Electron spin resonance observation of crossover behavior in antiferrodistortive $Al[CO(NH_2)_2]_6(ClO_4)_3$ and $Ga[CO(NH_2)_2]_6(ClO_4)_3$

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In an ESR investigation of the 300-K second-order structural phase transition in rhombohedral $Al\,ur_6(ClO_4)_3$ and $Ga\,ur_6(ClO_4)_3$ the critical exponent β has been obtained from the temperature dependence of the ESR parameter E below T_c. The change in β indicates a simultaneous lattice and order-parameter dimensionality crossover at $T \simeq T_c - 50$ K from $d=2$, $n=2$ to three-dimensional behavior. The two-dimensional behavior is associated with the occurrence of layers in the structure containing equivalent ions with a uniform phase of the local order parameter. In the $d=3$ region we suggest a six-dimensional order parameter with wave vectors contained in the star of $\{q_\zeta\} = \{(\bar{\zeta}02\zeta)\}$ (hexagonal setting) with $\zeta \simeq \frac{1}{2}$ near T_c.

I. INTRODUCTION

It is well known[1] that the exponents describing the critical behavior at phase transitions depend on the lattice dimensionality d, the dimensionality of the order parameter n, and on the symmetry of the interactions. For universality class with $d=2$ $n=2$ various examples are known for magnetic systems.[2] However, few systems are mentioned in the literature displaying $d=2$ $n=2$ behavior that undergo nonmagnetic structural transitions with short-range interactions.[3] It is the purpose of the present paper to show on the basis of the results of electron spin resonance (ESR) experiments[4] that $Al\,ur_6(ClO_4)_3$ and $Ga\,ur_6(ClO_4)_3$ belong to this class [ur = urea $=CO(NH_2)_2$].

The structure of rhombohedral $Al\,ur_6(ClO_4)_3$ and $Ga\,ur_6(ClO_4)_3$ consists of two sets of columns parallel to the trigonal axis C_3 containing ClO_4 groups and $M\,ur_6$ groups, respectively (M = Al,Ga). Each ClO_4 group can take on two positions (Fig. 1). The temperature variation of the ESR results can be formally envisaged as originating from the succession of two phase transitions: $D_{3d}^6(R\bar{3}c) \rightarrow S_6^2(R\bar{3}) \rightarrow S_2^1(P\bar{1})$. The former transition would take place at some temperature above the decomposition temperature of the crystals, while the latter one occurs at approximately 300 K. From the ESR results it is not possible to discriminate against predominantly order-disorder or displacive character of the transitions. However it is likely that the high-temperature transition is associated with the onset of ordering in the ClO_4 groups, which is linearly coupled to a $\vec{q}_\Gamma = (000)$ mode of $A_{2g}(\Gamma_2)$ symmetry of the $M\,ur_6$ units. The 300-K transition on the other hand is associated with the condensation of a $\{\vec{q}_X\} = \{(\frac{1}{2}00)(0\frac{1}{2}0)(\frac{1}{2}\frac{1}{2}0)\}$ mode of X_2 symmetry ($\vec{q}$ expressed in $2\pi \times$ reciprocal-lattice units for a hexagonal setting[5]). Symmetry and $\vec{q}$ values follow directly from a Landau-type argument. The high-temperature transition results in two domains in the S_6^2 phase. Due to the 300-K transition each of these domains is again split into three domains, each corresponding to one of the three $\vec{q}$ values. At the 300-K transition the volume of the unit cell is doubled.[6]

II. EXPERIMENTAL RESULTS

The ESR experiments have been performed[4] on Cr III doped single crystals, and are interpreted in terms of a spin Hamiltonian[7]

$$H = g\beta\vec{H}\cdot\vec{S} + D(S_z^2 - \tfrac{15}{4}) + E(S_x^2 - S_y^2) \quad .$$

The parameters D and E are related to the components D_{ij} of the EFG (electric field gradient) tensor at the metal ion site: $D \propto (2D_{zz} - D_{xx} - D_{yy})$ and $E \propto (D_{xx} - D_{yy})$. In this paper we focus on the temperature dependence of E.

