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The effect of pressure on incommensurate phases

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Abstract. The effect of pressure on incommensurate phases is studied on the basis of thermodynamic theory. It is shown that there are two types of pressure–temperature phase diagram and the influence of the pressure on different properties of incommensurate crystals is clarified. The character of the diagram and of this influence depends on the type of the incommensurate phase (existence or absence of the Lifshitz invariant, and the order of the anisotropy invariant). The results are compared with experiments and show good agreement.

The effect of pressure (in general, uniaxial stresses) on phase transitions, particularly on those with the formation of an incommensurate (I) phase, has been considered in many experimental studies. In theoretical treatments of the I phase such an effect is usually described by introducing terms $u_i \rho^2$ in the Landau thermodynamic potential, where u_i are the strain tensor components (here and subsequently $u_1 = u_{xx}$, $u_2 = u_{yy}$ and $u_3 = u_{zz}$) and ρ^2 is the quadratic invariant composed of the order parameter components (Mashiyama 1980, Sannikov and Golovko 1984, Chapelle 1986). Exclusion of u_i leads only to the appearance of an additional term, proportional to the pressure, in the coefficient of ρ^2 in the thermodynamic potential, which means that the variation in pressure must shift identically all transition temperatures without any other changes. However, experimental data have proved to be more complex, which suggests that other invariants would be important in the problem in question. In general, a substantial role can be played by those invariants which give corrections, depending on pressure, to the thermodynamic potential coefficients that have small values, because relative variations in these coefficients will be especially large when the pressure increases. The thermodynamic potential of the I phase contains two small coefficients, that of ρ^2 and that of the Lifshitz invariant (when a Lifshitz invariant exists, the I phase is often called type I; the case when the symmetry does not admit such an invariant, i.e. an I phase of the type II, will be considered below).

Let us first obtain some general results. We assume that the structure is modulated along the x direction and we represent the thermodynamic potential ϕ per unit length as

$$\phi = \frac{1}{d} \int_0^d \tilde{\phi}(x) dx \quad \tilde{\phi}(x) = \tilde{\phi}_1(x) + \tilde{\phi}_2(x) \quad (1)$$

where d is the period of the order parameter, $\tilde{\phi}_1$ is the part of the density $\tilde{\phi}$ which does not contain the strain tensor, and

$$\tilde{\phi}_2 = u_i F_i + \frac{1}{2} \lambda_{ij} u_i u_j - \sigma_i u_i. \quad (2)$$

Here λ_{ij} are the elastic moduli of the parent (P) phase, σ_i are the components of the stress

tensor, and summation from 1 to 3 over the repeated indices is implied. We assume that the P phase has orthorhombic symmetry (as is the case with many crystals with an I phase); then the components u_i are invariants. The quantities F_i can be arbitrary invariants composed of the order parameter components.

In minimising ϕ with respect to u_i the independent variables should be taken to be the components of the strain vector. Following a previously described procedure (Golovko 1985) and eliminating u_i from $\tilde{\phi}_2$, we get

$$\tilde{\phi}_2 = \frac{1}{2\lambda_{11}}(I_1^2 - F_1^2) - \frac{1}{2}\chi_{ij}I_iI_j + \chi_{ij}F_i\sigma_j - \frac{1}{2}\chi_{ij}\sigma_i\sigma_j \quad I_i = \frac{1}{d} \int_0^d F_i dx \quad (3)$$

where χ_{ij} are the elastic compliances ($\chi_{ij}\lambda_{jk} = \delta_{ik}$). The strain tensor components averaged over space are found to be

$$\bar{u}_i = \chi_{ij}(\sigma_j - I_j). \quad (4)$$

Let us consider a two-dimensional order parameter with components η and ξ written as $\eta = \rho \cos \varphi$ and $\xi = \rho \sin \varphi$ in polar coordinates. Since renormalisations of the coefficients of ρ^2 and of the Lifshitz invariant $\rho^2 d\varphi/dx$ are of interest, the quantities F_i should be taken in the form

