrate the memory effects in $TlInS_2$ and $TlGaSe_2$ crystals as they are usually observed in other crystals with incommensurate phase, that is the changes between dielectric constant temperature behaviour after and before annealing, $\nabla\varepsilon/\varepsilon$. In the case of experimental conditions realized during the registration of the $\varepsilon(T)$ curve, after annealing of the crystals for 2–5 h within the incommensurate phase, the classic memory effect is observed with inflexion points at the annealing temperature in both crystals. As is seen from figures 2, 3, the amplitude of $\nabla\varepsilon/\varepsilon$ increases with annealing time, but the shape of the $\nabla\varepsilon/\varepsilon$ curve depends on the annealing temperature also. For both crystals the memory effect is not observed if the annealing temperature is chosen within the commensurate phase. As for other crystals with a memory effect, the amplitude of the $\nabla\varepsilon/\varepsilon$ function gradually decreases and the memory effect totally disappears upon the crystals being heated to some temperature above T_i. However, obvious peculiarities of the memory effect manifestation in the crystals investigated also exist. First of all, the temperature interval in which anomalous behaviour of the dielectric constant is observed is very large, comprising almost the whole incommensurate phase interval. Usually (see for example [4–6]), the memory effect reveals itself in a 1–3 K temperature interval after 15–20 h

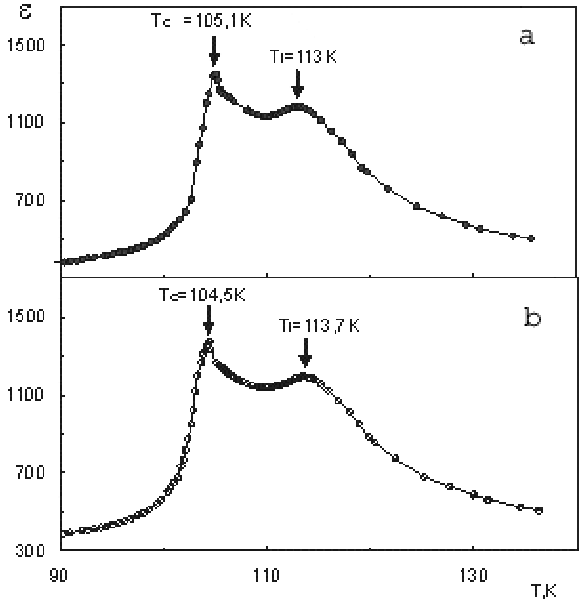

Figure 2. Temperature dependences of the real part of the dielectric constant of $TlGaSe_2$ crystal measured on heating at the rate 0.4 K min^{-1}: (a) without annealing, (b) after annealing for 3 h at 110 K.

Table 1. Heating rates and phase transition temperatures, T_c and T_i, for $TlInS_2$ crystal after annealing the sample at the temperature 210 K for 3 h.

Heating rate (K min^{-1})	T_c (K)	T_i (K)	ΔT_c (K)	ΔT_i (K)
0.7	198.6	215.8	2.3	1.8
0.79	197.6	214.8	1.4	0.7
0.9	197.2	213.4	0.9	−0.5
0.99	197.6	215.2	0.73	−0.95
1.11	196.8	212.5	0.6	−1.5
1.28	196.3	213.1	0.22	−1.66
2.38	195.5	213	−0.8	−1.8

of annealing within the incommensurate phase. Besides this, the amplitude of deviation of the dielectric constant in our case is almost twice larger in spite of the much shorter annealing time. Finally, when the annealing temperature shifts to lower temperatures, the $\nabla\varepsilon/\varepsilon$ curve becomes ‘asymmetric’ (figure 3(a)), proving once again that the memory effect covers the whole incommensurate phase.

