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Abstract
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Reference

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Ni-I Boracite: Latent Antiferromagnetism and Improper Ferroelectricity-Ferroelasticty

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A theoretical model of the 61.5 K transition in Nickel-iodine boracite is presented. Based on a six-dimensional irreducible representation of the F43cl' paramagnetic group, it shows, within the framework of the Landau theory, that the simultaneous onset of the magnetic ferroelectric and ferroelastic properties can be foreseen from the symmetry of the transition order-parameter. The primary order-parameter is identified as a latent antiferromagnetic ordering. The weak magnetization, polarization and strain components originate in an improper coupling of these quantities with the antiferromagnetic sublattice magnetization. The corresponding magnetic, dielectric, elastic and magnetoelectric anomalies are briefly discussed.

§1. Introduction

Nickel-iodine boracite (Ni-I) is the unique example of boracite in which a magnetic and structural transition occurs directly from the paramagnetic F43cl' phase to a monoclinic phase of magnetic class m'. The consistency of the preceding symmetries and the simultaneity of the onset of weak ferromagnetism and ferroelectricity have been demonstrated by magnetic, dielectric, piezoelectric and birefringence measurements. It is noteworthy that the smooth anomalies of various physical properties found around 120 K, or below the 61.5 K transition have been shown recently to be associated with relaxation mechanism due to defects and not with a structural transition, as was claimed by some authors. Besides, the domain pattern observed below Tc=61.5 K, shows the existence of twelve ferroelastic domains and twenty-four ferroelastic domains. The number and orientations of both types of domains are consistent respectively with the structural 43m'→m' and magnetic 43ml'→m' symmetry modifications.

In this paper, we present a theoretical analysis of the magnetostructural transition in Ni-I. Within the framework of the Landau theory, the symmetry of the order-parameter associated with the transition is identified (§2). It shows that the simultaneity of the magnetic and structural modifications is not accidental, but can be predicted on a phenomenological basis. Using the specific Landau-Dzialoshinskii approach to magnetic systems, the nature of the magnetic ordering arizing below Tc is precised (§3). Finally the critical behaviour of Ni-I is briefly discussed (§4).

§2. Identification of the order-parameter symmetry in Ni-I.

The F43cl' Shubnikov group possesses ten active irreducible corepresentations (IC's): five at the Brillouin-zone center I, and five at the X point of the face-centered Brillouin-zone surface (k,=0, 0, π/a) in the Kovalev notation. The results of the Landau symmetry analysis of these IC's are summarized in Table I. They reveal that the paramagnetic to ferromagnetic F43cl'→m' symmetry change observed in Ni-I can be unequivocally related to a six-dimensional IC, labelled , at the X point of the reciprocal lattice. Actually, as it can be seen in Table I, the other IC's lead either to antiferromagnetic groups, or to ferromagnetic groups of symmetry distinct from m'.

The change in magnetic structure induced by , has the remarkable property of being necessarily connected with a structural transition, a feature which is verified in Ni-I. This property deserves justification. In this respect, one must keep in mind that the magnetic symmetry of a paramagnetic crystal (the grey Shubnikov group) embodies its structural symmetry (the Fedorov group) in such a manner that the IC's of the paramagnetic group depict not only the degrees of freedom of the spin distribution, but also an eventual motion of the atoms in the crystal. This latter situation has been shown to be realized only for a small minority of zone-boundary IC's, the larger number of IC's inducing a purely magnetic modification. Let us stress that in Ni-I the structural change gives rise to spontaneous polar tensors (i.e. polarization and strain components). It thus differs in an essential manner from the mere magnetostriction in which only non-symmetry breaking polar tensors (transforming as the identity representation) are induced by the magnetic transition.