$$F_i = \frac{1}{2}b_i\rho^2 + r_i\rho^2 d\varphi/dx. \quad (5)$$

Let us turn now to equation (3) for $\tilde{\phi}_2$. The last term does not contain the order parameter and it can be omitted. The first two terms do not depend on σ_i . The quantity F_i^2 gives fixed corrections to coefficients in $\tilde{\phi}_1$. Close to the P-I transition, where ρ and $d\varphi/dx$ are constant in space (see, e.g., Golovko 1980), the terms with I_iI_j renormalise the coefficient of ρ^4 in $\tilde{\phi}_1$. Near the transition to the commensurate (C) phase the main role of these terms is that, owing to them, this transition becomes first order (Golovko 1985). If this fact is taken into account somewhat, the role of the terms with I_iI_j will be reduced to an effective renormalisation of the ρ^4 coefficient in $\tilde{\phi}_1$. Then only the third term in $\tilde{\phi}_2$ (equation (3)) will be essential. A method which greatly simplifies the problem and leads to an I-C transition of first order even without the first terms in equation (3), consists in utilising the constant-amplitude approximation, provided that the value of the amplitude ρ is determined by minimising ϕ (Golovko 1980). Strictly speaking, the constant-amplitude approximation is valid only in the case of weak anisotropy in the space of order parameter components (Sannikov 1980); if the anisotropy is not weak, this approximation can be used for qualitative and semi-quantitative estimates.

Let us write down the most essential terms in $\tilde{\phi}_1$, the above-mentioned renormalisation of the coefficients being implied:

$$\tilde{\phi}_1 = (\alpha/2)\rho^2 + (\beta/4)\rho^4 + (\gamma_n/n)\rho^n \cos n\varphi - \sigma\rho^2 d\varphi/dx + (\delta/2)[(d\rho/dx)^2 + \rho^2(d\varphi/dx)^2]. \quad (6)$$

Adding here the third term of $\tilde{\phi}_2$ (equation (3)) and substituting equation (5) for F_i leads only to replacement of α and σ by α^* and σ^* , respectively, with

$$\alpha^* = \alpha + \alpha_p \quad \sigma^* = \sigma + \sigma_p \quad \alpha_p = \chi_{ij}b_i\sigma_j \quad \sigma_p = -\chi_{ij}r_i\sigma_j. \quad (7)$$

If the question is of a hydrostatic pressure ($\sigma_1 = \sigma_2 = \sigma_3 = -p$) one has

$$\alpha_p = -bp \quad \sigma_p = rp \quad b = \sum_{j=1}^3 \chi_{ij} b_i \quad r = \sum_{j=1}^3 \chi_{ij} r_i. \quad (8)$$

For simplicity we shall discuss further only the effect of the pressure p . In the case of uniaxial stresses, one must utilise equation (7) for α_p and σ_p instead of (8).

Now we can analyse the influence of the pressure on I phases. First, let us consider the wavevector q of the incommensurate superstructure at the P-I transition. When $p = 0$ we have $q = \sigma/\delta$ (see, e.g., Golovko 1980). Replacing σ by σ^* yields

$$q = q_0 + (r/\delta)p \quad q_0 = \sigma/\delta. \quad (9)$$

The wavevector q_0 is small (compared with an ordinary value, in this case with the reciprocal-lattice constant), whereas the coefficient r is, in general, of ordinary magnitude. Therefore the pressure changes q appreciably. At $p = 0$ the point of the P-I transition is defined by the equation $\alpha = \sigma^2/\delta$. Replacing α and σ by α^* and σ^* , respectively, we get for this point, when $p \neq 0$,

$$\alpha = -\alpha_p + \alpha_0^* = \alpha_0 + bp + 2q_0rp + (1/\delta)r^2p^2 \quad \alpha_0 = \sigma^2/\delta \quad \alpha_0^* = (\sigma^*)^2/\delta. \quad (10)$$

The temperature T_i of the P-I transition can be found from (10) if, as usual, one assumes that $\alpha = \alpha_T(T - \theta)$. At small p the shift of T_i is determined essentially by the term bp because q_0 is small. Making use of (4), one can obtain expressions for jumps of the thermal expansion coefficients and of the elastic moduli at T_i , and also the pressure dependence of these jumps. It should be noted that invariants of type $\rho^2 h_{ij} u_i u_j$ which were not taken into account in (2), also play a role in the pressure dependence of the jumps (Luspin *et al* 1984).

