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Origin of Modulated Incommensurate Phases in Insulators

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We discuss the origin of incommensurate structural modulations as found in certain insulating crystals. The theory developed is based on the necessary existence of a second, independent, transformation mode which can have an energy-lowering interaction with the main mode of transformation *only* at nonzero wave vector, due to symmetry. The required subsidiary mode, of correct symmetry, has been directly observed, or strongly inferred, in four cases.

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Some crystals have a modulation of their structure with (usually) a fairly long wavelength incommensurate with the underlying lattice, which has aroused considerable interest in recent years.¹

In metals similar modulations have been well understood as due to effects near the Fermi surface, but in good insulators a different mechanism must be responsible and this has been an enigma up until now. Among many examples¹ of insulators showing such structural modulations, some are compounds, of which we have considered NaNO_2 ,^{2,3} while others are solid solutions, of which we have studied the intermediate plagioclase feldspars (IPF) $(\text{NaAlSi}_3\text{O}_8)_x(\text{CaAl}_2\text{Si}_2\text{O}_8)_{1-x}$,⁴ mullite $(\text{Al}_{12}\text{O}_{18}\square_2)_x(\text{Al}_8\text{Si}_4\text{O}_{20})_{1-x}$,^{5,6} and nepheline $K_x\square_{1-x}\text{Na}_3\text{Al}_{4-x}\text{Si}_{4+x}\text{O}_{16}$.^{5,6} Here \square represents a site vacancy.

Some crystals have a modulation of their structure with (usually) a fairly long wavelength incommensurate with the underlying lattice, which has aroused considerable interest in recent years.¹

If one interprets the long wavelength of the modulation as evidence for a long-range oscillating force, where can it come from? In the simplest cases, the incommensurate (IC) phase is thermodynamically stable in a temperature range $T_2 < T < T_1$ between a more symmetrical (usually disordered) high-temperature phase ($T > T_1$) and a fully transformed phase at $T < T_2$. The latter is not always observed in the solid solutions because

of kinetic reasons or instability to segregation of the components, but its form can easily be imagined. Either way it has a structure of lower symmetry as a result of some transformation, usually involving atomic ordering, at $q=0$ or with \vec{q} at the Brillouin-zone boundary such as $(0, 0, \frac{1}{2})$ in IPF⁴ and mullite,^{5,6} or at some other symmetry point such as $(\frac{1}{3}, \frac{1}{3}, 0)$ in reciprocal space as in nepheline.^{5,6} The IC phase shows the same transformation but modulated, with \vec{q} near the relevant symmetry point. For example, in NaNO₂ the O-N-O groups have the shape of an arrow or triangle, and below T_2 they order with $q=0$, i.e., all point in the same direction along the crystallographic \vec{b} axis (with an accompanying displacement of the Na⁺ ions) giving a ferroelectric material (Fig. 1).^{2,3} In the IC phase they point positively along the \vec{b} axis with sinusoidal probability

$$p(\vec{r}) = \frac{1}{2} + \psi_q \cos(qx) \quad (1)$$

and along $-\vec{b}$ with probability $1 - p(\vec{r})$,⁷ where \vec{q} varies from 0.10 to 0.12 times the reciprocal vector a^* .²

Recent study has revealed a new aspect of the modulation phenomenon in insulators, which in turn has immediately suggested the theoretical explanation to be presented below. We will return at the end to discuss how aspects of our analysis can be seen in other earlier work. Our explanation suggests new observations and makes possible the structure determination of materials hitherto found too complex, as well as unifying the discussion of IC phases in different situations. In all the cases investigated so far, the following phenomenology appears to apply.³⁻⁶

(i) The crystal has *two* possible transformation modes, not one, which we shall refer to as the main mode and subsidiary mode. The main mode refers to the transformation below T_2 .

(ii) The two transformation modes have different symmetry at $\vec{q}=0$ (or \vec{q} at the relevant symmetry point which we take as $\vec{q}=0$ for ease of

presentation). But when they occur modulated with the observed IC wave vector $\vec{q} \neq 0$, they have the same symmetry, i.e., they belong to the same irreducible representation of the group of \vec{q} .⁸ Thus by symmetry the two transformation modes *cannot* have an interaction energy at $q=0$ but they *do* interact at $\vec{q} \neq 0$.

(iii) *Both* transformation modes are present in the IC phase, with modulation in quadrature, but the subsidiary mode disappears (has zero amplitude) below T_2 .