The second effect, which is of special interest, is the shifting of the phase transition temperatures T_i and T_c upon annealing, depending on the heating rate. Different types of shifts of phase transition points were obtained on heating the sample at various heating rates. The results of such experiments for $TlInS_2$ crystal are presented in table 1 and figure 5. As can be seen from table 1 and figure 5, T_i and T_c for $TlInS_2$ can shift to lower and higher temperatures depending on the heating rate. It is important to note that the effects described can only be observed after thermal annealing of the crystals within the incommensurate phase. The following experimental details are of special interest. As is clearly seen from figure 5, the positive shifts of T_i and T_c at relatively small heating rates change to negative ones at

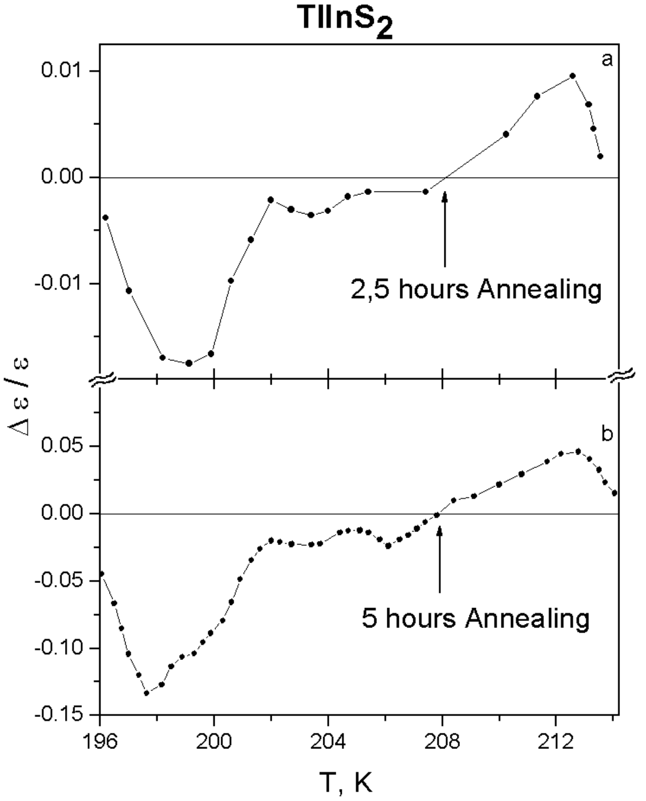

Figure 3. The temperature dependences of the deviations of the real part of the dielectric constant, $\nabla\varepsilon/\varepsilon$, for TlInS$_2$ crystals measured in a heating cycle after annealing at 208 K: (a) for 2.5 h; (b) 5 h.

higher heating rates. A clear saturation tendency is observed in the T_i and T_c behaviour at higher heating rates. The 'usual', that is unshifted, values of $T_c = 196$ K and $T_i = 214$ K are observed at heating rates close to 1 K min^{-1}.

For TlGaSe$_2$ crystal, the character of the behaviour of the phase transition temperatures with the heating rate is the same as for the TlInS$_2$ crystal. But in contrast to the case of TlInS$_2$ crystal, the values of the shift for T_i and T_c upon annealing of TlGaSe$_2$ lead to widening of the temperature interval over which the incommensurate phase exists. Figure 2(b) demonstrates the $\varepsilon(T)$ behaviour for TlGaSe$_2$ crystal. As in the case of TlInS$_2$ crystal, thermal annealing within the incommensurate phase leads to shifting of phase transition temperatures. Upon annealing the sample for 3 h at the temperature 110 K, T_c shifts to lower temperatures, whereas T_i shifts to higher temperatures under the experimental conditions realized in this case, that is at the heating rate 0.4 K min^{-1}.

4. Discussion

As is mentioned above, the mechanism of the memory effect in crystals with incommensurate phases is based on the interaction of a modulated wave with a periodic potential created by the DDW [4–6]. The modulation wave becomes locked in a temperature interval close to the annealing temperature leading to anomalies like those shown in figures 2, 3. Usually, this type