Next, let us consider the I-C transition ($\alpha = \alpha_c$, $T = T_c$). Here results depend on the integer n in the anisotropy invariant in (6). If $n = 4$ we denote, as usual, $\gamma_n = \beta'$. In this case, $\alpha_c = -\alpha_0 B$ where B depends only upon the ratio β'/β . The β'/β dependence of $B = |\alpha_c|/\alpha_0$ within the constant-amplitude approximation is shown in figure 2 of the paper by Golovko (1980). In order to evaluate α_c , one can take a close value $\alpha = \alpha_t$ at which the modulus of elliptic integrals equals unity. This gives

$$B = (\pi^2/4)(\beta/|\beta'| - 1). \quad (11)$$

Proceeding as before, we obtain for α_c , when $p \neq 0$,

$$\alpha_c = -\alpha_0 B + bp - 2q_0 B r p - (B/\delta)r^2 p^2. \quad (12)$$

Here, as in equation (10), the main p dependence is due to the term bp . Therefore, at small p the lines $T_i = T_i(p)$ and $T_c = T_c(p)$ run almost parallel. An exception is the case of weak anisotropy when the ratio $|\beta'|/\beta$ is small and hence B is large. Strictly speaking, according to the discussion at the beginning of this paper, when β' is small, equation (5) for F_i must be supplemented with a term containing $\rho^4 \cos 4\varphi$, but the qualitative result remains the same.

The p - T phase diagrams resulting from equations (10) and (12) are shown schematically in figures 1 and 2. Note point A (figure 2) where $\sigma^* = 0$ (and hence $q = 0$). The I phase also exists above point A because the sign of σ in (6) plays no role in the I phase (the sign of σ and that of r_i can be reversed in (5) and (6) by changing the sign of the coordinate x ; therefore only the sign of the ratio σ/r_i is of importance). Naturally,

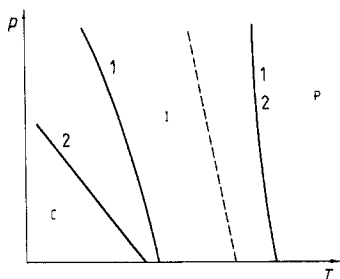


Figure 1. Phase diagram for $\sigma/r > 0$. The broken curve is the curve where $\alpha^* = 0$ (if $b < 0$); curve 1, $n = 4$; curve 2, $n = 6$.

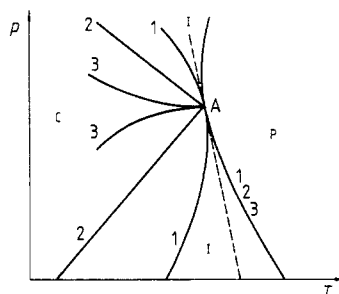


Figure 2. As for figure 1 but for $\sigma/r < 0$: curve 3, $n > 6$.

at high pressures, terms that were discarded in the above treatment may modify some details of the phase diagrams.

An example of a crystal having an *i* phase with $n = 4$ is $(\text{NH}_4)_2\text{BeF}_4$. According to experimental data (Gesi and Ozawa 1974) the phase diagram of $(\text{NH}_4)_2\text{BeF}_4$ is of the type shown in figure 1. Comparison of the p dependence of the temperatures T_i and T_c allows one to evaluate the magnitude of the anisotropy. Differentiating equations (10) and (12) with respect to p and taking into account that q_0 is small gives at $p = 0$