Since the temperature dependence of E near T_c is due to the local order parameter $\phi_1 = \sum_q \exp(i\vec{q}\cdot\vec{r}_1)\phi_{\vec{q}}$ we can expand E in terms of ϕ_1, the order of the leading term in the expansion being determined by symmetry considerations. The 300-K transition results from the condensation of an X_2 zone-boundary mode with $\{\vec{q}\} = \{(\frac{1}{2}00)\}$. In the S_6^2 phase the metal ion site symmetry is C_3. The local order parameter ϕ_1 and E transform according to the same representation $E(\Gamma_3)$. Thus we obtain $E = e\langle\phi_1\rangle$.

A preliminary interpretation[8] of the $E(T)$ data yielded $\beta \simeq \frac{1}{3}$ for $T \rightarrow T_c^-$. A more careful examination results in $\beta = 0.34(+0.04, -0.01)$ near T_c with

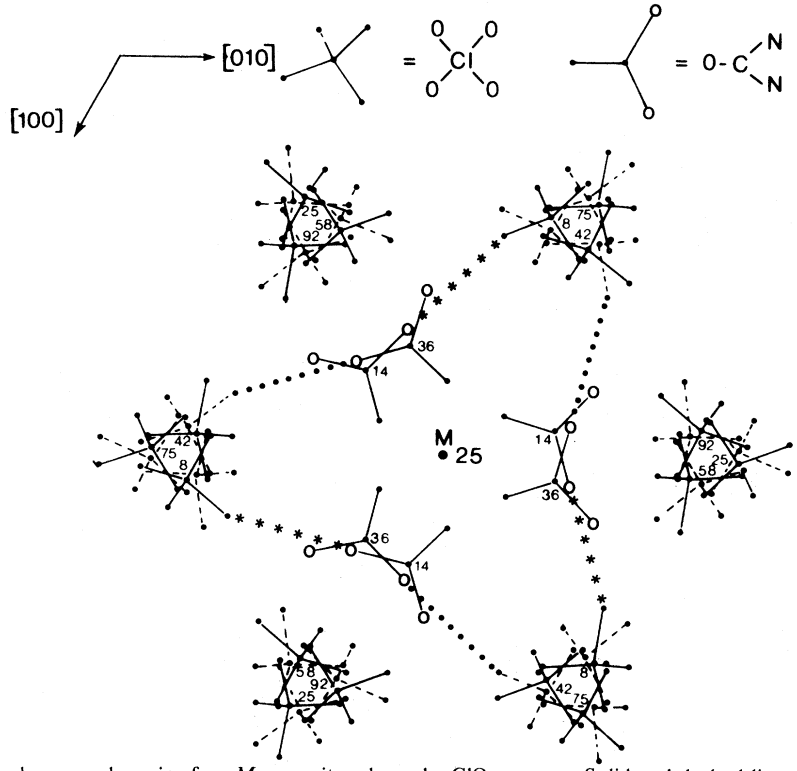

FIG. 1. View along hexagonal z axis of an $M\,ur_6$ unit and nearby ClO_4 groups. Solid and dashed lines (ClO_4 groups) and stars and dots (hydrogen bonds) correspond to the two completely ordered states of the ClO_4 groups in the S_6^2 phase. Z coordinates of some of the atoms are included (height of the hexagonal unit cell = 100). The position of the next $M\,ur_6$ unit in the column is obtained by inversion with respect to the center at $z = 50$.

