

Order-disorder versus soft mode behaviour of the ferroelectric phase transition in $\text{Sn}_2\text{P}_2\text{S}_6$

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1999 J. Phys.: Condens. Matter 11 3209

(<http://iopscience.iop.org/0953-8984/11/16/002>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.214

The article was downloaded on 15/05/2010 at 07:19

Please note that [terms and conditions apply](#).

Order–disorder versus soft mode behaviour of the ferroelectric phase transition in $\text{Sn}_2\text{P}_2\text{S}_6$

Jirka Hlinka[†], Ted Janssen[‡] and Vladimír Dvořák[†]

[†] Institute of Physics AVCR, Na Slovance 2, CZ-18221 Praha 8, Czech Republic

[‡] Institute for Theoretical Physics, University of Nijmegen, NL-6525ED Nijmegen, The Netherlands

Received 9 March 1999

Abstract. This paper explains the coexistence of the displacive and the order–disorder features of the ferroelectric phase transition in $\text{Sn}_2\text{P}_2\text{S}_6$ crystals. Both have been observed in experiments. The height of the potential barrier hindering the order parameter fluctuations, estimated from experimental data, shows that the phase transition in $\text{Sn}_2\text{P}_2\text{S}_6$ is actually very close to the theoretical case of the order–disorder versus displacive crossover. Moreover, previously performed model calculations can be used for the analysis of the temperature dependence of dielectric susceptibility and other physical properties which do not obey the predictions of standard Landau theory.

1. Introduction

Although the two very basic pictures for structural phase transitions—those of the displacive, soft mode driven phase transition and the order–disorder (o/d) phase transition—are intuitively clear and seemingly exclusive concepts, the actual behaviour of real crystals or theoretical models may often correspond to a less transparent intermediate case [1].

A good example of such an ambiguous case is realized in $\text{Sn}_2\text{P}_2\text{S}_6$, as well as in related isostructural compounds derived from $\text{Sn}_2\text{P}_2\text{S}_6$ by substitution of Sn by Pb or S by Se [2, 3]. The crystal of $\text{Sn}_2\text{P}_2\text{S}_6$ undergoes a second order phase transition from the paraelectric phase to the ferroelectric phase at $T = 337$ K, while $\text{Sn}_2\text{P}_2\text{Se}_6$ goes to the equivalent ferroelectric phase through an intermediate incommensurate phase with stability limits from $T = 193$ K to $T = 221$ K. The phase diagram of the solid solutions of these compounds contains a rather unique critical point; the Lifshitz point [4]. At the same time, the fortunate combination of ferroelectricity with semiconducting properties makes these crystals very interesting from the point of view of applications [5, 6].

Quite recently, several papers dealing with $\text{Sn}_2\text{P}_2\text{S}_6$ and $\text{Sn}_2\text{P}_2\text{Se}_6$ addressed the natural question of whether the phase transition in these compounds follows the o/d or the displacive scenario [7–14]. The spectrum of suggested answers is rather wide. The specific heat measurements [7] on both compounds seem to clearly support the o/d concept, and the structural model of $\text{Sn}_2\text{P}_2\text{Se}_6$ by Israel *et al* [8] also seems to favour the o/d concept. On the other hand, spectroscopic studies of $\text{Sn}_2\text{P}_2\text{Se}_6$ by Eijt *et al* [9–11] seem to support a soft mode behaviour, even though effects that ‘might be alternatively related to disorder’ are identified. Finally Enjalbert *et al* [12] and Drobnich and Vysochanski [13] consider these compounds as ‘mainly displacive with slight disorder effects’.

The aim of this paper is to establish quantitatively the degree of o/d versus soft mode behaviour in $\text{Sn}_2\text{P}_2\text{S}_6$ type crystals. For this purpose, we first discuss the o/d versus soft mode crossover for a simple theoretical model (in the next section). The crossover can be characterized by the ratio $U_m/k_B T_c$ where U_m is the energy barrier on the trajectory of the ferroelectric mode coordinate. In section 3, this energy barrier is determined from the experimental data of $\text{Sn}_2\text{P}_2\text{S}_6$. It turns out that the estimate obtained allows us to show that the $\text{Sn}_2\text{P}_2\text{S}_6$ type materials are close to the theoretical definitions of the o/d versus soft mode crossover. Some of the consequences are discussed in section 4.