$$(T'_i - T'_c)/T'_i = 2(1 + B)q_0r/b \quad (13)$$

where the primes denote derivatives of T_i and T_c with respect to p . The value of r can be found from the pressure dependence of q according to (9); that of b can be extracted from other independent experiments (Sannikov and Golovko 1984). Knowing r/b , from equation (13), one calculates B and hence β'/β . Because lack of data does not permit us to calculate r/b for $(\text{NH}_4)_2\text{BeF}_4$ let us confine ourselves to semi-quantitative estimates. From dimension considerations it follows that generally $b \sim a^*r$ where a^* is the reciprocal-lattice constant. For $(\text{NH}_4)_2\text{BeF}_4$, according to Kudo (1982), $q_0/a^* = 0.025$ and, according to Gesi and Ozawa (1974), $(T'_i - T'_c)/T'_i = -0.29$; consequently, from (13) $B \approx 4.8$. Now from (11) we obtain that $|\beta'/\beta| \approx \frac{1}{3}$.

Let us now consider the effect of pressure on other properties of incommensurate crystals with $n = 4$. Any expression for a physical quantity M in the *i* phase can be put into the form (see, e.g., Golovko 1980)

$$M = \tilde{M}f(\alpha/\alpha_0, \beta'/\beta, \dots) \quad (14)$$

where \tilde{M} is a dimension factor, f is a dimensionless function, and the ellipsis stands for combinations of parameters which are not explicitly written down in (6). Suppose that \tilde{M} does not contain α_0 , q_0 , p or T . Then all the dependence on p and T will be due to α^*/α_0^* ; that is with increasing p , only a shift and rescaling on the temperature axis without change in the heights of peaks and jumps occur. An example of such a quantity is the dielectric permittivity in the case of ferroelectrics (Golovko 1980), the result just obtained being in agreement with the experiment (Gesi and Ozawa 1974) on $(\text{NH}_4)_2\text{BeF}_4$ up to the maximum pressure used of 7.2 kbar. The specific heat C_p contains a factor T (Golovko 1980); therefore its p dependence will be insignificant and due to the variation in the temperature interval where the *i* phase exists. The *i*-*c* transition heat Q contains a factor α_0T_c (Golovko 1980), and the main p dependence of Q will be caused by the p dependence of α_0^* ; in particular, at point A (figure 2), Q becomes zero.

Next, let us consider the case when $n = 6$. Note that the dimensionless parameter which characterises the magnitude of the anisotropy is proportional to $\alpha_0^\nu \sim q_0^{2\nu}$ with $\nu > 0$ if $n > 4$ (Sannikov 1980). Therefore, when $n > 4$ the anisotropy is always weak and hence the constant-amplitude approximation is always satisfactory. In the work by Golovko (1980), only the $n = 4$ case was considered; proceeding likewise, instead of equations (7) of this reference, from equation (6) for $n = 6$ we get

$$\begin{aligned} \rho^4 &= 3\pi^2 \alpha_0 k^2 / 8|\gamma|E^2 \\ \alpha &= -(\pi\beta k/2E)\sqrt{3\alpha_0/2|\gamma|}[1 + (\pi/2\beta kE)\sqrt{\alpha_0|\gamma|/6(4E/K + 3k^2 - 6)}] \end{aligned} \quad (15)$$

where K and E are the complete elliptic integrals of the first and second kind, respectively, with the modulus k , and $\gamma = \gamma_n$. The thermodynamic potential can be written as

$$\phi = -(3\pi^2 \alpha_0 \beta k^2 / 32|\gamma|E^2)[1 - (\pi/\beta kE)\sqrt{2\alpha_0|\gamma|/3(2 - k^2 - 2E/K)}]. \quad (16)$$

