Novel Type of Phase Transition to Incommensurate Structure in Quartz and in Berlinite

D. Mukamel[(a)]
IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598

and

M. B. Walker
Department of Physics and Scarborough College, University of Toronto, Toronto, Ontario, Canada M5S 1A7
(Received 12 March 1987)

It is shown that the β-incommensurate transitions which take place in quartz at $T_S \simeq 8.46$ K and in berlinite at $T_S \simeq 870$ K are of a novel type which has recently been discussed theoretically. This transition has features in common with both instability and nucleation types. The wave vector $\mathbf{q}$ of the incommensurate phase rotates continuously away from the symmetry axis as the temperature is lowered below T_S. Renormalization-group and scaling arguments are presented, suggesting that the perpendicular component of the wave vector should vary as $q_\perp \sim t^\nu$, where $t=(T_S-T)/T_S$ and ν is the critical exponent associated with the correlation length.

PACS numbers: 64.70.Kb, 05.70.Jk, 61.50.Ks

Continuous phase transitions leading to incommensurate structures have been classified into two main types[1,2]: (a) instability and (b) nucleation. Instability-type transitions usually take place when a disordered phase becomes incommensurate. Such transitions are characterized by a small local order parameter $P(\mathbf{r})$ whose thermodynamic average vanishes in the disordered phase. Below the transition a certain Fourier component $P(\mathbf{q})$ of the order parameter with $\mathbf{q}\neq\mathbf{0}$ becomes nonzero, thus breaking the translational symmetry. In continuous transitions $P(\mathbf{q})$ grows continuously as the temperature is lowered below the critical temperature T_C. In addition to the fundamental Fourier component $P(\mathbf{q})$, one usually finds that higher harmonics $P(n\mathbf{q})$, $n>1$, become nonzero as well. However, the structure of the incommensurate phase is such that the ratios $P(n\mathbf{q})/P(\mathbf{q})$ vanish as the transition temperature is approached from below. Another characteristic feature of this type of transitions is that they are characterized by a diverging susceptibility.

On the other hand, nucleation-type transitions, which usually take place when a commensurate phase becomes incommensurate, are not associated with a small order parameter. They are, rather, described by a condensation of discommensurations or domain-wall structures. As the transition is approached, the average distance between discommensurations diverges, resulting in a continuous transition to an ordered commensurate state. The structure below the transition is periodic and is characterized by a fundamental Fourier mode $P(\mathbf{q})$ and its harmonics. However, since the incommensurate phase is composed of arrays of domain-wall-like structures, the ratios $P(n\mathbf{q})/P(\mathbf{q})$ do not vanish as the transition is approached from below. Moreover, unlike instability-type transitions, here $\mathbf{q}\rightarrow\mathbf{0}$ at the transition and there exists no diverging susceptibility associated with $P(\mathbf{q})$. Recently it has been pointed out[3] that a new class of transitions exists, which has properties of both instability and nucleation types. In these transitions the incommensurability is driven by a gradient cubic term in the free energy.[4-8] They are associated with a small order parameter and have a diverging susceptibility as do instability-type transitions. However, they are characterized by an infinite-wavelength structure and a nontrivial harmonic content at the transition, as is common in nucleation type. The existence of such transitions has been suggested on the basis of theoretical analysis of a certain Landau-Ginzburg-Wilson (LGW) model. No specific physical system in which such transitions take place has been found.

In the present Letter we suggest that the β-incommensurate transitions which take place in quartz (SiO_2) at $T_S \simeq 846$ K and in berlinite ($AlPO_4$) at $T_S \simeq 870$ K are in fact of the new type. These transitions have been studied extensively in recent years.[9-17] To be specific we consider here the transition in quartz; however, our analysis will also apply to berlinite. Quartz exhibits three phases at temperatures around $T \simeq 846$ K: a hexagonal D_6^4 ($P6_222$) β phase which exists at $T>T_S\simeq 846$ K, an α phase at $T<T_C\simeq T_S-1.8$ K which has a threefold symmetry D_3^4 ($P3_121$) (see Fig. 1), and an intermediate incommensurate phase which exists in the narrow temperature interval $T_C<T<T_S$. This incommensurate phase is characterized by a wave vector $\mathbf{q}$ which at the transition temperature T_S points along a symmetry axis in the x-y plane [see Fig. 2(a)]. One of the interesting features of this transition is that as the temperature is lowered below T_S, the $\mathbf{q}$ vector rotates in the x-y plane away from the symmetry axis. This behavior has been observed experimentally by electron microscopy[14,15] and by x-ray diffraction studies,[10] and discussed theoretically with use of Landau theory[13]