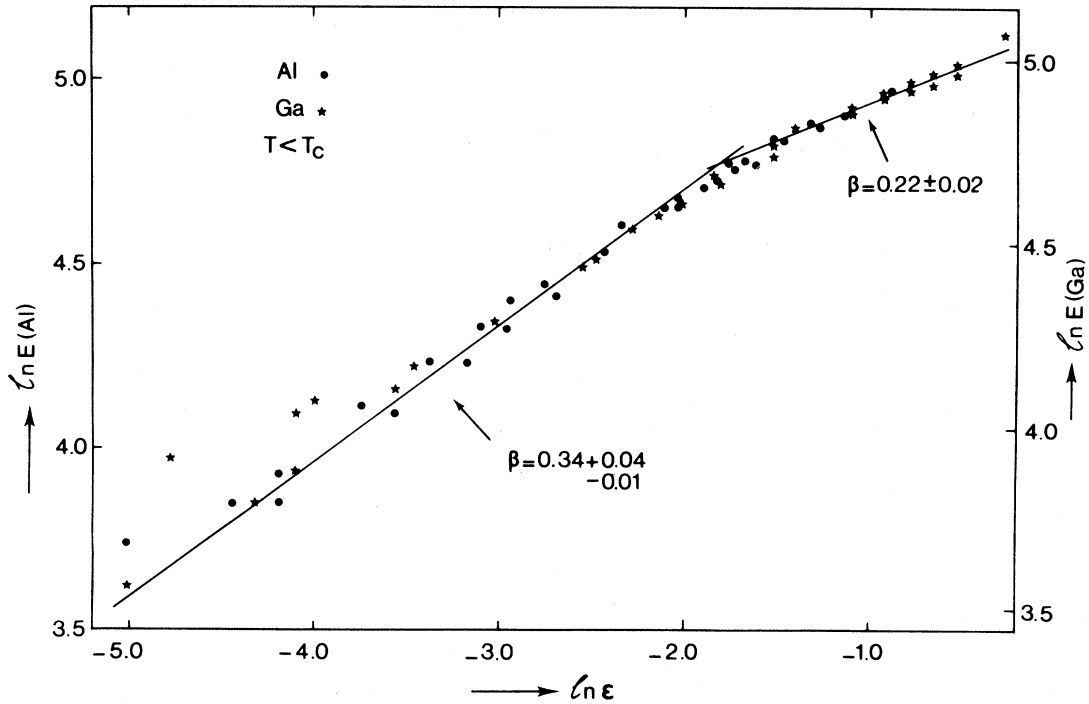

FIG. 2. Crossover behavior in the value of the critical exponent β from the temperature dependence of the ESR parameter E. Left- and right-hand scales correspond to M = Al and M = Ga, respectively.

$T_c = 298.0 \pm 0.5$ K for $Al\,ur_6(ClO_4)_3$ and $T_c = 301.5 \pm 0.5$ K for $Ga\,ur_6(ClO_4)_3$. From Fig. 2 it is clear that there exists another region at lower temperatures with $\beta = 0.22 \pm 0.02$. Crossover between the two regions takes place within a narrow temperature range at $\ln\epsilon \simeq -1.8$ ($T_c - T \simeq 50$ K). The deviation of β from the mean field value $\beta = \frac{1}{2}$ persists down to $\epsilon = 0.6$ indicating a large critical temperature region.

III. DISCUSSION

A. Lattice dimensionality crossover

From the Ginzburg criterion[9] concerning the extent of the critical temperature region, a crossover from lower dimensionality to $d = 3$ in $Al\,ur_6(ClO_4)_3$ and $Ga\,ur_6(ClO_4)_3$ seems very probable. This criterion relates the relative temperature difference ϵ_c at which critical effects become non-negligible to the zero temperature correlation length ξ_0. Analyzing the dependence of ϵ_c on d one finds $\epsilon_c(d=2) >> \epsilon_c(d=3)$. The large critical temperature region observed in the present systems thus is a strong indication for low dimensional critical behavior.

It has previously[8] been shown that the experimental data can also be interpreted in terms of $E \propto (T_c - T)^{\beta}$ with $\beta \simeq \frac{1}{3}$ near T_c and $E \propto (T_0 - T)^{\beta'}$ with $T_0 = T_c + 200$ K and $\beta' = \frac{1}{2}$ (mean field behavior) further away from T_c. However, apart from the extent of the critical region cited above there are other reasons which favor a crossover $d = 2 \rightarrow d = 3$.