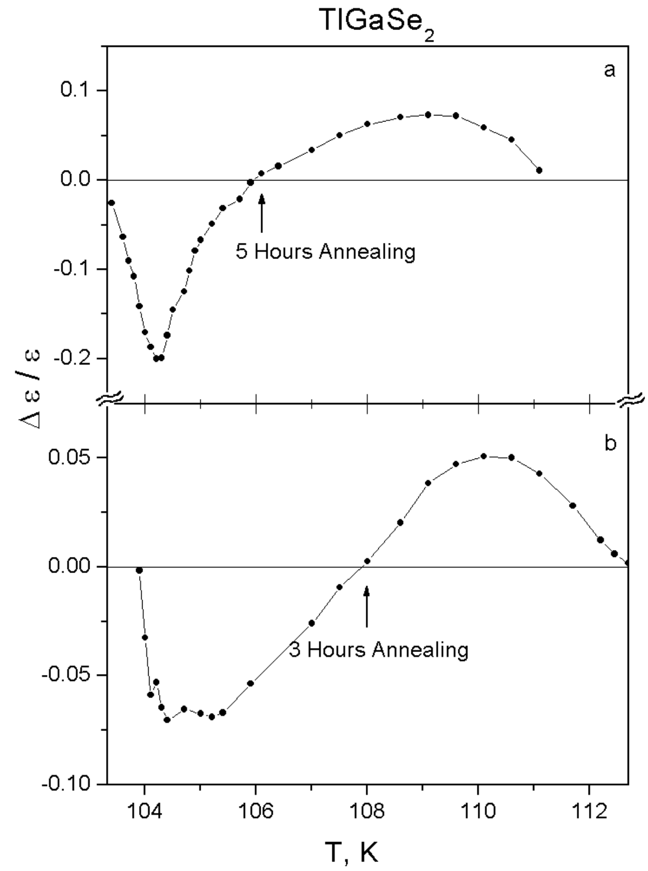

Figure 4. The temperature dependences of the deviations of the real part of the dielectric constant, $\nabla\varepsilon/\varepsilon$, for $TlGaSe_2$ crystals measured in a heating cycle after annealing for 5 h at 106 K (a) and 3 h at 108 K (b).

of artificial lock-in manifests itself in a temperature interval which depends on some parameters which describe the modulation wave, the defect subsystem and their interactions which each other, namely the modulation wave–defect interaction potential, the concentration of mobile defects, their diffusion constant, the annealing time, the temperature variation of the modulation wavelength, etc. In thiourea [5, 6], for example, the artificial lock-in temperature interval does not exceed 1–2 K after annealing for 10–15 h. The same order of lock-in temperature interval is characteristic for memory effects in other crystals. The substantially wider temperature interval which is typical for $TlInS_2$ and $TlGaSe_2$ needs special explanation and we think that this peculiarity of the memory effect is due to the peculiar character of mobile defects in layered crystals. In fact, it is well known [11, 12] that the most typical defects in layered crystals are interlayer defects which are very mobile and have very high concentration due to the weak interlayer bonding. The modulation wave in $TlInS_2$ and $TlGaSe_2$ is created in the direction perpendicular to the layers, so it can be strongly distorted by interplanar defects. Thus, all the important parameters which can lead to widening of the artificial lock-in interval in layered crystals are extremely large compared with those for other crystals in which a memory effect is observed.

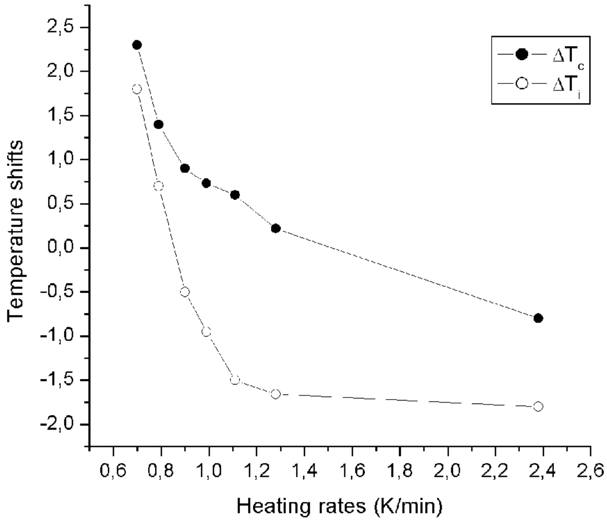

Figure 5. Heating rate dependences of the phase transition temperature shifts (ΔT_c and ΔT_i) in $TlInS_2$ crystal (according to data given in table 1).

