

## Resonance theory of the pressure-induced incommensurate phase in ammonium hydrogen oxalate hemihydrate

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

1990 J. Phys.: Condens. Matter 2 10249

(<http://iopscience.iop.org/0953-8984/2/51/003>)

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

Download details:

IP Address: 129.252.86.83

The article was downloaded on 27/05/2010 at 11:21

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

# Resonance theory of the pressure-induced incommensurate phase in ammonium hydrogen oxalate hemihydrate

Wilson C K Poon

Department of Physics, University of Edinburgh, James Clerk Maxwell Building, The King's Buildings, Mayfield Road, Edinburgh EH9 3JZ, UK

Received 11 July 1990

**Abstract.** The resonance theory of incommensurate (IC) phases in insulators studied by Heine and McConnell is reviewed and applied to ammonium hydrogen oxalate hemihydrate, in which an IC phase is stabilized above 3 kbar between the room-temperature paraelastic phase and the low-temperature ferroelastic phase. It is suggested that this IC phase is due to a structural resonance between the ferroelastic ordering mode and an incipient ferroelectric ordering mode. A simple pressure dependence of the latter reproduces the topology of the  $p$ - $T$  phase diagram and the pressure dependence of the IC wavevector at  $T_{1C}$ . Specific predictions concerning dielectric behaviour and diffuse scattering round satellite positions under pressure are made.

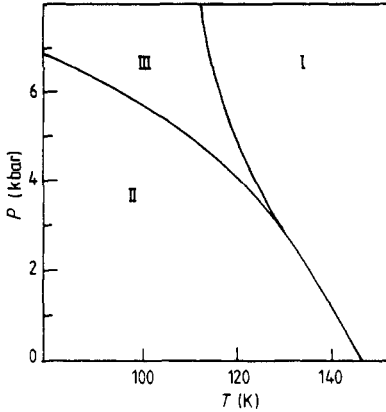
## 1. Introduction

Ammonium hydrogen oxalate hemihydrate (AHO),  $\text{NH}_4\text{HC}_2\text{O}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ , has attracted interest recently because, upon cooling, it goes through an incommensurate (IC) phase only under the application of hydrostatic pressure [1, 2]. Its phase diagram is shown in figure 1. Phase I is orthorhombic [3]. On cooling at ambient pressure, a second-order equitranslational ferroelastic phase transition occurs at  $T_C = 145.6$  K to a monoclinic structure (phase II) [4]. Above  $p_c = 3$  kbar, an IC phase appears [1] (phase III) with  $q$  along  $c^*$ .  $q$  shows a large pressure dependence, moving from  $0.147 c^*$  at 4.3 kbar to about  $0.25 c^*$  at 8 kbar but appears to be temperature independent [2].

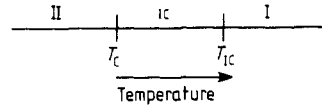
Heine and McConnell have published a series of papers in which they proposed a general theory to account for the occurrence of IC phases in insulators. They have applied this theory successfully to diverse materials such as  $\text{NaNO}_2$  and various minerals (see references in [5]). In this paper, we show that a slightly extended version of their theory can account for the topology of the AHO phase diagram. This leads to a number of specific predictions which should be susceptible to experimental verification.

## 2. The resonance theory of IC phases

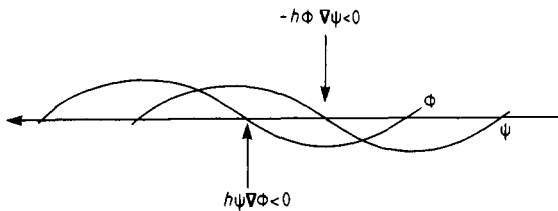
Heine and McConnell suggest that IC phases occur in insulators because of 'structural resonance' between two ordering modes. We review their theory in this section.



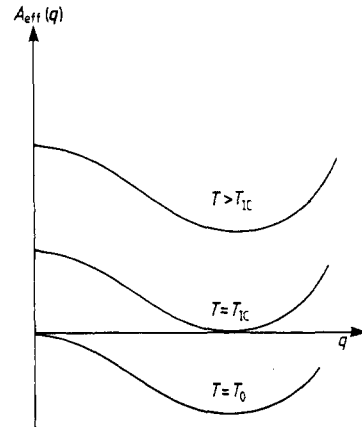
**Figure 1.** The  $p$ - $T$  phase diagram of AHO (after [2]). Phase I is orthorhombic; the ferroelastic phase II is monoclinic. Phase III is IC.