2. Theoretical analysis of the o/d versus soft mode behaviour

A simple model [1, 14–21], convenient for analysis of the o/d versus soft mode crossover, can be defined by a potential acting on a set of classical particles, each with a single continuum degree of freedom x_i attached to a 3D lattice of discrete sites i :

$$V = \sum_i V(x_i) + \frac{1}{2} \sum_i \sum_{j \neq i} C_{i,j} (x_i - x_j)^2 \quad (1)$$

that can also be expressed as

$$V = \sum_i V'(x_i) - \sum_i \sum_{j \neq i} C_{ij} x_i x_j. \quad (2)$$

Following [14–21], we assume a symmetric anharmonic ‘2–4’ on-site potential

$$V(x_i) = \frac{1}{2} A x_i^2 + \frac{1}{4} B x_i^4 \quad (3)$$

with $A < 0$ and $B > 0$. The intersite harmonic coupling is limited to nearest neighbour sites with $C > 0$ unless the opposite is stated explicitly. Since the essential effects of anisotropy can be taken into account by rescaling of the force constants, the lattice is considered to be cubic [1]. We expect this model to describe second order phase transitions in most uniaxial ferroelectrics, except for the cases when the phase transition is at low temperature so that the quantum effects have to be taken into account [1].

The ground state (and the equilibrium state at zero temperature) is a ferroelectric ordered state with all particles at the (same side) bottom of the local double well:

$$x_i = \pm X \quad X = \sqrt{-A/B}. \quad (4)$$

A simultaneous shift of all the particles towards the opposite domain state (between $x_i = X$ and $x_i = -X$) corresponds to a large fluctuation of the zone centre (‘ferroelectric’) soft mode. The energy barrier per site on this trajectory is entirely defined by the on-site potential (equation (3)):

$$U_m = A^2/(4B). \quad (5)$$

On the other hand, the energy increase corresponding to an isolated ‘flip’ (between $x_i = X$ and $x_i = -X$) of a single particle inside the ordered domain can be expressed as

$$U_f = 12CX^2 = 12 \frac{C|A|}{B}. \quad (6)$$

By an appropriate choice of units for energy and displacement [1, 14–16], the potential of equations (1)–(3) can be put in a form where the only free parameter is the ratio of the two characteristic energies $U_f/U_m = 3C/|A|$. When this ratio is very small, the model displays an o/d phase transition. In the opposite case, in the displacive limit, the phase transition can

be described as freezing of the soft mode. The transition temperature itself may be expressed through a dimensionless function $f(t)$:

$$k_B T_c = f \left(\frac{U_f}{U_m} \right) C X^2$$

Analytical methods were previously used to determine the phase transition temperatures in these two limiting cases [1, 16–18]:

$$f(0) \doteq 9.12 \quad f(\infty) \doteq 2.638. \quad (7)$$

It is natural to ask for the position and sharpness of the ‘crossover’ between the two asymptotic cases. Obviously, we expect that this crossover happens when U_f and U_m are of the same order of magnitude, but it would be convenient to have a more quantitative and meaningful clear cut criterion. Two possibilities for such a criterion have been proposed previously [15]. According to the first one, the crossover is put at the point where the diagonal elements of the quadratic part of the potential change sign, i.e. when the on-site potential $V'(x)$ in the ‘Ising’ expression of equation (2) just changes from a single well to a double well profile. This condition corresponds to $U_f = 4U_m$. There is a related proposal based on an assumption that the soft mode frequency extrapolated linearly to the phase transition would vanish completely on the ‘displacive side’ of the crossover point [15]. Note that if this were to hold exactly, it would imply a kind of phase transition with the ‘extrapolated soft mode gap’ as an order parameter, rather than a crossover situation. Nevertheless, this type of criterion seems to be useful for the analysis of some numerical studies [15]. After all, according to Padlewski *et al* [15], such a criterion localizes the crossover at the same place as the former criterion based on the form of $V'(x)$, that is at $U_f = 4U_m$.