Usually the role of mobile defects is restricted to the creation of DDW and memory effects of the type described above. However, charge carriers localized at such defects may play an important role in phase transitions taking place in ferroelectric semiconductors.

As was shown above, the annealing within the incommensurate phase in $TlInS_2$ and $TlGaSe_2$ crystals leads to shifting of the phase transition temperatures. It seems natural to suggest that a model of extremely mobile defects with high concentration could help in understanding these phenomena also. Below we propose a mechanism explaining the results obtained, based on theoretical investigations of the role of charge carriers in the memory effect and phase transitions in ferroelectric semiconductors [13–16].

It is well known that the incommensurate–commensurate phase transition temperature depends on the rate of temperature scanning even without any annealing: T_c shifts to lower temperatures with increasing heating rate. In this sense it must be emphasized that at least at the heating rates realized in the present work, no shifts of phase transition temperatures were observed without annealing. We think that the observed effects can be explained taking into account the role of charge carriers in these crystals.

The study of the role of a charge carrier subsystem in the memory effects in ferroelectric semiconductors with incommensurate phases is of a great interest. In a series of works [13–15] it was shown that these phenomena are greatly influenced by the charge carriers localized at defect states and interacting with a modulation wave.

It is well known [16] that in ferroelectric semiconductors the temperature at which the phase transition into the ferroelectric state occurs shifts to lower temperatures due to the influence of the electronic subsystem. In [17] the contribution of charge carriers to phase transition temperatures for semiconductors with incommensurate phases is considered within the framework of a phenomenological theory of the structural phase transitions. According to this approach, both T_i and T_c will shift to lower temperatures when trapping centres are full as compared with the case where they are empty. However, it is worth mentioning that the occupation of trapping levels and as a result the position of the phase transition temperatures will depend on the interrelation between the heating rate and the relaxation time for electrons on the trapping levels, τ. In fact, if the heating time was to be much higher than τ (slow heating rates) electrons would release from trapping centres and the phase transition temperatures would correspond to the case of empty centres. In the case of fast heating when the heating time is much less than τ, trapping centres will be 'overfilled' and phase transition temperatures will shift to lower temperatures in comparison with the previous case. It is clear that in the real experimental conditions both types of shifting for the phase transition temperatures can be observed, depending on the heating rate. In this case the negative (to lower temperatures) shifts will be observed at higher heating rates and positive ones will be registered at smaller heating rates. Besides this, increasing the heating rate, the 'saturation' of shifting values must be observed, because all traps will be filled and no additional traps available. As is seen from figure 5 and table 1, all above-mentioned phenomena are observed experimentally in the case of $TlInS_2$ crystals. It becomes clear from the results obtained that heating rates of 2.4 K min^{-1} are fast rates, whereas heating with rates of 0.5 K min^{-1} corresponds to slow heating. The same tendency in phase transition temperature behaviour is characteristic for $TlGaSe_2$ crystals also.

Two main problems arise from the considerations given above. The first problem is connected with the experimental investigations of trapping centres in $TlInS_2$ and $TlGaSe_2$ crystals. As a matter of fact, theoretical analysis requires the existence of trapping centres with appropriate parameters. First of all these traps must be activated in the temperature region where the phase transitions take place; then the corresponding relaxation times for charge carriers must be comparable with the real experimental conditions during the heating or cooling process. According to thermally stimulated current investigations of $TlInS_2$ crystals [18], the first and main requirement of the theory is fulfilled: thermally activated current really exists in the temperature region of incommensurate and commensurate phase transitions in this crystal. Our recent investigations of thermally stimulated current in $TlGaSe_2$ showed that the same is true for this crystal. However, there is no information about the relaxation times of charge carriers in the two crystals. The second problem that must be considered is that the theory described in [13, 14, 17] did not require thermal annealing within the incommensurate phase to observe the shifts of phase transition points. However, the results obtained definitely show that only thermal annealing within the incommensurate phase gives the effects described above. We suppose that the impurity centre parameters are modified during the annealing.