**Figure 2.** Typical phase diagram of a material showing an IC phase under ambient pressure.



**Figure 3.** A schematic diagram showing how an interaction of the form (2.1) will stabilize spatially inhomogeneous  $\varphi$  and  $\psi$  modes varying in quadrature.



**Figure 4.** Curves of  $A_{\text{eff}}(q)$  at successively lower temperatures near the IC transition.

Consider a material (such as  $\text{NaNO}_2$ ) with a phase diagram such as that shown in figure 2. Heine and McConnell propose that the high-symmetry phase I has two possible modes of transformation,  $\psi$  and  $\varphi$ , where  $\psi$  acting alone will give the  $\text{I} \rightarrow \text{II}$  transition. The interaction between  $\psi$  and  $\varphi$  has the form

$$G_{\text{int}} = h(\varphi \nabla \psi - \psi \nabla \varphi). \tag{2.1}$$

This means that there is no interaction at  $\mathbf{k} = \mathbf{0}$  (cf equation (2.3)), and the variation in  $\psi$  and  $\varphi$  must be such that they are always in quadrature (figure 3). An interaction of the form (2.1) stabilizes a spatially inhomogeneous  $\psi$  (or  $\varphi$ ) because the condensation of  $\varphi$  (or  $\psi$ ) in regions of large  $\nabla \psi$  (or  $\nabla \varphi$ ) allows relief of stress.

Working in Fourier space, the free energy is then written as

$$G = G_0 + \sum_q A(\mathbf{q})\psi_q^* \psi_q + H(\mathbf{q})\psi_q^* \varphi_q + B(\mathbf{q})\varphi_q^* \varphi_q. \quad (2.2)$$

An interaction of the form (2.1) is obtained as the second term in the Taylor expansion of

$$G_{\text{int}} = 2 \sum_{l'} \psi(l)H(l-l')\varphi(l') \quad (2.3a)$$

the first term of which is zero for symmetry reasons. Fourier transform of (2.3a) shows that, to first order,  $H(\mathbf{q})$  takes the form

$$H(\mathbf{q}) = i\mathbf{q} \cdot \mathbf{H}_1 \quad (2.3b)$$

in equation (2.2) with

$$\mathbf{H}_1 = \sum_{\lambda} \lambda H(\lambda) \quad (2.3c)$$

where  $\lambda = l - l'$  is a nearest-neighbour lattice vector.

If  $\psi$  acting on its own leads to a phase transition at  $T = T_0$  with  $q = 0$ , we can write

$$A(q, T) = a(T - T_0) + A_2 q^2 + A_4 q^4 + \dots \quad (2.4)$$

The change in sign of the first term results in an instability which gives the commensurate low-temperature phase.

The heart of the argument of Heine and McConnell then runs as follows. Rewrite equation (2.2) as

$$G = G_0 + A_{\text{eff}}(\mathbf{q})\psi_q^* \psi_q \quad (2.5a)$$

(dropping the summation sign from here on, considering only one particular  $q$ ) with

$$A_{\text{eff}}(\mathbf{q}) = A(\mathbf{q}) + H(\mathbf{q})\varphi_q/\psi_q + H^*(\mathbf{q})\varphi_q^*/\psi_q^* + B(\mathbf{q})\varphi_q^* \varphi_q/\psi_q^* \psi_q. \quad (2.5b)$$

Minimizing (2.5b) with respect to  $\varphi_q/\psi_q$  and its complex conjugate and substituting back into (2.5b) then gives

$$A_{\text{eff}}(\mathbf{q}) = A(\mathbf{q}) - H^*(\mathbf{q})H(\mathbf{q})/B(\mathbf{q}). \quad (2.6)$$

This means that  $A_{\text{eff}}(\mathbf{q})$  may go through zero and precipitate an instability at  $T = T_{\text{IC}} > T_0$ . Using (2.3b) and (2.4) and expanding

$$B(\mathbf{q}) = B_0 + B_2 q^2 + \dots \quad (2.7)$$

Heine and McConnell obtain from (2.6)

$$A_{\text{eff}}(\mathbf{q}, T) = a(T - T_0) + (A_2 - H_1^2/B_0)q^2 + A_4 q^4 + \dots \quad (2.8)$$