(i) The crossover from $\beta = 0.22$ to $\beta = 0.34$ strongly suggest crossover from $d = 2$ $n = 2$ to $d = 3$. For comparison, from Ref. 1 one obtains in the $d = 2$ $n = 2$ region for short-range interaction $\beta = 0.23$.

(ii) A fit to classical behavior can only be obtained by invoking an improbably large difference $T_0 - T_c$.

(iii) For increasing values of $T_c - T$ the present systems exhibit *negative* values for $(\phi_{obs} - \phi_c)$ where $\phi_c = \phi_0 \epsilon^{0.34}$. This is contrary to the case of $SrTiO_3$ where outside the $\beta \simeq \frac{1}{3}$ region classical behavior is well established.[10]

(iv) The decrease in the slope of the $\ln E \leftrightarrow \ln\epsilon$ plot for increasing $\ln\epsilon$ indicates a *smaller* value of β for increasing values of $T_c - T$. These considerations provide a firm basis for the interpretation of the experimental results in terms of a crossover from $d = 2$ $n = 2$ to $d = 3$ behavior.

The two-dimensional behavior in the present systems can be explained by referring to the change of the translational symmetry at the 300-K transition. Due to the antiferrodistortive nature of the phase transition, the local order parameter has opposite phase for equivalent ions separated by $\vec{r} = m\vec{b} + n\vec{c} + p\vec{\tau}$ ($m + n + p = \text{odd}$) for domains or clusters with $\vec{q}_1 = (0\frac{1}{2}\frac{1}{2})_r$, $\vec{r} = m\vec{a} + n\vec{c} + p\vec{\tau}$ for $\vec{q}_2 = (\frac{1}{2}0\frac{1}{2})_r$, and $\vec{r} = m\vec{a} + n\vec{b} + p\vec{\tau}$ for $\vec{q}_3 = (\frac{1}{2}\frac{1}{2}0)_r$ (see Fig. 3). The corresponding vectors in a hexagonal setting are $\vec{q}_1 = (0\frac{1}{2}0)$, $\vec{q}_2 = (\frac{1}{2}\frac{1}{2}0)$, and $\vec{q}_3 = (\frac{1}{2}00)$. For all other equivalent ions the local order parameter has the same phase. The result of these phase relations is the occurrence of layers containing ions moving with uniform phase. For instance, Fig. 4 (and Fig. 3) clearly demonstrates the layered structure for $\vec{q}_2 = (\frac{1}{2}\frac{1}{2}0)$ domains. Open and full circles refer to ions with opposite phase for the local order parameter. For simplicity only the metal ions are indicated in the figure. The layers are parallel to the $(1\bar{1}2)$ plane for $\vec{q}_2$ (Fig. 4), and parallel to (012) for $\vec{q}_1$ and $(\bar{1}02)$ for $\vec{q}_3$.

From the occurrence of these layers we expect for $T \rightarrow T_c$ a softening of the appropriate phonon modes extending over a wide range in $\vec{q}$ along $\{\vec{q}_\zeta\} = \{\pm(\bar{\zeta}02\zeta) \pm (\zeta\bar{\zeta}2\zeta) \pm (0\zeta2\zeta)\}$ (each value corresponding with a particular layer direction). It would be of interest to see if this could be observed directly from the dynamic structure factor $S(\vec{q}, \omega)$ in quasielastic x-ray or neutron scattering.

It is noteworthy that $\{\vec{q}_\zeta\}$ contains both $\vec{q}_\Gamma = (000)$ (wave vector of the high-temperature transition) and $\{\vec{q}_X\} = \{(\frac{1}{2}00)(0\frac{1}{2}0)(\frac{1}{2}\frac{1}{2}0)\}$ (300-K transition). Thus one may envisage a situation where the initial condensation of the Γ-point mode is followed by the softening of the X-point mode. A similar situation is encountered in various other systems displaying a strong anisotropy in the fluctuations [for instance NH_4Br (Ref. 11) and $KMnF_3$ (Ref. 12)].