The I-C transition point $\alpha = \alpha_c$ is obtained by equating expression (16) and the thermodynamic potential of the C phase. The result can be substantially simplified when use is made of the fact that $\alpha_0\gamma/\beta^2$ is small; then the corresponding value $k = k_c$ approaches unity and is determined by the equation

$$\alpha_0|\gamma|/\beta^2 = (3/2\pi^2)(1 - k_c^2)^2 K^4(k_c). \quad (17)$$

Now from (15) we have in a first approximation ($k_c \rightarrow 1$)

$$\alpha_c = -(\pi\beta/2)\sqrt{3\alpha_0/2|\gamma|} = -(\pi\beta|\sigma|/2)\sqrt{3/2|\gamma|\delta} \quad (18)$$

from which we get the p dependence of α_c :

$$\alpha_c = bp - \frac{1}{2}\pi\beta|\sigma + rp|\sqrt{3/2|\gamma|\delta}. \quad (19)$$

The corresponding p dependence of T_c is represented by straight lines in figures 1 and 2. In reality, the shape of the $T_c(p)$ curve is more complex and may be specified with the help of (15) and (17). However, in the vicinity of point A the phase diagram is such as shown in figure 2. In contrast with (12) the rp term in (19) does not contain the small factor q_0 ; therefore the slopes of the curves $T_i = T_i(p)$ and $T_c = T_c(p)$ as $p \rightarrow 0$ can be quite different. We note that equations (17)–(19) do not change if a ρ^6 term is taken into account in (6), as usually done when $n = 6$, since the coefficient of this term vanishes from (17)–(19) in the limit of small $\alpha_0\gamma/\beta^2$.

Let us discuss examples of the $n = 6$ crystals. For K_2SeO_4 , Rb_2ZnCl_4 and K_2ZnCl_4 the phase diagrams are of the type presented in figure 1 (Press *et al* 1980, Kudo and Ikeda 1981, Samara *et al* 1981, Aleksandrova 1980, Gesi 1985), although in the cited papers there are disagreements as to the details of the diagrams. More serious discrepancies concern the diagram for Rb_2ZnBr_4 (Gesi 1985, Aleksandrova *et al* 1987). An example of the diagram in figure 2 is that for $[N(CH_3)_4]_2ZnCl_4$ (Marion *et al* 1984) at high pressures (point A was not reached); at low pressures the diagram is complicated because of the occurrence of several c phases.

For K_2SeO_4 there are measurements permitting us to calculate r ; this can be done in two ways. According to (9), $r = \delta dq/dp$. We find the value of dq/dp from a graph of Press *et al* (1980) putting $a^* = 8.28 \times 10^7 \text{ cm}^{-1}$; this gives $dq/dp =$

$3.3 \times 10^{-4} \text{ cm dyn}^{-1}$. Using the value of δ (Sannikov and Golovko 1984)[†] we have $r/\alpha_0 = 9 \times 10^{-17} \text{ cm}^3 \text{ dyn}^{-1}$. On the other hand, from (10) and (19), one obtains at $p = 0$

$$dT_i/dp - dT_c/dp = (\pi\beta r/2\alpha_T)\sqrt{3/2|\gamma|\delta} \text{sgn } \sigma. \quad (20)$$

Experiments by Press *et al* (1980), Kudo and Ikeda (1981) and Samara *et al* (1981) give 2.5 K kbar⁻¹, 9.9 K kbar⁻¹ and 3.1 K kbar⁻¹, respectively, for $T_i - T_c$ at $p = 0$. When use is made of the values (Sannikov and Golovko 1984) of the coefficients in (20), this equation yields 4, 15 and $5 \times 10^{-17} \text{ cm}^3 \text{ dyn}^{-1}$ for r/α_0 . The above-calculated value of r/α_0 lies within this range. Such a large dispersion of the r/α_0 values is due to the marked disagreement between the p dependences of T_i and, in particular, T_c given by different workers, as mentioned above in the discussion of the phase diagrams. In connection with the above estimate $b \sim a^*r$, note that, for K_2SeO_4 , $|b| = 1.6a^*r$, if one takes $r/\alpha_0 = 9 \times 10^{-17} \text{ cm}^3 \text{ dyn}^{-1}$ and utilises the results of Sannikov and Golovko (1984) ($b/2 = B_1 + B_2 + B_3$ and the values (24) of the above-cited paper are taken for B_i).