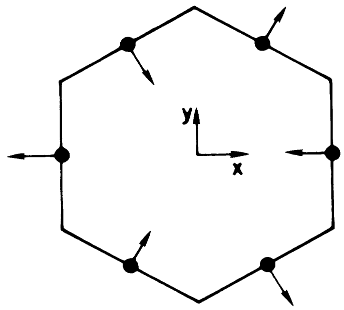

FIG. 1. Basal-plane projection of the position of the silicon ions in quartz. The circles indicate the positions in the β phase while the arrows give the directions of the silicon displacements in the α phase.

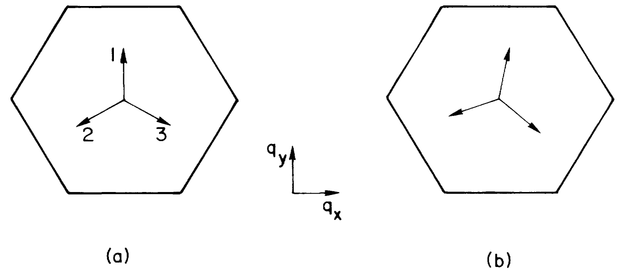

FIG. 2. The three $\mathbf{q}$ vectors associated with the order parameter of the incommensurate phase (a) at the transition point T_S and (b) for $T < T_S$. Below the transition point the $\mathbf{q}$ vectors are rotated in the x-y plane away from the symmetry axes.

and domain-wall–type arguments.[14] Here we present scaling and renormalization-group arguments suggesting that close to T_S the component of $\mathbf{q}$ perpendicular to the symmetry axis should vary as $q_\perp \sim t^\nu$, where $t = (T_S - T)/T_S$ and ν is the critical exponent associated with the correlation length.

To study the β-incommensurate transition we construct the LGW Hamiltonian associated with this system. Let η be the order parameter of the α phase. This is a single-component Ising-type order parameter which represents the distortion given in Fig. 1. The intermediate incommensurate phase is characterized by a modulated α-type distortion. At the transition the modulation vector points along one of the symmetry axes in the x-y plane. The order parameter for the β-incommensurate transition has therefore six components $\eta_{\pm q_i}$, $i = 1$, 2, and 3, where the wave vectors $\mathbf{q}_i$ are given in Fig. 2(a), and $\eta_{\pm q_i}$ are the $\pm \mathbf{q}_i$ Fourier components of the order parameter $\eta(\mathbf{r})$. For simplicity we denote $\eta_{\pm q_i}$ by $\eta_{\pm i}$. Since the order parameter $\eta(\mathbf{r})$ is real, one has $\eta_{-i} = \eta_i^*$, where η_i^* is the complex conjugate (c.c.) of η_i. The LGW effective Hamiltonian associated with this order parameter takes the form[18]

$$\mathcal{H} = \int dV\, H(\eta_i, \nabla\eta_i),$$

with

$$H = \frac{1}{2} r \sum_{i=1}^{3} |\eta_i|^2 + \frac{1}{2} a \sum_{i=1}^{3} |\nabla\eta_i|^2 + \frac{1}{2} w [(\hat{\mathbf{x}}_1 \cdot \nabla\eta_1)\eta_2\eta_3 + (\hat{\mathbf{x}}_2 \cdot \nabla\eta_2)\eta_3\eta_1 + (\hat{\mathbf{x}}_3 \cdot \nabla\eta_3)\eta_1\eta_2 + \text{c.c.}] + u \left(\sum_{i=1}^{3} |\eta_i|^2 \right)^2 + v \sum_{i=1}^{3} |\eta_i|^4, \quad (1)$$