Figure 4 shows  $A_{\text{eff}}(\mathbf{Q})$  at successively lower temperatures. These plots assume that

$$A_2 - H_1^2/B_0 < 0 \quad (2.9)$$

i.e. there is a downward curvature at  $q = 0$ . Then

$$A_{\text{eff}}(\text{min}) = a(T - T_0) - \frac{1}{2}A_4(H_1^2/B_0 - A_2)^2 \quad (2.10)$$

(where the  $\frac{1}{2}$  in the second term was given incorrectly as  $\frac{1}{4}$  in the paper of Heine and

McConnell).  $A_{\text{eff}}(\text{min})$  first hits zero at the *non-zero value of  $Q$*  given by

$$Q^2 = (1/2A_4)(H_1^2/B_0 - A_2) \quad (2.11)$$

at the IC transition temperature

$$T_{\text{IC}} = T_0 + \Delta \quad (2.12)$$

where  $\Delta$  is given by

$$\Delta = (1/4aA_4)(H_1^2/B_0 - A_2)^2. \quad (2.13)$$

Equation (2.9) is therefore seen to be the condition for the occurrence of an IC phase. By considering higher-order terms in  $\psi_q$  which will limit the IC amplitude below  $T_{\text{IC}}$ , Heine and McConnell show further that the commensurate transition temperature is

$$T_C = T_0 - 4.45\Delta. \quad (2.14)$$

At this temperature, a *uniform* high value of  $\psi$  becomes energetically more favourable than the inhomogeneous  $\psi$  and  $\varphi$  in resonance (figure 3) in the IC structure.

We need to mention one further aspect of the work of Heine and McConnell—symmetry. The free energy  $G$  must have the full symmetry of the high-temperature symmetry phase. Since

$$H(\mathbf{q})\varphi_q\psi_q^* = i\mathbf{q} \cdot \mathbf{H}_1\varphi_q\psi_q^*$$

occurs in (2.2), then the direct products of the irreducible representations (the  $\Gamma$ -values) of  $\mathbf{q}$ ,  $\varphi$  and  $\psi$  must contain the identity representation. Equivalently

$$\Gamma(\mathbf{q}) = \Gamma(\varphi)\Gamma(\psi). \quad (2.15)$$

This imposes severe restrictions on the kinds of modes  $\psi$  and  $\varphi$  which can interact via (2.1) to give an IC structure with a particular observed direction of  $\mathbf{q}$ .

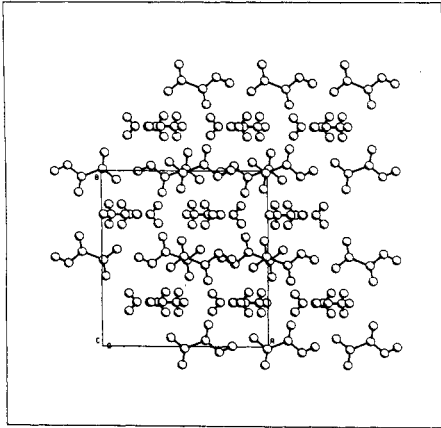
Such is the outline of the resonance theory of IC phases in insulators. Heine and McConnell recognize that detailed extensions will be necessary for applications to particular materials. We shall attempt such an extension for AHO in the rest of this work.

### 3. Phase transitions in AHO

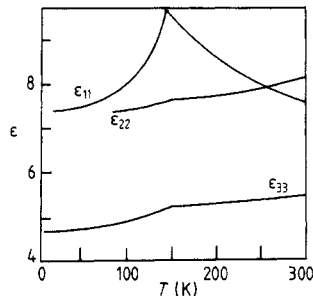
Under ambient condition, AHO is orthorhombic ( $Pmnb$ ,  $Z = 8$ ) [3]. In this structure, each  $\text{HC}_2\text{O}_4^-$  ion occupies a general position, while both the  $\text{H}_2\text{O}$  and  $\text{NH}_4^+$  lie on a mirror plane perpendicular to  $\mathbf{a}$  (figure 5). The  $\text{NH}_4^+$  ions are further subdivided into two groups, the mirror plane being only statistical for one of these groups of ammonium ions, which are in fact disordered at room temperature.

The original motivation [4, 6] for looking for a low-temperature phase transition in AHO was driven by the consideration that the arrangement of  $\text{NH}_4^+$  groups in the unit cell is very similar to that in the room-temperature phase of  $(\text{NH}_4)_2\text{SO}_4$  ( $Pnam$ ,  $Z = 4$ ), which undergoes a *displacive* transition [7] at 223 K into a ferroelectric phase ( $Pna2_1$ ,  $Z = 4$ ).