The Shubnikov group of the low-temperature phase in Ni-I can be identified as Cc'. On Fig. 1 we have represented schematically the magnetostructural lattice change corresponding to the F43cl'→Cc' transition. It in-

Table I. Results of the Landau symmetry analysis for active IC's of the paramagnetic group F43cl', (b) High symmetry points of the paramagnetic Brillouin zone (c) Ferromagnetic (F) and antiferromagnetic (AF) low symmetry group (d) Primitive translations and antitranslations of the low-temperature phase primitive cells, with reference to the paramagnetic primitive translations.

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<td>AF II P43m (τ2, τ3)</td>
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In Ni-I, a number of experimental facts strongly suggest that the primary order-parameter is an antiferromagnetic ordering of the magnetic moments. These facts are: 1) neutron-diffraction evidences of antiferromagnetic sublattices below \( T_c \); 2) the typical negative asymptotic Curie-Weiss temperature deduced from the magnetic susceptibility; 3) the weak value of the measured magnetization compared to the sum of the effective magnetic moments. In this respect it must be pointed out that one cannot assume the spontaneous polarization \( P \) (or strain components \( e_{ij} \)) to be the primary order-parameter (as suggested in ref. 24), the polarization being a secondary order-parameter, as the two quantities would be necessarily connected by a coupling term of the form \( P^a M \) (or \( e_{ij} M \) with \( n > 1 \)). Such a coupling is forbidden by the time-reversal operation which belongs to the paramagnetic phase.

The monoclinic \( Cc' \) cell has the same volume (4V) as the conventional cubic cell of symmetry \( F43c' \), assuming, without loss of generality, that the lowering of symmetry is entirely connected with the displacement of the nickel ions, the twenty-four metallic ions will thus be distributed among twelve independent monoclinic sublattices. The position of the ions forming each sublattice are denoted (1, 2, 3, 4), (5, 6, 7, 8), and (9, 10, 11, 12) on Fig. 2.

Let us symbolize the spins of the ions by \( S_i \) (\( i = 1 \) to 24). The exchange interactions, can be written (omitting the superscript \( a \)):

\[
F_a = \frac{\alpha}{2} \sum_i (L_i)^2 + \frac{B_1}{4} \sum_i [L_i(L_i)^2 + \frac{B_2}{4} \sum_i (L_i)^4 \\
+ \frac{B_3}{4} \sum_i (L_i)^2 + \frac{C}{2} M^2 \\
+ D((M_1 L_1 L_2) + (M_2 L_2 L_3) + (M_3 L_3 L_1))
\]

where the \( B_i \), \( D \), \( M \), \( C \) are constant coefficients, and \( L = (T - T_c) \). One of the absolute minima of \( F_a \) corresponding to:

\[
L^\dagger = \pm L^\ddagger = \pm L^\gamma
\]

is associated with the non-zero magnetization.

\[
M^a = -\frac{D}{C} [L^\gamma (L^\gamma L^\gamma) + L^\dagger (L^\dagger L^\dagger) + L^\ddagger (L^\ddagger L^\ddagger)]
\]

As the \( L^\gamma \) vary as \( L^\gamma = (T_c - T)^{\gamma/2} \), \( M^a \) is proportional to \( (T_c - T)^{\gamma/2} \). Besides, introducing (3.3) in (3.1) leads to:

\[
S_i + S_i_{12} = \frac{1}{4} (M^a + 3 L^\gamma)
\]
and \( S_j + S_{j+1} = \frac{1}{4} (M^+ + L^-) (j \neq i) \) \( (3.5) \)

where the number \( i \) in (3.5) is determined by the signs in eq. (3.3) (e.g. for \( L_1 = L_2 = L_3, i = 1, j = 2, 3, 4 \)).

From Eq. (3.5) it can be seen that the average spins of the ions can be divided into two groups, the absolute magnitude of the spins differing from one group to the other. Such a property is usual for ferrimagnets. However, here the spins are associated with one identical type of magnetic ions, which is found in equivalent crystallographic positions in the paramagnetic phase.