At $n = 6$ the second dimensionless parameter in (14) is $\alpha_0\gamma/\beta^2$ which will depend on p after the substitution $\alpha_0 \rightarrow \alpha_0^*$. Therefore, here the pressure dependence of quantities need not be the same as and, in general, is more complex than in the $n = 4$ case. Let us elucidate the main features of this dependence in terms of ferroelectrics. Denoting the corresponding component of the polarisation by P_y , we supplement ϕ_1 (equation (6)) with the terms

$$\frac{1}{2}a_1 P_y \rho^3 \sin 3\varphi + \frac{1}{2}\kappa_1 P_y^2 - P_y E_y. \quad (21)$$

Proceeding in the usual way (Golovko 1980) we get the dielectric susceptibility χ_{yy} as (for simplicity the renormalisation of γ is not taken into account)

$$\begin{aligned} \chi_{yy} &= (3a_1^2/8|\gamma|\kappa_1^2)[E/(1-k^2)K-1] + 1/\kappa_1 \\ \zeta &= (3a_2^2/8|\gamma|\kappa_2^2)(1-E/K) + 1/\kappa_2. \end{aligned} \quad (22)$$

Here we have also written the susceptibility ζ with respect to a field transforming like $\rho^3 \cos 3\varphi$ (in K_2SeO_4 -type crystals this is the elastic compliance χ_{xyxy}). Consider the value of χ_{yy} at the I-C transition (the peak of χ_{yy}). Substituting $1 - k_c^2$ from (17) into (22) and taking into account the relatively weak k dependence of K ($K \approx \ln(4/\sqrt{1-k^2})$ as $k \rightarrow 1$), one finds that the main p dependence of the χ_{yy} peak is due to the factor $(\alpha_0^*)^{-1/2} \sim 1/\sigma^*$. Thus, for crystals having a phase diagram as in figure 1, the χ_{yy} peak decreases with increasing p , which agrees with experiment (Kudo and Ikeda 1981, Samara *et al* 1981, Gesi 1985). On approaching point A (figure 2) the value of the χ_{yy} peak should increase. Note the different behaviour of the χ_{yy} peak in the cases $n = 4$ and $n = 6$. The quantity ζ is $1/\kappa_2$ in the P phase and $3a_2^2/8|\gamma|\kappa_2^2 + 1/\kappa_2$ in the C phase. As the temperature decreases from T_i , ζ increases and undergoes an upward jump at $T = T_c$. The magnitude of the jump should be only weakly pressure dependent

[†] The thermodynamic potential used by Sannikov and Golovko (1984) has coefficients which differ from those of (6) in the multipliers; in particular the present value of α_0 is twice that used by Sannikov and Golovko. Note that the above-mentioned paper contains errors and the most important are as follows: in (28) the exponent should be +3, in (30) the first two numbers should be 60 and -3, and in (22) 1.8 should read 2.7.

($\sim 1/\ln(4/|\sigma^*|^{1/2})$). Calculating the specific heat C_p of the I phase and the heat Q of the I-C transition (Golovko 1980), we get, taking into account that $k_c \approx 1$ according to (17),

$$C_p(T = T_c) = \alpha_T^2 T_c / 2\beta [1 - 1/K(k_c)] \quad Q = \pi^2 \alpha_0 \alpha_T T_c / 4\beta K(k_c). \quad (23)$$

These expressions show that the pressure dependences of C_p and Q are almost the same as in the case $n = 4$.

Let us discuss in brief the case $n > 6$. Calculations analogous to those which have led to (19) allows one to write

$$\alpha_c = bp - D|\sigma^*|^{4/(n-2)} \quad \alpha_T dT_c/dp = b - [4r/(n-2)]D \operatorname{sgn} \sigma^* |\sigma^*|^{(6-n)/(n-2)} \quad (24)$$

with

$$D = \beta(\pi^2 n / 16 |\gamma_n| \delta)^{2/(n-2)}.$$

Since the exponent of $|\sigma^*|$ in the second term of the expression for dT_c/dp is negative when $n > 6$, this term will prevail over the first term, and the value of dT_c/dp will be large. This result agrees with the experimental phase diagrams given by Gesi (1986), namely at large n the temperature T_c varies more rapidly with increasing p than at small n (note that n is equal to the doubled denominator of the fraction expressing the wavevector of the C phase in terms of a^*). The behaviour of the I-C transition line near point A where $\sigma^* = 0$ is shown in figure 2.