Low-temperature work on AHO shows that it indeed undergoes a phase transition at  $T_C = 145.6$  K, transforming into a monoclinic ferroelastic phase ( $P2_1/n$ ,  $Z = 8$ ) owing to the ordering of one family of  $\text{NH}_4^+$  ions, destroying the mirror plane. The ferroelastic order parameter has  $B_{2g}$  symmetry. This transition has been studied in some detail [8, 9].



**Figure 5.** The structure of AHO at room temperature projected onto (001).



**Figure 6.** The temperature behaviour of the principal dielectric constants of AHO at 1 bar (after [6]).

Early dielectric measurements on AHO did, however, show some interesting results which have *not* been commented upon since the recent revival of interest in this material. While  $\epsilon_{22}$  and  $\epsilon_{33}$  show only very slight discontinuities in slope at  $T_C = 145.6$  K,  $\epsilon_{11}$  shows a large anomalous behaviour [6] (figure 6). (Note that  $\epsilon_{11}$  and  $\epsilon_{22}$  here correspond to  $\epsilon_{22}$  and  $\epsilon_{11}$  in [6], owing to different space group settings.) Above  $T_C = 145.6$  K, the behaviour of  $\epsilon_{11}$  could be very accurately (to 0.3%) described by a Curie–Weiss law

$$\epsilon_{11} = \epsilon_g + C/(T - T_{tr}) \quad (3.1)$$

with  $\epsilon_g = 5.10$ ,  $C = 735$  K and  $T_{tr} = -20$  K. That is to say, AHO is an *incipient ferroelectric*. The polarization of the hypothetical ferroelectric phase would be along the orthorhombic  $a$  direction; in other words, the ferroelectric order parameter would have symmetry  $B_{3u}$ .

We have shown elsewhere [10] that the collapse of  $\epsilon_{11}$  at the *ferroelastic* phase transition temperature is explained by a strain-induced biquadratic coupling between the ferroelastic ( $B_{2g}$ ) and ferroelectric ( $B_{3u}$ ) order parameters.

#### 4. Resonance theory of the IC phase in AHA

In the notation of Heine and McConnell, we take the ferroelastic ( $B_{2g}$ ) order parameter in AHO as the  $\psi$  mode. The condensation of this mode at ambient pressure gives the

I  $\rightarrow$  II ferroelastic transition at 145.6 K. We know that the IC wavevector is along  $\mathbf{e}^*$ , which transforms as  $B_{1u}$ . Application of (2.15) then gives the result that the resonance mode  $\varphi$  in the IC phase of AHO must transform as  $B_{3u}$  (i.e.  $\mathbf{x}$ ). The discussion at the end of the last section shows that there indeed exists a mode ordering in AHO with this symmetry—the ferroelectric mode! We propose that this is the  $\varphi$  mode which, in structural resonance with the ferroelastic  $\psi$  mode, leads to IC behaviour in AHO.

Reference to (2.9) shows that the occurrence of an IC phase due to structural resonance depends on having a large  $H_1^2/B_0$ , i.e. a large gradient interaction (large  $H_1$ ), or soft  $\varphi$  mode (small  $B_0$ ). The lack of an IC phase in AHO at ambient pressure will then arise because  $\varphi$  never becomes soft enough; at  $p = 0$  kbar, AHO is only an incipient ferroelectric, with  $T_{tr} = -20$  K in (3.1). However, a positive pressure coefficient for  $T_{tr}$  will lead to a drop in  $B_0$  with increasing pressure, leading to the possibility of stabilizing the IC phase.

Let us write

$$B_0 = b[T - \omega_0^2(p)] \quad (4.1)$$

and use the simplest form of  $\omega_0^2(p)$  that will give a positive pressure coefficient:

$$\omega_0^2(p) = \Omega_0^2(p - p_c). \quad (4.2)$$

For  $p < p_c$ ,  $B_0$  will always be too large for condition (2.19) to be satisfied. In other words, the coefficient of  $q_2$  in equation (2.8) will always be positive for all  $T \geq T_0$ , so that cooling will result in a phase transition at  $T_0 = 146$  K when the ferroelastic ( $\varphi$ ) mode condenses out (figure 7(a)). An increase in pressure will, however, lead to a drop in  $B_0$ . At  $p = p_c$ , the coefficient of  $q^2$  in equation (2.8) becomes zero at  $T = T_0$ . The IC phase just appears but has an infinitesimal stability range. At higher pressures still, a minimum for  $A_{\text{eff}}(q)$  away from the origin will appear at a temperature  $T^* > T_0$ . Further cooling from  $T^*$  will bring about the transition into the IC phase which now has a finite stability range (figure 7(b)).