This is in contrast with the situation found in standard ferrimagnets such as ferrites or garnets.\(^{\text{20}}\) Dzialoshinskii and Man'ko\(^{\text{13}}\) suggested to denominate this new type of uncompensated antiferromagnetism, latent antiferromagnetism. As noted by the authors of Ref. 13, is that, despite its exchange origin, the magnetization must be expected to assume very weak values at any temperature below \( T_c \). This is connected with the improper character of the transition, i.e. to the fact that \( M \) results from a coupling to the third power of the antiferromagnetic sublattices. In Ni-I, the magnetization at 4.2 K is found to be about 0.9 Gauss \(^{\text{27}}\) which represents 1% of the nominal value. Furthermore, as for the case of Ni-I, it can be shown \(^{\text{27}}\) that latent antiferromagnetic transitions should always be accompanied by marked structural modifications, possibly involving spontaneous polar tensors.

\section*{4. Magnetostructural Anomalies}

The existence of a coupling between the magnetization components \( M_x, M_y, M_z \) and the antiferromagnetic sublattices \( L_x, \) with a \( \nu = 3 \) faintness index, \(^{\text{18}}\) allows to explain \(^{\text{18}}\) the remarkable magnetic anomalies which have been observed at the transition in Ni-I, namely 1) a magnetic susceptibility which shows a sharp decrease on cooling to about 30 K, where it starts increasing again down to 4 K; \(^{\text{22}}\) 2) an asymmetric hysteresis loop \(^{\text{3}}\) for a magnetic field \( H \|[\text{III}] \), the curve \( M_x(H) \) decreases above 3 K near and changes sign above 20 kOe. \(^{\text{27}}\) On the other hand, the dielectric and elastic anomalies clearly denote the improper character of the ferroelectric-ferroelastic transition. In particular the value of the spontaneous polarization \( P \) at 4.5 K \((P \sim 0.07 \mu \text{C/cm}^2) \) is about two orders of magnitude smaller than the corresponding value for GMO. Besides, near below \( T_c \), a linear variation \( P = (T_c - T) \) is observed \(^{\text{10}}\) in agreement with the theoretical prediction of a faintness index \( \nu = 2.10 \) \(^{\text{10}}\). Herebelow we will restrain ourselves to discuss the spontaneous magnetoelectric properties of Ni-I, which are among the most distinctive features of this material.

Magnetoelectric effects were evidenced experimentally by the switching of electric and magnetic domains under conjugated fields. In our model such effects are accounted by the coupling term:

\[ F_{\text{ME}} = P_x M_x + P_y M_y + P_z M_z \] \( (4.1) \)

From the minimization of the Landau free-energy \(^{\text{10}}\) including (4.1), one gets the equation of state:

\[ \frac{P_x}{x^2 \phi} - E_x - (M_x)^2 \sin \theta \cos \theta \] \( (4.2) \)

where the spontaneous magnetization \( M_x^s \) is located in the \( x, y \) plane, \( \theta \) being the angle between \( M_x^s \) and the \( x \) axis (Fig. 3(a)). Eq. (4.2) shows that a change of sign of \( P_x \) under application of a field-\( E_x \), should result in a 90° rotation of \( M_x^s \) in the \( xy \) plane \((\theta = \theta + \pi/2)\). This effect was obtained by Ascher \(^{\text{21}}\) et al. (1978) by applying of \(-5 \text{ kV/cm} \) field at 56 K. The inverse effect, i.e. the reversal of \( P_x \), when an external magnetic field is applied perpendicular to the magnetization, evidenced by the same authors near \( T_c^0 \), is expressed by the equation:

\[ [(x^2)^{-1} M_x^s - H_x] \sin \theta - M_x; P_x \cos \theta \] \( (4.3) \)

One can see (Fig. 3(b)) that when turning the magnetization by \( 90° \) from the initial position \( \theta = \pi/4 \), under application of the corresponding magnetic field \((\theta = \theta + \pi/2)\) one has the reverse sign of \( P_x \), for eq. (4.3) to remain unchanged.

References

16) O. V. Kavelev: Irreducible representations of the space groups (Gordon and Breach, New-York, 1963).