Let us illustrate these bare remarks. The main transformation in each of the four cases studied so far is an ordering as follows: In NaNO₂, the direction of the NO₂ groups as already described; in IPF and the mineral mullite, the spatial ordering of the Al and Si atoms^{5,6}; in nepheline, the K⁺ and cation site vacancies^{5,6}; and in hollandite, Ba⁺⁺ and vacancies.⁵ All are described by a scalar order parameter such as ψ_q in (1), and the existence of a second type of modulation in the IC phase *is required*⁹ by the observation of different x-ray diffraction intensities at $\vec{g} \pm \vec{q}$. This point has been understood for some time but only taken into account in the most recent structural determinations.³⁻⁶ In NaNO₂ the subsidiary transformation is a local shear of the unit cell,

$$\epsilon_{xy}(\vec{r}) = \varphi_q \sin(qx) \quad (2)$$

with amplitude φ_q , as has recently been deduced directly by x-ray structure analysis³ after many studies of this material over many years.² The unit cell of NaNO₂ in the high-temperature phase has point-group symmetry *mmm* if the $\pm \vec{b}$ orientations of the NO₂ group are taken as occupied with equal probability, which reduces to *m2m* when the NO₂ groups order uniformly and to the *different* symmetry $2_z/m$ under *xy* shear. Alternatively we can say⁸ that the group of $\vec{q}=0$ is *mmm* and the two transformation modes belong to the two different irreducible representations B_{2u} and B_{1g} , respectively. The corresponding group of $\vec{q}=(q, 0, 0)$ for the IC phase is *2mm*, the symmetry of the frozen-in phonon (2) following in the usual manner of lattice dynamics⁸ and that of the ordering (1) analogously. Both can easily be seen to belong to the *same* irreducible representation B_2 (Σ_4 in the Bouckaert-Smolouchowski-Wigner notation⁸) of the group of \vec{q} , namely odd under 2_x and m_y but even under m_z .¹⁰ Thus the NO₂ ordering and *xy* shear can interact at $\vec{q} \neq 0$ but not at $\vec{q}=0$.

The same kind of symmetry situation has been found in the ordering complex solid solutions in

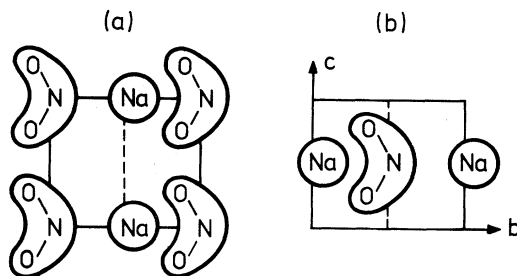


FIG. 1. Geometry of structures.

IPF,⁴ mullite, and nepheline.^{5,6} In the case of nepheline it has led to the identification of a subsidiary acoustic mode, and then from x-ray data a solution for the modulated structure. This illustrates how the symmetry analysis provides precise constraints on possible structures, which are invaluable in the structure determination of materials previously found to be insoluble by normal methods.

In some modulated solid solutions it may be a simple matter to identify the subsidiary mode as a second type of atomic ordering from the end members of the solid solution series. For example, in mullite the subsidiary mode involving O/□ ordering is observed^{5,6} in the end member (composition $x=1$) ι -alumina, while in the IPF a subsidiary Ca/Na ordering was suggested as an intermediate compound and established by kinetic studies.⁴ Clearly the presence of two transformation modes suggests studying them individually by using a range of techniques such as electron microscopy, thermal kinetics, neutron diffraction, etc., chosen to be preferentially sensitive to one or the other.

We turn now to the energetics of the interaction between the two transformation modes, and the origin of the IC phase. Let us consider a Landau expansion of the free energy F for the high-temperature phase in terms of the order parameters ψ_q and φ_q for the main and subsidiary transformation modes as in (1) and (2). Ignoring algebraic complications from the fact that in general ψ_q and φ_q should be treated as complex numbers with $\psi_q^* = \psi_{-q}$, etc., we have

$$F = \sum_q \{ A_q \psi_q^2 + 2H_q \psi_q \varphi_q + B_q \varphi_q^2 \}, \quad (3)$$