where $\hat{\mathbf{x}}_i$ are unit vectors pointing along $\hat{\mathbf{z}} \times \mathbf{q}_i$, respectively, $i = 1$, 2, and 3, and $\hat{\mathbf{z}}$ is a unit vector along the z axis. This LGW Hamiltonian has the basic features associated with the new class of transitions discussed previously.[3] Namely, it does not possess a Lifshitz-type term which is quadratic in η and linear in the ∇ operator, and the leading cubic term in η is linear in ∇. Note that the w term is invariant under the space group D_6^4. It is clearly invariant under the sixfold axis. It is also invariant under the twofold axes in the x-y plane. Within the mean-field approximation, the ordered phases associated with this model are obtained by our minimizing the Hamiltonian with respect to $\eta_i(\mathbf{r})$. Two kinds of ordered phases are found: a single-$\mathbf{q}$ structure in which, say, $|\eta_1| \neq 0$ but $\eta_2 = \eta_3 = 0$, and a triple-$\mathbf{q}$ structure characterized by $\eta_i \neq 0$, $i = 1$, 2, and 3. The (r,w) phase diagram associated with this model is given in Fig. 3. For $v > 0$ the model exhibits a triple-$\mathbf{q}$ structure. However, for $v < 0$ one finds both ordered phases: a single-$\mathbf{q}$ phase for $w < |v|$ and a triple-$\mathbf{q}$ phase for $x > |v|$. The two phases are separated by a first-order line.

The transition from the β to the triple-$\mathbf{q}$ phase is of the type which has recently been discussed theoretically. It is characterized by a small order parameter η_i and diverging susceptibility, as in ordinary instability transitions. On the other hand, as a result of the w term which tends to favor nonzero $\hat{\mathbf{x}}_i \cdot \nabla\eta_i$, the $\mathbf{q}$ vectors associated with the order parameter rotate continuously below the transition.[10,19] Let the modulation vectors below the transition be $\mathbf{q}_i + \mathbf{k}_i$, where the vectors $\mathbf{k}_i$ are perpendicular to $\mathbf{q}_i$, $i = 1$, 2, 3, respectively, and they all lie in the x-y plane. The order parameters associated with these wave vectors will be denoted by η_{i,k_i}. Within the mean-field approximation, the vectors $\mathbf{k}_i$ are found to satisfy[20]

$$|\mathbf{k}_i| \sim t^{1/2}. \quad (2)$$

It has been suggested that usually, in this class of phase transitions, the structure of the low-temperature phase should exhibit nontrivial harmonic content. This would mean that higher harmonics of the order parameter η_{i,nk_i}, $n>1$ (i.e., Fourier components associated with $\mathbf{q}_i+n\mathbf{k}_i$), should become nonzero with nonvanishing ratios $\eta_{i,nk_i}/\eta_{i,k_i}$ at T_S. However, because of the particular structure of the model (1) this is *not* the case here, and higher harmonics vanish identically below T_S. To see that this indeed is the case one should consider the Euler-Lagrange equations of the model (1). They take the form

$$r\eta_i+4u\left(\sum_{j=1}^{3}|\eta_j|^2\right)\eta_i+4v|\eta_i|^2\eta_i-a\nabla^2\eta_i+\frac{\sqrt{3}}{2}w[(\hat{\mathbf{q}}_{i+2}\cdot\nabla\eta^*_{i+1})\eta^*_{i+2}-(\hat{\mathbf{q}}_{i+1}\cdot\nabla\eta^*_{i+2})\eta^*_{i+1}]=0,\quad i=1,2,3, \tag{3}$$

where $\hat{\mathbf{q}}_i$ is a unit vector along $\mathbf{q}_i$, and in the last term the indices $i+1$ and $i+2$ are taken modulo 3. These equations have an exact solution of the form

$$\eta_l=\bar{\eta}_l\exp(ik\hat{\mathbf{x}}_l\cdot\mathbf{r}), \tag{4}$$

where $\bar{\eta}_l$ are independent of $\mathbf{r}$. This solution does not contain harmonics other than the fundamental ones. In general, however, since the Euler-Lagrange equations are nonlinear, higher harmonics do not vanish. In particular for vectors $\mathbf{q}_i$ such that $4\mathbf{q}_i$ are reciprocal-lattice vectors (which is *not* the case for quartz or berlinite) one expects an additional term in the LGW model:

$$\bar{u}\sum\eta_i^4. \tag{5}$$

It is easy to verify that in this case the structure below T_S will contain higher harmonics, and that the harmonic content will be nontrivial at T_S.

