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Antiferroelectric transition in β -alumina, a realization of the $D = 2, s = 3$ Potts model ?

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Résumé. — Un modèle basé sur des interactions dipôle-dipôle électriques est proposé pour expliquer la transition d'ordre récemment observée dans l'alumine bêta stœchiométrique à l'argent.

La phase basse température est un réseau antiferroélectrique de dipôles, trois fois dégénéré, associé aux ions Ag^+ et O_5^- . Quand $T \rightarrow T_c$ avec $(T - T_c)/T_c > 10^{-2}$, la longueur de corrélation ξ croît dans les couches bidimensionnelles avec un comportement critique $\xi \sim (T - T_c)^{-\nu}$ que l'on considère comme appartenant à la même classe d'universalité que le modèle de Potts $D = 2, s = 3$: nous trouvons $\nu_{\text{exp}} = 0,85 \pm 0,1$ tandis que $\nu_{\text{th}} \simeq 0,83$.

Abstract. — A model based on electric dipole-dipole interactions is proposed to explain the recently observed ordering transition in stoichiometric silver β -alumina. The low temperature phase is a three-fold degenerate antiferroelectric array of dipoles associated with Ag^+ and O_5^- ions. When $T \rightarrow T_c$ with $(T - T_c)/T_c > 10^{-2}$, the correlation length ξ increases in the $D = 2$ layers with a critical behaviour $\xi \sim (T - T_c)^{-\nu}$ which is supposed to belong to the $D = 2, s = 3$ Potts model universality class : we find $\nu_{\text{exp}} = 0.85 \pm 0.1$ as $\nu_{\text{th}} \sim 0.83$.

It has recently been observed that stoichiometric [1] Ag^+ β -alumina undergoes a structural ordering around 300 K, the low temperature structure being an hexagonal superlattice structure [2, 3] with $a' = a/\sqrt{3}$. The purpose of this paper is first to remark that the observed structure can be predicted in a simple picture which takes into account the existence of off-centred positions (o.c.p.) for the Ag^+ and O_5^- ions. The model is basically that of an order-disorder antiferroelectric transition in *two dimensions* [4]. Antiferroelectric interactions between o.c.p. have been already claimed to be responsible for the anomalous static and dynamic behaviour of Cu_3VS_4 at low temperature and the existence of off-centred positions seems to play an important role in a number of fast ion conductors [5, 6].

We show that the transition can be related to recent

theoretical and experimental studies of phase transition in 2-dimensions and that it constitutes the first physical realization of the $D = 2$, three states Potts model [7] where the critical exponent ν for the correlation length ξ can be measured from scattering techniques.

To clarify the following discussion one should stress that in fast ion conductors one can consider two kinds of order-disorder transitions : the first is the classical transition concerning the occupation of Beevers-Ross (BR) and the anti-Beevers-Ross (aBR) sites. We shall call it the BR-aBR transition and is usually considered as closely related to fast ion conduction (lattice gas models [8]). Here we shall consider an other type of transition in which what is considered is the ordering between the equivalent off-centre positions of the ions.

We show in this letter that the order-disorder transition in β -alumina when studied in the quasi-2D regime belongs to the same universality class as the $D = 2$ three states ($s = 3$) Potts model [7]. The only other realization [9] of this model is the transition

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from a liquid to a commensurate solid for adsorbed helium and Kr atoms on graphite [10, 11]. For ^4He specific heat measurements have given a critical exponent [10, 12] $\alpha = 0.36$ and $\alpha = 0.28$. Contrary to Landau theory which predicts a first-order transition, the strong fluctuations in 2D lead for the Potts model with $s \leq 4$ to a second-order transition [13]. Recent conjectures [14] and real space renormalization group calculations [15] predict for the three states $D=2$ Potts model $\nu \simeq 5/6$ and $\alpha = 2 - 2\nu \simeq 1/3$.

The fact that the ordering seems to take place between a liquid like phase at high temperature (probably highly conducting) and an antiferroelectric phase at low temperature suggests that both phenomena are not independent.

The superstructure which exists below $T_c = 300$ K is shown in figure 1. It is due to an ordering of the silver and the oxygen ions between the otherwise equivalent o.c.p. It is reminiscent of the $\sqrt{3} \times \sqrt{3}$ superstructure found in commensurate solid phases of rare gas adsorbed on graphite [10] (see also ref. [15] for further references).

Microdensitometer readings of the X-rays pattern show that approaching T_c from above there exists a region $T > T^*$ for which correlations are purely 2D. $[(T^* - T_c)/T_c \sim \text{a few } 10^{-2}]$. When $T > T^*$ the system behaves as if it was 2-dimensional and only very close to T_c , ($T < T^*$) the behaviour crosses over to the truly 3-dimensional regime. If the two-dimensional regime is *second order* a critical behaviour is expected in the region $T \rightarrow T_c$; $T > T^*$ with $\xi \sim (T - T_c)^{-\nu}$.