Now let us consider type II of the I phase when there is no Lifshitz invariant. For a system described by a one-component order parameter η the thermodynamic potential density $\tilde{\phi}_1$ is

$$\tilde{\phi}_1 = (\alpha/2)\eta^2 + (\beta/4)\eta^4 + (\delta/2)(d\eta/dx)^2 + (\lambda/2)(d^2\eta/dx^2)^2. \quad (25)$$

Here we have retained only typical terms although other terms may be of importance in some cases (Ishibashi and Shiba 1978, Jacobs *et al* 1984, Golovko 1988). The I phase can exist if $\delta < 0$, and the P-I transition occurs at $\alpha = \alpha_0$ while $q = q_0$ with

$$\alpha_0 = \delta^2/4\lambda \quad q_0^2 = -\delta/2\lambda. \quad (26)$$

Since $|\delta| \sim q_0^2$, now the coefficients which have small values are α and δ , and instead of (5) we take

$$F_i = \frac{1}{2}b_i\eta^2 + \frac{1}{2}s_i(d\eta/dx)^2. \quad (27)$$

In the case of $\tilde{\phi}_1$ (25) the I-C transition is first order (Ishibashi and Shiba 1978, Jacobs *et al* 1984). Hence the role of the two first terms in (3) is not major and can be taken into account by renormalising the coefficients in $\tilde{\phi}_1$ (cf the discussion after expression (5)). Therefore, again the expression for $\tilde{\phi}_1$ must be supplemented only with the third term from $\tilde{\phi}_2$ (equation (3)), which leads to replacing α and δ by α^* and δ^* with α^* determined by the same expressions (7) and (8) and

$$\delta^* = \delta + \delta_p \quad \delta_p = \chi_{ij}s_i\sigma_j \quad \delta_p = -sp \quad s = \sum_{j=1}^3 \chi_{ij}s_i \quad (28)$$

where the second expression for δ_p is written assuming the effect of hydrostatic pressure p .

The p dependence of the wavevector q at $T = T_i$ is found from (26). If $\delta < 0$ we get (the case $\delta > 0$ is considered below)

$$q = q_0 \sqrt{1 - (s/\delta)p} \approx q_0 + (s/4q_0\lambda)p. \quad (29)$$

The second expression written in the limit of small p shows that here, because of the presence of the small factor q_0 in the denominator, the effect of pressure on q is much more pronounced than in the case of type I of the I phase (cf (9)). The p dependence of the P-I transition temperature is obtained from the first equation (26):

$$\alpha = \alpha_0 + bp + q_0^2 sp + (1/4\lambda)s^2 p^2. \quad (30)$$

The I-C transition at $p = 0$ occurs when $\alpha = -\alpha_0 C$ with $C = 4.60$ according to Ishibashi and Shiba (1978) or $C = 4.71$ according to Jacobs *et al* (1984). Therefore the p dependence of the I-C transition temperature is given by

$$\alpha_c = -\alpha_0 C + bp - q_0^2 Csp - (1/4\lambda)Cs^2 p^2. \quad (31)$$

Comparing equations (30) and (31) with (10) and (12) we see that, on the whole, the p - T phase diagrams in this case are similar to those for the $n = 4$ I phase of type I with one essential exception. Since the condition $\delta^* < 0$ must hold, the I phase in figure 2 exists only below point A if $\delta < 0$ (and $s < 0$) or only above point A if $\delta > 0$ (and $s > 0$). Here point A is a Lifshitz point where $\delta^* = 0$ and $q = 0$.