In our opinion, the problem of modification of impurity centre parameters under the influence of modulation waves in the incommensurate phase is of special interest and must be considered separately. We note here only that according to investigations of $TlInS_2$ crystals [18] and our preliminary results obtained on $TlGaSe_2$ crystals, the incommensurate phase in both crystals greatly influences the parameters for impurity centres. As was shown theoretically in [14], the annealing within the incommensurate phase may lead to modification of impurity state parameters: non-uniform distribution of charge carriers density is realized which is characterized by long relaxation times (5–300 min). Thus, it appeared to be possible to observe the emptying of impurity states during the heating procedure realized in actual experimental conditions. Perhaps, before annealing, the impurities have very short relaxation times.

5. Conclusion

Thus, various shifts of the incommensurate and commensurate phase transition points both to higher and lower temperatures after annealing within the incommensurate phase temperature interval, depending on the heating rate, were observed for the first time in $TlInS_2$ and $TlGaSe_2$ crystals, together with the 'classic' memory effect with an 'inflexion' point in the $\nabla\varepsilon/\varepsilon(T)$ curve. The peculiarities of the giant 'classic' memory effect in the crystals investigated can be considered in the framework of the model of defect density waves (DDW), so such a memory effect for layered crystals would embrace the wide temperature interval due to the specific type of mobile defects in crystals with layered crystalline structure.

Widening and narrowing of the incommensurate phase temperature interval are considered in the framework of the model, which takes into account the role of charge carriers localized on the defects in commensurate–incommensurate and incommensurate–paraelectric phase transitions. The thermally activated population of these states is responsible for changes of phase transition temperatures.

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References

[1] Muller D and Hahn H 1978 *Z. Anorg. Allg. Chem.* **38** 258
[2] Vakhrushev S B, Zhdanova V V, Kvyatkovsky B E, Okuneva V N, Allakhverdiev K R, Aliev R A and Sardarly R M 1984 *JETP Lett.* **39** 292
[3] McMorrow D F, Cowley R A, Hatton P D and Banys J 1990 *J. Phys.: Condens. Matter* **2** 3699
[4] Folcia C L, Tello M J and Perez-Mato J M 1987 *Phys. Rev.* B **36** 7181
[5] Lederer P, Montambaux G, Jamet J P and Chauvin M 1984 *J. Physique Lett.* **45** L627
[6] Lederer P, Jamet J P and Montambaux G 1986 *Ferroelectrics* **66** 25
[7] Hamano K, Ema K and Hirotsu S 1981 *Ferroelectrics* **36** 343
[8] Gupta S K, Gladkii V V and Lal Krishan 1992 *J. Phys.: Condens. Matter* **4** 855
[9] Allakhverdiev K R, Mikailov F A, Kulibekov A M and Turetken N 1998 *Phase Transit.* **67** 457
[10] Aliyev V P, Babayev S S, Mammadov T G, Seyidov Mir-Hasan Yu and Suleymanov R A 2003 *Solid State Commun.* **128** 25
[11] Manfredotti C, Murri R and Rizzo A 1974 *Phys. Rev.* B **10** 3387
[12] Amelinckx S 1964 *The Direct Observation of Dislocations* (New York: Academic)
[13] Mamin R F 1990 *JETP Lett.* **52** 952
[14] Mamin R F 1991 *Sov. Phys.—Solid State* **33** 2609
[15] Maior M M, Rasing Th, Eijt S W H, van Loosdrecht P H M, van Kempen H, Molnar S B, Vysochanskii Yu M, Motrij S F and Slivka V Yu 1994 *J. Phys.: Condens. Matter* **6** 11211
[16] Fridkin V M 1979 *Photoferroelectrics* (Moscow: Nauka) (in Russian)
[17] Mamin R F and Teitelbaum G B 1988 *Sov. Phys.—Solid State* **30** 3536
[18] Ozdemir S, Suleymanov R A, Civan E and Firat T 1996 *Solid State Commun.* **98** 385