We can now calculate the phase diagram of AHO based on this model. First, the IC phase is stable above 3 kbar, so that  $p_c = 3$  kbar. At this pressure, as we have already discussed, the coefficient of  $q^2$  in equation (2.8) becomes zero at  $T = T_0$ . Using equations (4.1) and (4.2) we therefore get

$$A_2 = H_1^2/bT_0 \quad (4.3)$$

at  $p = p_c$ . From the  $\epsilon_{11}(T)$  data of Albers and Küppers we get  $\omega_0^2(p = 0) = -20$  K in equation (4.1), so that equation (4.2) gives  $\Omega_0^2 p_c = 20$  K, or  $\Omega_0^2 = 6.67$  K kbar $^{-1}$ .

Using equation (4.3), we write the coefficient of  $q^2$  in equation (2.8) as

$$(H_1^2/b)\{1/T_0 - 1/[T - \Omega_0^2(p - p_c)]\}.$$

This changes sign at

$$T^* = T_0 + \Omega_0^2(p - p_c). \quad (4.4)$$

Again, substituting equation (4.3) into equation (2.10) gives

$$A_{\text{eff}}(\text{min}) = a(T - T_0) - (B^2/2A_4)\{1/[T - \Omega_0^2(p - p_c)]\} \quad (4.5)$$

where

$$B = H_1^2/b. \quad (4.6)$$

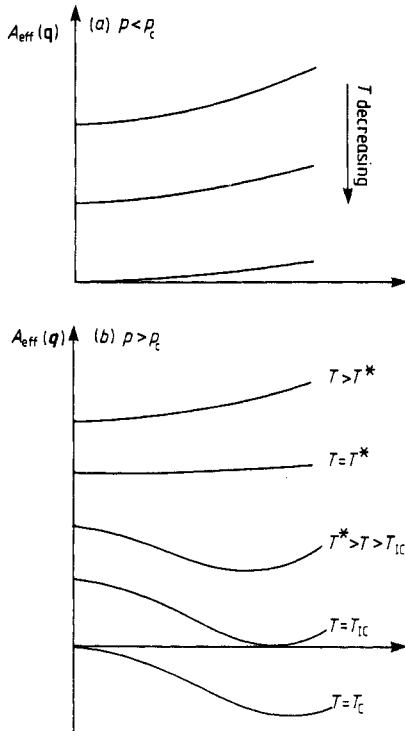


Figure 7. Curves of  $A_{\text{eff}}(q)$  at successively lower temperatures (a) below and (b) above the critical pressure  $p_c$ , above which an IC phase is stabilized.

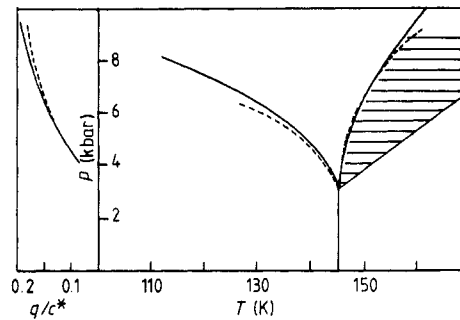


Figure 8. The calculated phase diagram and pressure dependence of the IC wavevector ( $|q|$ , in units of  $|c^*|$ ) of AHO (—) compared with experimental data (---). See text for details concerning the position of the broken lines in the phase diagram. The shaded area is the  $p$ - $T$  region in which diffuse scattering round satellite positions should be observable.

The locus of  $(p, T)$  satisfying

$$A_{\text{eff}}(\text{min}) = 0 \tag{4.7}$$

will then map out the boundary between phase I and phase III of AHO.

At each pressure we can calculate (see equation (2.12))  $\Delta = T_{\text{IC}} - T_0$ , and then equation (2.14) to get  $T_C$  for the III  $\rightarrow$  I (IC  $\rightarrow$  commensurate) transition.

Note that the actual calculated phase boundaries obtained depend only on the ratio of  $B^2/2A_4$  to  $a$ .

Finally, substituting equation (4.3) into equation (2.11), we get an equation for the IC wavevector

$$Q = \sqrt{B/2A_4} \sqrt{1/[T - \Omega_0^2(p - p_c)] - 1/T_0} \tag{4.8}$$

to within a multiplicative factor  $\sqrt{B/2A_4}$ .