where the main mode by itself would go soft at $T = T_c$ when¹¹

$$A_q(q=0, T=T_c) = 0. \quad (4)$$

To see the effect of the subsidiary mode we write each q component of (3) as

$$[A_q + 2H_q(\varphi_q/\psi_q) + B_q(\varphi_q/\psi_q)^2] \psi_q^2 \quad (5)$$

and minimize the coefficient in square brackets by mixing in the optimum ratio

$$\varphi_q/\psi_q = -H_q/B_q \quad (6)$$

of the subsidiary mode to achieve the lowest energy which then equals

$$[A_q - H_q^2/B_q] \psi_q^2. \quad (7)$$

The mixed (ψ_q, φ_q) mode goes soft when¹¹

$$A_q - H_q^2/B_q = 0, \quad (8)$$

which clearly occurs at a higher temperature than when A_q by itself (at the same q) goes soft. We note that with the ratio (6) and when (8) is satisfied, the three terms in the energy (3) or (5) are in the ratio 1:(-2):1 so that the two transformation modes contribute equally in energy at the instability point which we call a *structural resonance*⁴ between them. This equality is true even though B_q may be quite stiff with the φ_q mode nowhere near instability by itself, in which case the amplitude ratio (6) is simply small.

We now have the explanation of incommensurate phases. With the phenomenology condition (ii) we have $H_q = 0$ (no interaction) at the symmetry point $q=0$ but $H_q \neq 0$ at $q \neq 0$. It is therefore clearly possible that the instability (8) sets in more easily at some $q_0 \neq 0$ than the $q=0$ transformation (4). We can make this more precise by expanding (8) in powers of q , retaining the most significant terms:

$$A_q \approx A_0(T) + a_2 q^2 + a_4 q^4, \quad (9a)$$

$$H_q \approx h q, \text{ and } B_q \approx B. \quad (9b)$$

Since H_q is zero at $q=0$ it must be (at least) linear in q , and B_q to lowest order is a constant, namely in NaNO_2 the relevant elastic constant. The dominant temperature dependence lies in $A_0(T)$ which goes linearly to zero at $T = T_c$. Now (8) becomes

$$A_0(T) + (a_2 - h^2/B)q^2 + a_4 q^4 = 0, \quad (10)$$

which has a solution $q_0 \neq 0$ when $A_0(T)$ is still slightly positive if

$$h^2/B > a_2. \quad (11)$$

This then is the condition for the onset of an instability and IC phase at $T_1 > T_c$.

Our analysis relates to some earlier work on IC phases. The cooperative Jahn-Teller effect in $\text{K}_2\text{PbCu}(\text{NO}_2)_6$ coupled to lattice distortions appears to be an example of our mechanism,¹²⁻¹⁴ although the symmetry analysis to show the coupling vanishes at the symmetry point is missing.¹⁴ Periodic lattice distortions in metallic systems¹⁵ can be subsumed under our equations by attaching ψ and φ to the atomic motion and the conduction charge-density wave, respectively, but the incommensurateness arises from a maximum of H_q related to the Fermi surface and not for symmetry reasons as here. The organic compound

tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ)¹⁶ is metallic, but the coupling between the distortions in the TTF and TCNQ stacks has been described¹⁶ by equations and symmetry arguments analogous to ours. Finally, a few situations are known¹⁷ where IC structures result from two competing interactions with only a single order parameter: These could be put under our analysis but at the expense of some artificiality.

It helps to see the physical origin of the causative interaction energy H_q for NaNO_2 . As an exaggeration consider an abrupt antiphase boundary in an otherwise perfectly ordered material. The layers shown in Figs. 1(a) and 1(b) are stacked alternately on top of one another, until after a layer of type (a) let us add one of type (b) but reversed left to right. The O atoms of the reversed layer are now too close to the nearest Na atoms in the previous layer and vice versa, these atoms having the tightest contacts⁷ in the crystal. The resultant stress is relieved by sliding the reversed type-(b) layer to the left relative to the underlying type-(a) layer, thus producing an xy shear. More generally this mechanism yields an energy $h(\partial\psi/\partial x)\varphi$ which in Fourier transform becomes $H_q = iqh$, where the factor i gives ψ and φ in quadrature, as also follows from symmetry.¹⁸

Finally it can be shown¹⁸ that the existence range T_1-T_2 of the IC phase becomes wide if B is small, i.e., if the subsidiary mode is also nearly soft by itself as can easily happen if it too is an ordering process, e.g., in mullite.

Fuller accounts of the individual cases⁶ and of the theory with its implications for structural analysis¹⁷ are planned, with quantitative calcula-

tions⁷ for NaNO_2 . We thank Professor K. H. Michel for helpful discussions.

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