Examples of crystals with an I phase of type II having the phase diagram presented in figure 1 are sodium nitrite (Gesi *et al* 1965) and thiourea (Gesi 1969, Denoyer *et al* 1982). Crystals having a phase diagram as in figure 2 where the I phase exists below point A are $[\text{N}(\text{CH}_3)_4]_2\text{CuBr}_4$ at high p (Gesi and Ozawa 1982, Gesi 1986) and Cs_2CdBr_4 (Vlokh *et al* 1988); those where the I phase exists above point A include $\text{C}_2\text{O}_4\text{H}_2\text{NH}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ (Krauzman *et al* 1988). Note that the P-C transition above point A in $[\text{N}(\text{CH}_3)_4]_2\text{CuBr}_4$ is first order (Gesi and Ozawa 1982); therefore the form of the diagram in the vicinity of point A differs from that shown in figure 2. For this crystal, $\beta < 0$ in (25), and a term with η^6 must be taken into account. It should be mentioned that the sign of β may change when the pressure increases; the p dependence of β can be easily taken into account by adding a term with η^4 to (27).

Let us clarify what estimates can be obtained from the shape of the p - T phase diagram. From (30) and (31) we get the relation, at $p = 0$,

$$(T'_i - T'_c)/T'_i = (1 + C)q_0^2 s/b. \quad (32)$$

This permits us to calculate s/b . For sodium nitrite $(T'_i - T'_c)/T'_i = 0.125$ (Gesi *et al* 1965) and $q_0/a^* = 0.119$ (Hoshino and Motegi 1967); putting $C = 4.71$ one has $s/b = 1.5(a^*)^2$. For thiourea $(T'_i - T'_c)/T'_i = -0.368$ (Gesi 1969) and $q_0/a^* = 0.125$ (Shiozaki 1971), which gives $s/b = -4.1(a^*)^2$; the same value of s/b is obtained for deuterated thiourea where $(T'_i - T'_c)/T'_i = -0.464$ and $q_0/a^* = 0.141$ (Denoyer *et al* 1982). On the other hand, since from dimension considerations, generally $s \sim b(a^*)^2$, equation (32) permits us to estimate the value of q_0/a^* from the form of the p - T diagram. Note that, in like manner, q_0/a^* can be estimated also for an I phase of type I with $n = 4$, making use of (13) if β'/β is known.

From (25) it follows that, for type II of the I phase, an expression of the type (14) contains only one dimensionless parameter $\alpha/\alpha_0 \sim \alpha\lambda/\delta^2$ instead of the first two. As an example, let us consider again ferroelectrics where η in (25) means the polarisation. Then in the P phase the dielectric susceptibility χ is $1/\alpha$, and at the P-I transition, when $\alpha = \alpha_0$, it is $1/\alpha_0 = 4\lambda/\delta^2$. Therefore, for χ we have $\tilde{M} = \lambda/\delta^2$ in (14), and the function

f changes from 4 at $\alpha = \alpha_0$ to a definite number at $\alpha = \alpha_c$. From this it follows that, when increasing p , the susceptibility χ will vary as $(\delta^*)^{-2}$ but the form of the curve $\chi(T)$ will remain unchanged except for rescaling on the T axis. If the p - T diagram is that of figure 1, χ decreases with increasing p , which is observed in sodium nitrite (Gesi *et al* 1965). The same is observed, on the whole, in thiourea but the form of the curve $\chi(T)$ and its variation are more complex because of the appearance of a ferroelectric phase in the region where the I phase exists (Gesi 1969, Shiozaki 1971), which is not described by $\tilde{\phi}_1$ (equation (25)) (Jacobs *et al* 1984). The p dependence of the specific heat C_p and of the I-C transition heat Q are the same as for the I phase of type I at $n = 4$.

In conclusion, we see that experimental studies of the effect of pressure on I phases may permit us to clarify such non-trivial questions as the type of the I phase, the value of the number n , the degree of anisotropy and the magnitude of the wavevector q . It is not only the effect of pressure that the above results concern; analogous effects can be produced by varying, for example, the composition of mixed compounds since, in (8) and (28), p can be any scalar quantity.

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