The second proposal consists in putting the crossover at the point where $k_B T_c = U_m$. Obviously, if the energy fluctuations at the phase transition are much larger than the potential barrier in the soft mode coordinate, oscillations over the barrier would take place that would lead to soft mode behaviour. In the opposite case, soft mode like oscillations above the phase transition are expected to be impossible and the particles would occupy only the bottoms of the double wells. By interpolation of $k_B T_c$ data of [15] and [16], we have found that the second proposal puts the crossover at $U_f \approx 2.5U_m$.

Crossover positions related to the above proposals are shown in figure 1, together with the plot of the ratio $f = k_B T_c / C X^2$ versus U_f / U_m . The discrete points correspond to the Monte Carlo and molecular dynamic simulations taken from references [15], [16] and [21], respectively. Note that the data can be rather well approximated by a heuristic formula

$$k_B T_c = C X^2 \left[\frac{f(0) + f(\infty)}{2} - \frac{f(0) - f(\infty)}{2} \tanh \lg \left(\frac{10 C X^2}{U_m} \right) \right] \quad (8)$$

with $f(0)$ and $f(\infty)$ fixed by equation (7).

Since the difference between the two proposals is quite small, we will choose as the relevant parameter $k_B T_c / U_m$, since it is easier to obtain from the experimental data than U_f / U_m . Figure 2 shows a plot of $k_B T_c / U_m$ versus U_f / U_m according to this model.

Finally, previous studies shed some new light on the Landau thermodynamic potential of the model [15, 16, 19, 20]. It has been found that, at temperatures well out of the critical region, the calculated free energy per site can be reasonably well approximated by the usual expansion in the powers of the spatially averaged displacement $x = \langle x_i \rangle$ as

$$U(T) = \frac{\alpha(T)}{2} x^2 + \frac{\beta(T)}{4} x^4 + \frac{\gamma(T)}{6} x^6 + \dots \quad (9)$$

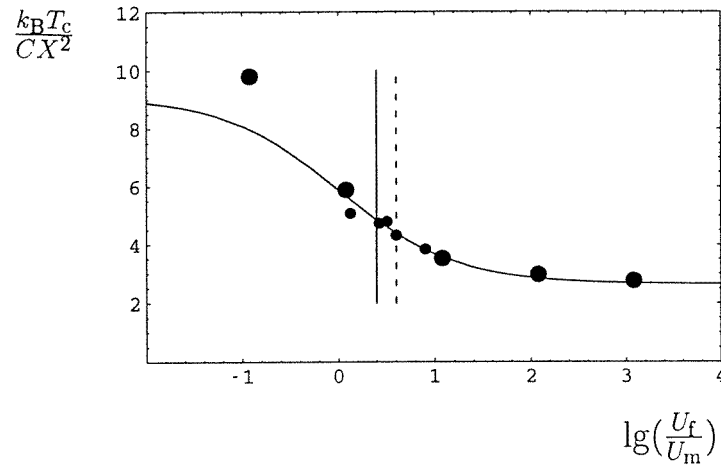


Figure 1. Reduced phase transition temperature $k_B T_c / U_f$ as a function of the ratio of characteristic energies U_f / U_m for the model defined in the text. Large circles: Monte Carlo simulations of Radescu *et al* [16]. Small circles: molecular dynamics results of Padlewski *et al* [15] and Schneider and Stoll [21]. Continuum curve: phenomenological interpolation (equation (8)) between the two asymptotic results (equation (7)) obtained by more exact methods. Vertical lines show theoretical ‘crossover positions’ defined in the text.