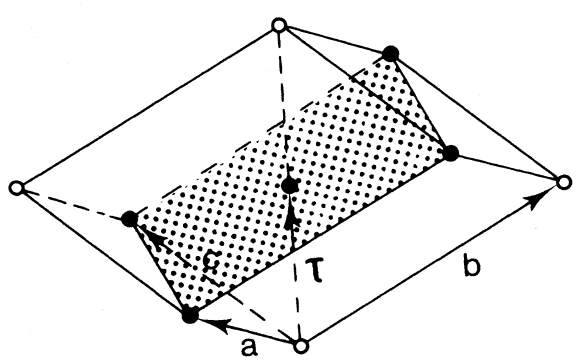

FIG. 3. Definition of the rhombohedral unit cell. Open and full circles refer to metal ions with opposite phase of the local order parameter.

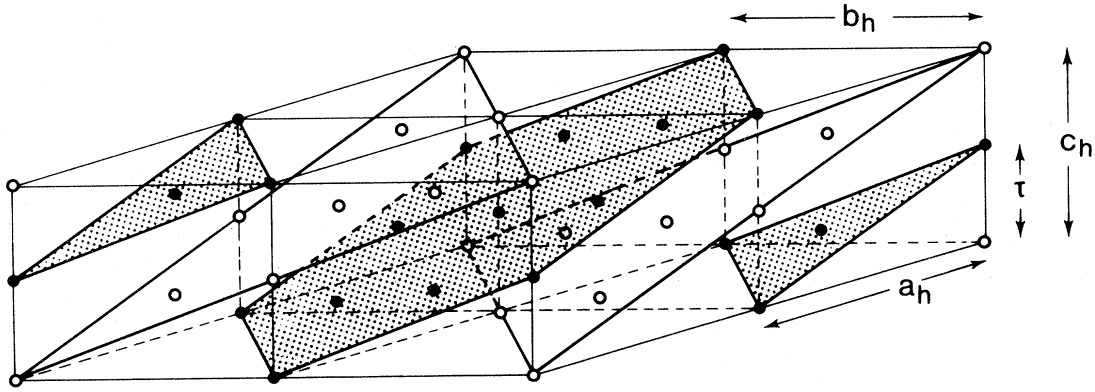

FIG. 4. Occurrence of a layered structure as a consequence of the phase relations between the local order parameters of equivalent ions. The figure includes a set of 2×2 hexagonal cells. For simplicity only metal ions have been indicated, open and full circles referring to ions moving with opposite phase. Layer orientation for other domains is obtained by rotating about C_3 over $\pm 120°$.

B. Order parameter dimensionality

The order parameter dimensionality is obtained[13] by multiplying the number of inequivalent vectors in the star of $\vec{q}$ by the dimensionality of the small representations. For rhombohedral systems all $\vec{q}$ except (000) have small representations that are one dimensional. Thus n equals the number of vectors in the star.

The experimental data on β lead unambiguously to $n=2$ in the $d=2$ region, while they are not conclusive with respect to n in the $d=3$ region. Elastic x-ray scattering in the low-temperature phase shows superlattice reflections[6] with $\{\vec{q}\} = \{(\frac{1}{2}00)(0\frac{1}{2}0)(\frac{1}{2}\frac{1}{2}0)\}$. These values of $\vec{q}$ satisfy the symmetry conditions of a Lifshitz "central point," ensuring by symmetry a minimum in the free energy at T_c.[14] Thus one arrives at $n=3$ in the $d=3$ region.

At this point we notice that the lattice dimensionality crossover can be accompanied by a simultaneous reduction of the value of n [cf. NbO_2 (Ref. 3)]. This is because the onset of large anisotropy in the correlations singles out one or more of the possible $\vec{q}$. For instance, out of the three vectors mentioned above, strong correlations within $(1\bar{1}2)$ planes correspond to $\vec{q}=(\frac{1}{2}\frac{1}{2}0)$ fluctuations. In this way the complete system can be described by three sets of independent systems, each corresponding with strong correlations within layers parallel to one of the planes $(\bar{1}02)$, $(1\bar{1}2)$, (012).

The observation of $n=2$ away from T_c leads to the following conclusions:

(i) The low value of n calls for a decoupling of the system into three independent systems as described above.