We now apply scaling and renormalization-group considerations to study the behavior of the perpendicular components $\mathbf{k}_i$ of the wave vectors near T_S. We first consider the LGW model (1) with $w=0$. This model is composed of three XY models which are coupled by an energy-energy–type term u. The crossover exponent associated with this coupling is[21] α, the specific-heat critical exponent, which for the XY model in $d=3$ dimensions is negative. Hence, near the decoupled fixed point $u^*=w^*=0$, u is an irrelevant operator. Moreover, one can relate the crossover exponent ϕ associated with w to the critical exponents η and ν which govern the behavior of the $\langle\eta_i(0)\eta_i(\mathbf{r})\rangle$ correlation function. One finds

$$\phi=\tfrac{1}{2}\nu(4-d-3\eta), \tag{6}$$

where d is the dimensionality of the system. Since[22] $\eta\simeq0.05$ for the $d=3$ XY model one has $\phi>0$ and w is relevant. Therefore if the model (1) has a stable fixed point in $d=3$ dimensions, it has to be one with u^*, w^*, and $v^*\neq0$. In this case the scaling form of the correlation function is given by

$$\langle\eta_{ik}\eta_{i-k}\rangle\sim t^{-\gamma}G(k\xi,u^*,v^*,w^*), \tag{7}$$

where γ is the critical exponent associated with the ordering susceptibility, and ξ is the correlation length. For $T<T_S$ this correlation function exhibits a singularity at some nonzero $\mathbf{k}$. In terms of the scaling variables the $\mathbf{k}$ at which the singularity takes place is given by $k\xi=C$, where C is a constant depending on u^*, v^*, and w^*. Therefore below the transition one has

$$|\mathbf{k}|\sim\xi^{-1}\sim t^{\nu}. \tag{8}$$

It is therefore suggested that the perpendicular component of the order parameter vanishes as $T\rightarrow T_S$ with the same critical exponent as that of the inverse correlation length. It would therefore be of interest to measure the correlation length and compare its behavior with that of the perpendicular component of the wave vector. Note that this result is not valid in general. For other models of the type (1) (e.g., models which have different fourth-order terms) the $w^*=0$ fixed point may be stable. The w term may then become a dangerous irrelevant variable. In this case the scaling form of the correlation function is $t^{-\gamma}G(k\xi,wt^{-\phi})$, where ϕ is the (negative) crossover exponent associated with w. The wave vector $\mathbf{k}$ below the transition is given by $k\xi=C$, where C is a function of $wt^{-\phi}$. Assuming that this is an analytic function, and noting that for $w=0$ the $\mathbf{k}$ vector vanishes, one finds that below the transition k is given by

$$k\xi\sim wt^{-\phi}\ \text{or}\ k\sim t^{\nu-\phi}. \tag{9}$$

In this case k is expected to vanish with an exponent larger than ν.

In summary, we have demonstrated that the β-incommensurate transitions in quartz and in berlinite belong to a class of transitions which has features in common with both instability and nucleation types. It is

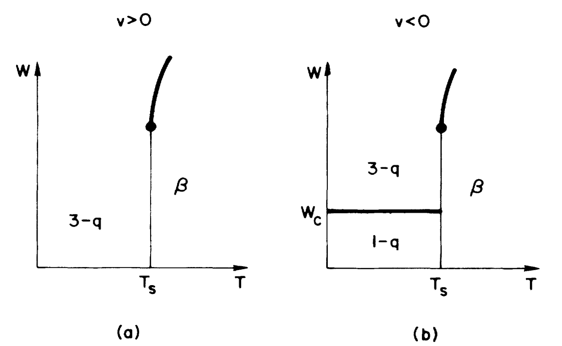

FIG. 3. Schematic (T,w) phase diagram of the model (1): (a) for $v>0$ and (b) for $v<0$. Thin lines represent second-order transitions while thick lines represent first-order transitions.

shown that the **q** vector associated with the incommensurate phase is expected to rotate below the transition, and that the perpendicular component of **q** should vanish at T_S as t^{ν}. This result is valid provided the transitions in quartz or in berlinite could be established to be continuous. It would be of interest to study the correlation length in these systems and compare its behavior to that of the perpendicular component of **q**.

We thank D. DiVincenzo, G. Grinstein, P. Horn, and J. Toner for illuminating discussions. This work was supported by the Israel Commission for Basic Research, by the Minerva Foundation (Munich, Germany), and by the Natural Sciences and Engineering Research Council of Canada.