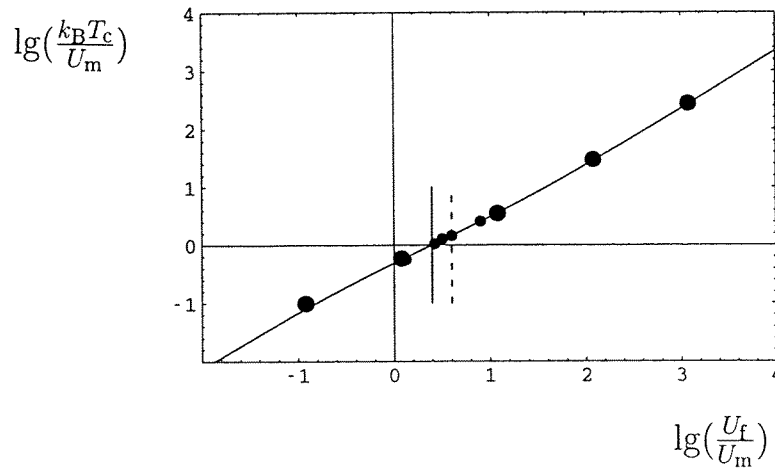


Figure 2. Relation between characteristic ratios $k_B T_c / U_m$, better suited to the characterization of a real crystal and ratio U_f / E_m more convenient when the theoretical model is introduced. Symbols and continuum guide line have the same meaning as in figure 1.

Obviously, in the low temperature limit we find again the original microscopic potential given by equation (3):

$$U(0) = \frac{A}{2}x^2 + \frac{B}{4}x^4. \quad (10)$$

The temperature dependence of the coefficients in equation (9) is, however, somewhat different to the standard phenomenological ansatz. We will use here the following three important conclusions that can be drawn from the investigations published in [15, 16, 19, 20]:

- (1) The coefficient α is a roughly linear function of the temperature below the phase transition, and it can be approximated by (see figure 3 of Radescu *et al* [16])

$$\alpha(T) \approx |\alpha(0)| \left(\frac{T}{T_c} - 1 \right) \quad T < T_c. \quad (11)$$

- (2) The coefficient α is also a roughly linear function of the temperature above the phase transition but the slope is the same as below T_c only in the displacive limit. In the o/d case the slope of $\alpha(T)$ is several times larger below T_c than above. This suggests a natural explanation for the often observed deviations from the prediction of standard Landau theory for the ratios of the Curie constants and soft mode slopes above and below the phase transition.
- (3) The coefficient $\beta(T)$ is temperature independent only in the displacive limit. Calculations performed in the o/d domain show that β decreases as T_c is approached. This leads to a temperature dependence of the order parameter that differs from the square root law prediction of the usual Landau theory. The reduction of the value of $\beta(T)$ compared to B in equation (10) may be so important that the sixth and higher order terms in the Landau potential expansion may become necessary. This seems to be a natural explanation for tricritical behaviour in many compounds, and may possibly even lead to a weakly first order phase transition.

3. Energy barrier for the ferroelectric mode in $\text{Sn}_2\text{P}_2\text{S}_6$

Let us now estimate the soft mode coordinate energy barrier in $\text{Sn}_2\text{P}_2\text{S}_6$. We start with a Landau expansion of the free energy density (per unit volume) in terms of the polarization P :

$$\frac{U}{V} = \frac{\alpha_P(T)}{2} P^2 + \frac{\beta_P(T)}{4} P^4 + \frac{\gamma_P(T)}{6} P^6 + \dots - EP. \quad (12)$$

We assume that the Landau energy density of the real $\text{Sn}_2\text{P}_2\text{S}_6$ crystal has the same properties as those derived for the simple model discussed in the previous paragraph. Then at low temperatures only the first two terms are relevant. This means that the barrier may be actually approximated by the 2–4 potential, that is by the first two terms of the Taylor expansion allowed by symmetry. Note that by this assumption we do not rule out the possible role of the sixth order term in the *Landau thermodynamical potential near the phase transition*.

The saturated spontaneous polarization P_s is given by

$$P_s^2 = \frac{|\alpha_P(0)|}{\beta_P(0)} \quad (13)$$

where $\alpha_P(0) < 0$, $\beta_P(T) > 0$, and the Curie constant below T_c can be approximated using equations (11) and (12) as

$$\epsilon_0 C_- = T_c/2|\alpha_P(0)|. \quad (14)$$

From these relations, using the experimental values of $P_s = 0.16 \text{ C m}^{-2}$ [22] and the Curie constant $C_- = 7 \times 10^3$ (here the high frequency value of C_- is taken from figure 1 of the paper by Grigas *et al* [23] in order to avoid contribution of domain walls [24]), we can estimate the potential parameters as:

$$\alpha_P(0) = 2.7 \times 10^9 \text{ J m C}^{-2} \quad \beta_P(0) = 10^{11} \text{ J m}^5 \text{ C}^{-4}. \quad (15)$$