(ii) To obtain $n=2$ in each of these subsytems, the total n should be six in the case of three-dimensional correlations, i.e., the star of $\vec{q}$ should contain six vectors.

This leads to wave vectors $\{\vec{q}_\zeta\} = \{\pm(\bar{\zeta}02\zeta) \pm(\zeta\bar{\zeta}2\zeta) \pm(0\zeta2\zeta)\}$ with $\zeta\neq\frac{1}{2}$. These wave vectors do not possess a special symmetry in the reciprocal lattice that precludes the occurrence of a gradient term $\phi\nabla\phi$ in the free energy as is required by the Lifshitz condition for the occurrence of a continuous phase transition. Thus, if the transformation keeps locked on a wave vector with $\zeta\neq\frac{1}{2}$ up to $T=T_c$, the necessary occurrence of a minimum in the free energy at T_c for $\{\vec{q}_\zeta\}$ must be accidental: the value $\vec{q}_0(T)$ which corresponds to a minimum in the free energy $F(\vec{q})$ changes with temperature, passing through $\{\vec{q}_\zeta\}$ at $T=T_c$. The occurrence of such an "accidental" minimum in $F(\vec{q})$ would mean that the critical exponents are those of the $n=6$ $d=3$ model for T near T_c. From the position of the x-ray superlattice reflections it seems difficult to exclude the possibility of a small difference $\delta=\zeta-\frac{1}{2}$ different from zero [cf. the comparison of neutron and x-ray data for NbO_2 (Ref. 15)]. In that case the 300-K transition would result in an incommensurate phase.

Another possibility is that the critical wave vector is $\{\vec{q}_\zeta\}$ with ζ initially only slightly different from $\frac{1}{2}$ for larger values of T_c-T, while $\zeta\rightarrow\frac{1}{2}$ for $T\rightarrow T_c$. In this description n changes from $n=6$ to $n=3$ somewhere in the $d=3$ region. This crossover will not be detectable in the critical exponent β as the theoretical values for both models are identical[16]: $\beta=0.38$ for both $n=6$ $d=3$ and $n=3$ $d=3$ [to $O(\epsilon^2)$]. The minimum in $F(\vec{q})$ now results from the symmetry of the X point in the Brillouin zone.

When the latter point of view is adopted we arrive

at the following conclusions: In the $d=2$ region there exist three indepenent $n=2$ subsystems with $\vec{q}=\{\pm(\bar{\zeta}02\zeta)\}$; $\pm\{(\zeta\bar{\zeta}2\zeta)\}$; $\pm\{(0\zeta2\zeta)\}$, corresponding to strong correlations in $(\bar{1}02)$; $(1\bar{1}2)$; (012) planes, respectively. Together with the lattice dimensionality crossover $d=2\rightarrow d=3$ (at $T=T_c-50$ K) the three $n=2$ systems couple to an $n=6$ system due to the growing importance of the interlayer correlations. Finally the order parameter dimensionality shifts from $n=6$ to $n=3$ near T_c as $\zeta\rightarrow\frac{1}{2}$.

Recently it has been shown by Bak[17] for the case of $Hg_{3-\delta}AsF_6$ ($n=4$) that a stable fixed point of the LGW (Landau-Ginzburg-Wilson) Hamiltonian as determined in renormalization-group calculations may not be accessible, depending on whether below T_c a "single-$\vec{q}$" or a "multiple-$\vec{q}$" structure is realized. Similar reasoning for the present systems leads to the conclusion that the unique stable fixed point for $n=6$ is only accessible if the low-temperature phase is characterized by a "triple-$\vec{q}$" structure where $\phi_{\vec{q}_\zeta}$ is the same for each value in $\{\vec{q}_\zeta\}$. However, from the experimental observation of six domains below T_c where only one of the order parameters $\phi_{\vec{q}_\zeta}$ is nonzero in each domain it follows that the transition is either first order, or that there is an additional crossover to lower n. The observation that the transition is second order within experimental accuracy favors the latter possibility, in accordance with the conclusions concerning crossover reached above.

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