In our case, the interaction between the o.c.p. can be modeled by electric dipole-dipole interactions [5]

$$\mathcal{H} = \sum_{ij} \left\{ \frac{\mathbf{d}_i \cdot \mathbf{d}_j}{r_{ij}^3} - 3 \frac{(\mathbf{d}_i \cdot \mathbf{r}_{ij})(\mathbf{d}_j \cdot \mathbf{r}_{ij})}{r_{ij}^5} \right\} \quad (1)$$

Fig. 1. — Low temperature structure of stoichiometric silver β -alumina. The unit cell of size $a\sqrt{3}$ is represented by the dotted line. The full circles represent the classical BR sites. The open circles represent the classical O_5^- sites. The square represent the aBR sites. The Ag^+ ions in BR sites and the O_5^- ions are found displaced towards an aBR site represented by an open square (site A). The other two degenerate fundamental states corresponds to displacement towards the B and C sites.

where the dipoles $\mathbf{d}_i$ can take six different values (3 for O_5^- and 3 for Ag^+).

The ground state of a layer is obtained numerically through the following iterative process : we first consider a small cluster and find the lower energy configurations. We then put several clusters together and determine the lower energy configurations of this larger cluster from a combination of the lower states of the small clusters. The ground state structure is found to depend on the ratio of the electric dipole associated with the two species Ag^+ and O_5^- . The structure represented in figure 1 is obtained only if this ratio is smaller than 2.583. Experimentally we can estimate from [2] that

$$d_{(\text{Ag}^+)}/d_{(\text{O}_5^-)} \simeq 0.8/2 \times 0.3 \simeq 1.33$$

a value compatible with the limit of 2.583 obtained from the numerical calculation. The fundamental state is found three-fold degenerate. One of these states is shown in figure 1. It is obtained by letting the Ag^+ and O_5^- ions move towards the aBR site named A in the figure. There are two other states of same energy named B and C in which the ions move respectively towards the sites B and C. In fact each of these states can be build by a *tile* pavement of only three types of rigid hexagons of dipoles. It is important to stress that the first excitations of this system corresponds to a domain structure of the three degenerate ground states and that excited states corresponding to the destruction of the basic hexagons by letting the Ag^+ and O_5^- ions move independently are much higher in energy. They can be neglected near the transition.

The ions positions in the ordered phase can then be expressed in terms of the two functions $\psi_1 = \exp(i\mathbf{k}_1 \cdot \mathbf{R})$ and $\psi_2 = \exp(i\mathbf{k}_2 \cdot \mathbf{R})$ where

$$\mathbf{k}_1 = \pi/a(1, 0, 0), \quad \mathbf{k}_2 = \pi/a(1/2, \sqrt{3}/2, 0)$$

as for the order parameter corresponding to the superlattice structure of He on graphite. The Landau-Ginzburg Hamiltonian takes the form :

$$\mathcal{H}_{\text{LG}} = \frac{1}{2} \{ (\nabla \varphi_1)^2 + (\nabla \varphi_2)^2 \} + \frac{1}{2} \Omega (\varphi_1^2 + \varphi_2^2) + \omega (\varphi_1^3 - 3 \varphi_1 \varphi_2^2)$$

where $\{\varphi_1, \varphi_2\}$ is the real basis of the irreducible representation to which belongs the order parameter. Up to the third-order this system and the three states Potts [7] model have the same Landau-Ginzburg Hamiltonians. Strong universality assumption implies the same critical behaviour for both systems. The same assumption was made for helium adsorbed layers and seems to be confirmed by experiments [12, 13]. For β -alumina a preliminary analysis of the experimental correlation length (Fig. 2) gives $\nu_{\text{exp}} = 0.85 \pm 0.1$ while theory [14, 15] predicts $\nu_{\text{th}} \simeq 0.83$. The uncertainty in this analysis comes from the difficulty to choose T_c and from the onset of the 2D-3D crossover.

Fig. 2. — Log. Log plot of the correlation length ξ as a function of $T - T_c$. These data are the best obtained by Boilot *et al.* [17]. The data of reference [2] has been also analysed and give compatible results. The vertical error bars are estimated errors in the measurement of ξ . In this figure T_c has been chosen to be equal to 300 K. Other choice of T_c compatible with the experiment, results in the quoted error for the exponent ν . For $(T - T_c)/T_c > 0.2$ the effective exponent $\nu_{\text{eff}} = -\text{Log } \xi / \text{Log } \Delta T$ crosses over to the mean field value 0.5

The observed 3D low temperature superstructure is a superposition of layer superstructures. One layer is of type A. The next layer is of type B with a permutation between the oxygen and the silver ions. This keeps the value of the lattice spacing c . Preliminary

calculations using dipolar interactions for two layers cannot decide between AA and AB for the lowest energy configuration. In fact the basic hexagonal *tiles* with which the fundamental states are constructed have no net dipolar moment. These hexagons have only quadrupolar interaction varying as r^{-5} . Moreover the difference between the AA and AB structure goes more like r^{-6} . Experimentally [3] the crossover to the 3D ordering occurs within a few degrees from T_c , in agreement with the weak interaction between planes. Because of the permutation of ions from one layer to the next the 3D structure can be only either AAA... or ABAB... We cannot exclude that the observed 3D arrangement comes from weak interactions through the spinel structure between the layers. The 3D ground state is six-fold degenerate and the order parameter has now four components. The Landau-Ginzburg Hamiltonian would have the same form as for two coupled $s = 3$ Potts models. In 3D a first-order transition is certainly expected. (The 3D, $s > 2$ Potts model is considered to lead to a first-order transition [16].)

More experimental work including detailed measurements of ξ between 300 and 330 K and specific heat measurements are needed to verify our model for the transition. Measurements of the conductivity in the same temperature range should give information about the relation between the o.c.p. ordering and the BR-aBR ordering.

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