The energy barrier per active entity, one molecular unit of $\text{Sn}_2\text{P}_2\text{S}_6$, is obtained as the product of the potential barrier energy density $\alpha_P(0)^2/4\beta_P(0)$, and the corresponding volume (half of the unit cell [2]):

$$U_m = \frac{1}{2} V_{\text{unit cell}} \alpha(0)^2/(4\beta(0)) \approx 4 \times 10^{-21} \text{ J}. \quad (16)$$

Alternatively, the energy barrier can be expressed using the low temperature limit of the soft mode frequency, the atomic masses and the amplitude of the frozen displacements in the ferroelectric phase. To this end, it is convenient to expand the free energy density (per unit of mass) in terms of the normalized soft phonon coordinate

$$\frac{U}{M} = \frac{\alpha_\eta(T)}{2}\eta^2 + \frac{\beta_\eta(T)}{4}\eta^4 + \dots \quad (17)$$

Here $2\alpha_\eta = 4\pi^2\nu^2$ is just the square of the saturated angular frequency of the soft mode. Since the temperature dependence of the soft mode in $\text{Sn}_2\text{P}_2\text{S}_6$, and its anticrossing with another mode was rather thoroughly studied by Raman spectroscopy [9, 25, 26] and inelastic neutron scattering [9, 11], the saturated low temperature frequency of the soft mode can be accurately determined. The experimental value [9, 25] of $\nu \approx 48 \text{ cm}^{-1}$ leads to $|\alpha_\eta(0)| \approx 42 \text{ THz}^2$. The amplitude of the frozen phonon displacement in equation (17) can, in principle, be calculated directly from the structural data at low temperatures. Unfortunately, at the moment only the room temperature structural data [27] are available. These results show that the soft mode eigenvector can be approximately regarded as a shift of the two Sn^{2+} ions in a direction close to that of the spontaneous polarization, by 0.032 and 0.022 nm, respectively [27]. The corresponding mass-averaged displacement at room temperature is about 0.014 nm. Anticipating a further increase of the frozen phonon displacement with further lowering of the temperature, we expect $\eta(0)$ to be about 0.02 nm. This rather rough estimate gives $\beta_\eta(0) \approx 10 \text{ THz}^2 \text{ nm}^2$. The energy barrier per molecular unit, obtained as product of the mass of the $\text{Sn}_2\text{P}_2\text{S}_6$ formula unit and the potential barrier energy density $|\alpha_\eta(0)|^2/4\beta_\eta(0)$:

$$U_m = \frac{1}{2}M_{\text{unit cell}}|\alpha_\eta(0)|^2/4\beta_\eta(0) \approx 3 \times 10^{-21} \text{ J}. \quad (18)$$

Since both these values ((16), (18)) are close to $k_B T_c = k_B \times 337 \text{ K} = 4.65 \times 10^{-21} \text{ J}$, we conclude that the ratio $k_B T_c/U_m$ for a $\text{Sn}_2\text{P}_2\text{S}_6$ crystal is close to unity. Thus, this crystal is actually a prototype for an o/d versus soft mode crossover system.

4. Discussion and conclusion

The estimation of the energy barrier in the $\text{Sn}_2\text{P}_2\text{S}_6$ allows us to establish the realization of the o/d versus displacive crossover in this material in a quantitative manner. The closeness to the theoretical definitions of the crossover enables us to understand seemingly contradictory conclusions of recent investigations [7–13], although more detailed analyses would be necessary for detailed interpretation of the related experimental results.

Still, there is a certain number of consequences that might be immediately derived from the value of the potential barrier:

- (1) The crossover situation actually implies that the compound should reveal a soft mode, which, however, does not soften completely, and is actually observed in experiment [9, 11, 25, 26].
- (2) From the molecular dynamics simulation performed for the simple model in the corresponding regime [15], it follows that the ratio of the soft mode temperature dependence is between $R = 2.7$ and $R = 9.5$, depending on the actual form of the dispersion (the case of $R = 2.7$ – 3 corresponds to the unrealistic case of infinitely long range interactions while $R = 8$ – 9.5 corresponds exactly to the nearest neighbour model so far considered.) This again agrees with the experimental estimate $R = -7.5 \pm 2.5$ from the inelastic neutron scattering study of Eijt *et al* [9, 11].