The phase diagram of AHO calculated from our model using

$$(B^2/2A_4)/a = 5 \times 10^6$$



is shown in figure 8, while the value of the IC wavevector as a function of pressure calculated using

$$\sqrt{B/2A_4} = 7c^*$$

is also shown in figure 8.

## 5. Comparison with experiment

It is immediately obvious that our calculated phase diagram reproduces the topology of the observed phase diagram (see figure 1). One feature in the real phase diagram which is *not* expected to be reproducible by our model is the pressure dependence of the I  $\rightarrow$  II phase transition temperature. This feature has not been built in, so that in our results the I  $\rightarrow$  II phase boundary at low pressures is vertical. In reality,  $dT_C/dp \approx -5 \text{ K kbar}^{-1}$ .

Bearing this feature in mind, we can attempt a more quantitative comparison between our calculations and experimental observation. The observed I  $\rightarrow$  II phase boundary was extrapolated into the phase III region in figure 1. The dispositions of the actual I  $\rightarrow$  III and III  $\rightarrow$  I boundaries relative to this extrapolated line were then noted, and the values transferred to figure 8 as points similarly disposed on either sides of the vertical line  $T = T_0$ . The resultant curves agree remarkably well with the calculated boundaries.

There is also good agreement between the calculated and observed behaviours of  $|q|$  at  $T_{IC}$  (figure 8). A naive application of equation (4.8), however, would suggest a very strong *increase* in  $|q|$  with decreasing temperature at any particular pressure. Preliminary observations [2] in restricted temperature ranges, however, show apparently that  $|q|$  is temperature independent.

The above discussion, of course, assumes that the pre-factor in equation (4.8) is temperature independent. Heine and McConnell have pointed out that this is often not the case. This pre-factor written out in full is (using equation (4.3))

$$H_1^2/2bA_4 = A_2T_0/2A_4.$$

Heine and McConnell have argued that  $A_2$  and  $A_4$  should both be very sensitive to the amount of short-range order in the vicinity of  $T_{IC}$  and therefore can be very sensitively temperature dependent. This is, for example, the case in  $\text{NaNO}_2$ , where the large degree of short-range order just below  $T_{IC}$  in fact leads to a decreasing  $|q|$  with decreasing temperature. A similar effect in AHO could compensate for the more obvious temperature dependence of  $|q|$  in equation (4.8) to give the observed behaviour.

## 6. Predictions of the theory

Our phenomenological theory of the IC phase in AHO as developed in section 4 makes two predictions that should be susceptible to experimental verification.

(i) The incipient ferroelectric ordering should be stabilized by pressure. If the work of Albers and Küppers shown in figure 6 is repeated under pressure, the value of  $T_{tr}$  obtained by the Curie–Weiss fit (3.1) is predicted to reach 0 K at  $p_c = 3 \text{ kbar}$  (see equation (4.21)).

(ii) Reference to figure 7(b) shows that, within the range of temperature  $T_{IC} < T < T^*$ , diffuse scattering should be observable at the  $q$  where  $A_{\text{eff}}(\text{min})$  occurs

at each pressure.  $T^*$  at each pressure is given by equation (4.4) and is plotted in figure 8. The shaded area between  $T^*(p)$  and the I  $\rightarrow$  III phase boundary is the region where one could expect to observe diffuse scattering at satellite positions.

Work along these two directions is under way in our laboratory.

## References

- [1] Bosio L, Oumezzine M and Pick R 1988 *Revue Phys. Appl.* **23** 105–9
- [2] Krauzman M, Godet J L, Pick R M, Poulet H, Toupry J, Bosio L, Debeau M, Launois P and Moussa F 1988 *Europhys. Lett.* **6** 37–42
- [3] Küppers H 1973 *Acta Crystallogr. B* **29** 318–26
- [4] Keller H L, Kucharczyk D and Küppers H 1982 *Z. Kristallogr.* **158** 221–32
- [5] Heine V and McConnell J D 1984 *J. Phys. C: Solid State Phys.* **17** 1199–220
- [6] Albers J and Küppers H 1977 *Phys. Status Solidi a* **39** K49–51
- [7] Schlemper E O and Hamilton W C 1966 *J. Chem. Phys.* **44** 1198–4509
- [8] Benoit J P, Berger J, Krauzman M and Godet J K 1986 *J. Physique* **47** 815–9
- [9] Godet J L, Krauzman M, Mathieu J P, Poulet H and Toupry N 1987 *J. Physique* **48** 809–19
- [10] Poon W C K 1990 unpublished.