[a]Permanent address: Department of Physics, The Weizmann Institute of Science, 76100 Rehovot, Israel.

[1]P. G. de Gennes, in *Fluctuations, Instabilities, and Phase Transitions,* edited by T. Riste, NATO Advanced Study Institute, Series B, Vol. 29 (Plenum, New York, 1975).

[2]B. Schaub and D. Mukamel, Phys. Rev. B **32**, 6385 (1985).

[3]J. W. Felix, D. Mukamel, and R. M. Hornreich, Phys. Rev. Lett. **57**, 2180 (1986).

[4]A. Michelson, Ph.D. thesis, Technion–Israel Institute of Technology, 1977 (unpublished); T. A. Aslanyan and A. P. Levanyuk, Fiz. Tverd. Tela (Leningrad) **20**, 804 (1978) [Sov. Phys. Solid State **20**, 466 (1978)].

[5]S. Alexander, R. M. Hornreich, and S. Shtrikman, in *Symmetries and Broken Symmetries in Condensed Matter Physics,* edited by N. Boccara (Institut pour le Developpement de la Science, l'Education, et la Technologie, Paris, 1981), p. 379.

[6]A. L. Korzenevskii, Zh. Eksp. Teor. Fiz. **81**, 1071 (1981) [Sov. Phys. JETP **54**, 568 (1981)].

[7]D. Blanckschtein, E. Domany, and R. M. Hornreich, Phys. Rev. Lett. **49**, 1716 (1982); D. Blanckschtein and R. M. Hornreich, Phys. Rev. B **32**, 3214 (1985).

[8]J. W. Felix and D. M. Hatch, Phys. Rev. Lett. **53**, 2425 (1984), and Jpn. J. Appl. Phys. Suppl. **24**, Pt. 2, 176 (1985).

[9]G. Van Tendeloo, J. Van Landuyt, and S. Amelinckx, Phys. Status Solidi A **30**, K11 (1975), and **33**, 723 (1976).

[10]K. Gouhara and N. Kato, J. Phys. Soc. Jpn. **53**, 2177 (1984), and **54**, 1868, 1882 (1985).

[11]G. Dolino, J. P. Bachheimer, B. Berge, C. M. E. Zeyen, G. Van Tendeloo, J. Van Landuyt, and S. Amelinckx, J. Phys. (Paris) **45**, 901 (1984).

[12]T. A. Aslanyan and A. P. Levanyuk, Solid State Commun. **31**, 547 (1979).

[13]T. A. Aslanyan, A. P. Levanyuk, M. Vallade, and J. Lajzerowicz, J. Phys. C **16**, 6705 (1983).

[14]M. B. Walker, Phys. Rev. B **28**, 6407 (1983).

[15]J. Van Landuyt, G. Van Tendeloo, S. Amelinckx, and M. B. Walker, Phys. Rev. B **31**, 2986 (1985).

[16]N. Kato and K. Gouhara, Phys. Rev. B **34**, 2001 (1986); J. Van Landuyt, G. Van Tendeloo, and S. Amelinckx, Phys Rev. B **34**, 2004 (1986).

[17]E. Snoeck, C. Roucau, and P. Saint-Grégorie, J. Phys. (Paris) **47**, 2041 (1986).

[18]This transition has previously been studied with use of the Landau theory (see Refs. 13 and 14). However, in these studies the LGW model was written in terms of the scalar order parameter $\eta(\mathbf{r})$ rather than its six Fourier components $\eta_{\pm i}$, $i=1$, 2, and 3. Writing the Hamiltonian in terms of these Fourier components makes the fact that the transition to the incommensurate phase is of an intermediate type more transparent. Also this form is more appropriate for carrying out scaling and renormalization-group analyses.

[19]Such rotation does not take place in the single-**q** phase. In this case the contribution of the w term to the free energy vanishes.

[20]Note that in this model one expects the perpendicular component of the wave vector $|\mathbf{k}_i|$ rather than the wave vector itself to vanish at the transition.

[21]See, e.g., A. Aharony, in *Phase Transitions and Critical Phenomena,* edited by C. Domb and M. S. Green (Academic, New York, 1976), Vol. 6.

[22]M. E. Fisher, Rev. Mod. Phys. **46**, 597 (1974).