- (3) As the condition $k_B T_c \approx U_m$ corresponds to the case $U_m \approx 4CX^2$, we may estimate the interaction constant $C \approx \alpha_\eta(0)/16$. Using $\alpha_\eta(0)$ of equation (17), we get quite a small value of $C \approx 2.6 \text{ THz}^2$, which is in perfect agreement with the experimental result, showing that the dispersion curves in all three directions are very flat (change of the frequency along dispersion of the x-polarized mode is within the 5 per cent, except for the regions where obvious mixing with acoustic branches takes place) [11].
- (4) The Monte Carlo (MC) simulations performed on the model at $U_m \approx 1CX^2$ and $U_m \approx 10CX^2$ showed a clear jump of the slope of the temperature dependence of the Landau expansion coefficient $\alpha(T)$ (see figure 3 of Radescu *et al* [16]). This would lead to a nonstandard ratio of the Curie constants below and above the phase transition ($C_-/C_+ = 4$ and 10, respectively.) Since the value of the barrier in $\text{Sn}_2\text{P}_2\text{S}_6$ places this system between the two model situations, it seems natural to claim that it is the o/d crossover that is responsible for the large value of $C_-/C_+ \approx 9$ observed experimentally [23].
- (5) Using the results of the above mentioned MC simulations, it can also be claimed that the *quartic coefficient of the Landau potential for $\text{Sn}_2\text{P}_2\text{S}_6$ should be considered as temperature dependent* on the temperature scales comparable with T_c . Reduction of its value at T_c should be significant, by a factor of 10 at least, so that the sixth-order term in the Landau expansion really may play an important role in the vicinity of T_c , as anticipated by phenomenological theory [28]. This suggests that the crossover behaviour is most probably responsible for all ‘tricritical’ features of the $\text{Sn}_2\text{P}_2\text{S}_6$ phase transition.
- (6) The temperature dependence of the quartic term itself is sufficient to produce a nonstandard temperature dependence of the spontaneous polarization. According to the above mentioned MC simulations, the ‘pseudo-critical’ coefficient β in

$$P_s = K(T - T_c)^\beta \quad (19)$$

fitted to experimental data in the region of about $0.5T_c$ – $0.95T_c$ should give a value between 0.26 and 0.33 (see figure 6 of Radescu *et al* [16]. Note that this essentially means that saturation is achieved faster than would be expected for a usual displacive phase transition. In this way the crossover effect contributes to the enhancement of the pyroelectric coefficient dP_s/dT [5].

Finally, the reason why we did not provide an analogous estimate of the energy barrier in $\text{Sn}_2\text{P}_2\text{Se}_6$ is because the experimental data are less transparent—neither the Curie constant in the ferroelectric constant, nor the saturated frequency of the ferroelectric mode can be estimated with the same precision as in $\text{Sn}_2\text{P}_2\text{S}_6$. Nevertheless, it is clear that the energy barriers in both compounds are of the same order of magnitude. It may perhaps be somewhat lower in $\text{Sn}_2\text{P}_2\text{Se}_6$, since the phase transition temperatures are also lower. Moreover, the presence of the intermediate incommensurate phase itself is probably more important for the actual soft mode versus o/d behaviour. To analyse this point, a detailed analysis of the o/d versus soft mode crossover in the DIFFOUR (discrete frustrated ϕ^4) model [29] would be highly desirable. The merit of such a study, which is currently under development, should be a description of the tricritical features of the phase transitions in the mixed $\text{Sn}_2\text{P}_2\text{S}_x\text{Se}_{6-x}$ system in a model without *ad hoc* assumptions on the form and temperature dependence of the Landau potential.

Acknowledgments

This work has been supported by the INCO-COPERNICUS project No ERB3512PL964434. One of the authors (JH) is grateful for the warm hospitality shown during his stay at the Institute

for Theoretical Physics of the University of Nijmegen, to Professor Yu M Vysochanski of Uzhgorod University for providing useful reprints and preprints of scientific papers and to Professor S I Ben-Abraham of Ben-Gurion University and Dr J Petzelt of the Institute of Physics of AVCR in Prague for useful comments on the manuscript.

References

- [1] Bruce A D and Cowley R A 1981 *Structural Phase Transitions* (London: Taylor and Francis) p 112
- [2] Barsamian T K, Khasanov S S and Shekhtman V Sh 1993 *Ferroelectrics* **138** 63
- [3] Vysochanski Yu V, Gurzan M I, Maior M M, Motrya S F, Potorii M V, Salo L A, Khoma M M, Voroshilov Yu M and Slivka V Yu 1984 *Fiz. Tver. Tela (Leningrad)* **27** 858
- [4] Vysochanski Yu V, Maior M M, Rizak V M, Slivka V Yu and Khoma M 1989 *Zh. Eksp. Teor. Fiz.* **95** 1355
- [5] Maior M M, Vysochanskij Yu M, Prits I P, Molnar S B, Seikovskaya L A and Slivka V Yu 1990 *Kristallogr. (Sov. Phys. Crystallogr.)* **35** 1300
- [6] Cleary D A, Willet R D, Ghebremichael F and Kuzyk M G 1993 *Solid State Commun.* **88** 39
- [7] Moria K, Kuniyoshi H, Tashita K, Ozaki Y, Yano S and Matsuo T 1998 *J. Phys. Soc. Japan* **67** 3505
- [8] Israel R, de Gelder R, Smits J M M, Beurskens P T, Eijt S W H, Rasing Th, van Kempen H, Maior M M and Motrija S F 1998 *Z. Kristallogr.* **213** 34
- [9] Eijt S W H 1998 *PhD thesis* University of Nijmegen
- [10] Eijt S W H, Currat R, Lorenzo J E, Saint-Gregoire P, Katano S, Janssen T, Hennion B and Vysochanskii Yu M 1998 *J. Phys.: Condens. Matter* **10** 4811
- [11] Eijt S W H, Currat R, Lorentzo J E, Saint-Gregoire P, Hennion B and Vysochanski Yu M 1998 *Eur. Phys. J. B* **5** 169
- [12] Enjalbert R, R Galy J, Vysochanski Yu, Ouedrago A and Saint-Gregoire P 1999 *Eur. Phys. J. B* to be published
- [13] Droblich A and Vysochanski Yu V 1998 *Condens. Matter Phys.* **1** 331
- [14] Aubry S 1975 *J. Chem. Phys.* **62** 3217
- [15] Padlewski S, Evans A K, Ayling C and Heine V 1992 *J. Phys.: Condens. Matter* **4** 4895
- [16] Radescu S, Etxebarria I and Perez-Mato J M 1995 *J. Phys.: Condens. Matter* **7** 585
- [17] Bruce A D 1980 *Adv. Phys.* **29** 111
- [18] Oppermann R and Thomas H 1975 *Z. Phys.* **B 22** 387
- [19] Giddy A P, Dove M T and Heine V 1989 *J. Phys.: Condens. Matter* **1** 8327
- [20] Heine V et al 1992 *Ferroelectrics* **128** 255
- [21] Schneider T and Stoll E 1978 *Phys. Rev.* **B 17** 1302
- [22] Vysochanski Yu V 1999 private communication
- [23] Grigas J, Kalesinskas V, Lapinskas S and Paprotny W 1988 *Phase Transitions* **12** 263
- [24] Petzelt J, Kozlov G V and Volkov A A 1987 *Ferroelectrics* **73** 101
- [25] Gomonnai A V, Vysochanski Yu M, Grabar A A and Slivka V Yu 1981 *Fiz. Tver. Tela (Leningrad)* **23** 3623
- [26] Slivka V Yu, Vysochanski Yu M, Gurzan M I and Chepur D V 1979 *Fiz. Tver. Tela (Leningrad)* **21** 1378
- [27] Scott B, Pressprich M, Willet R D and Cleary D A 1992 *J. Solid State Chem.* **96** 294
- [28] Vysochanskii Yu M, Khoma M M and Molnar A A 1997 *Ferroelectrics* **191** 231
- [29] Janssen T and Tjon J A 1982 *Phys. Rev. B* **25** 3767