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HAL Id: jpa-00210501
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Submitted on 4 Feb 2008

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Phase transitions in C₂O₄HNH₄, 1/2 H₂O.
A light scattering study at normal pressure

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(Reçu le 20 juin 1986, accepté sous forme définitive le 28 octobre 1986)

Résumé. — Dans C₂O₄HNH₄, 1/2 H₂O, il existe une transition ferroélastique du deuxième ordre à Tᵣ = 145 K. L'étude par diffusion Raman présentée ici permet de montrer que le degré de liberté responsable de la transition est la mise en ordre d'une famille d'ions NH⁺₄. La dynamique correspondante apparaît sous la forme d'un pic central qui présente un rétrécissement critique à Tᵣ. La largeur de ce pic n'est cependant pas minimale à Tᵣ, mais à environ 10 degrés en dessous. L'analyse simultanée de son intensité et de sa largeur a montré que ce comportement inhabituel est dû à l'évolution du temps de relaxation individuel des ions. Celui-ci varie fortement en dessous de Tᵣ à cause de l'inéquivalence entre les deux puits de potentiel, et aussi à cause du changement de la hauteur de cette barrière. Ce modèle permet un accord quantitatif avec nos résultats.

Abstract. — C₂O₄HNH₄, 1/2 H₂O undergoes, at Tᵣ = 145 K, a second order ferroelastic transition. The present Raman study allows us to identify the soft degree of freedom responsible for the transition as the ordering of one family of NH⁺₄ ions. This ordering process appears as a central peak which displays a critical narrowing in the vicinity of Tᵣ. Nevertheless, its linewidth is minimum not at Tᵣ but below Tᵣ. The combined analysis of its intensity and linewidth shows that this unusual behaviour is due to the evolution of the individual ionic relaxation time. The latter is strongly modified, below Tᵣ, by the inequivalence between the two potential wells, as well as by the change of the potential barrier. This model gives quantitative agreement with our results.

1. Introduction.

Structural phase transitions in solids have been widely studied for more than two decades and are still a subject of large interest. They are usually classified either as displacive or as order-disorder, which represent two extreme cases for classical phase transitions, but, in fact, real cases always lie somewhere in between [1]. This paper is the second of a series of three devoted to the study, by light scattering techniques, of the phase transitions which take place in C₂O₄HNH₄, 1/2 H₂O (hereafter called Ammonium Hydrogen Oxalate AHO) where we shall show that, at least, one of the transitions that AHO undergoes is typical of the order-disorder type.

At room temperature AHO crystallizes in the space group Pmn0 (D₁₆h) [2, 3] with Z = 8 (phase I). In this structure, the C₂O₄H⁻ form a single family, each ion being in a general position, while both the water molecule and the NH⁺₄ ions lie on a mirror plane. This implies the existence of two distinct ammonium families and X ray studies have shown that for one of them, this mirror plane has only a statistical character, each NH⁺₄ ion taking at random, one of two orientations, symmetric with respect to this mirror plane (Fig. 1 [3]). At normal pressure, AHO undergoes at Tᵣ = 145 K, a second order, ferroelastic, equitranslational phase transition [4] which leads to a P₂₁/n (C₅₅h) structure (phase II). Below Tᵣ, the monoclinic angle β has a typical meanfield behaviour:

$$\beta = \frac{\pi}{2} \pm \beta₀ \left(1 - \frac{T}{Tᵣ}\right)^{1/2}$$

and the net result of the phase transition is an ordering of NH⁺₄ ions, which, in turn, implies the loss of the m mirror planes. The ferroelastic behaviour of the transition at Tᵣ and the characteristic mean field law for the monoclinic angle suggested that the corresponding elastic constant C₅₅ would vanish at Tᵣ. This was verified in the first paper [5] of this series (hereafter referred to as I), through a...
Brillouin scattering study. In this experiment, the speed of a T.A. mode (or a pseudo T.A. mode) propagating along a, and polarized perpendicular to both a and b, was recorded above and below \(T_c\). The analysis showed that the light scattering and X ray experiments could be made consistent with each other, provided that:

- above \(T_c\), the elastic deformation was linearly coupled with another degree of freedom having the same \(B_{2g}\) symmetry, which would, in the absence of this coupling, become soft around \(T_c = 4 \pm 10\) K [5]. The strong linear coupling with \(e_5\) increased the transition temperature from \(T_0\) to \(T_c = 145\) K leading to a nearly complete vanishing of \(C_{55}\) at \(T_c\);

- below \(T_c\), an additional coupling between the same \(B_{2g}\) variable and the three principal deformations \(e_i\) (with \(i = 1, 2, 3\)) had to be taken into account. This third order coupling linear in \(e_i\) and quadratic in the \(B_{2g}\) variable, explained that the ratio

\[
R = \left. \frac{dC_{55}}{dT} \right|_{T - T_c} / \left. \frac{dC_{55}}{dT} \right|_{T = T_c} \tag{1a}
\]

was equal to

\[
R = \frac{-2K}{1 - \alpha} \tag{1b}
\]

with \(\alpha = 0.1\) instead of \(\alpha = 0\) and \(K = 1.1\) instead of 1 in the absence of coupling.

The purpose of this second paper is to elucidate the nature of this \(B_{2g}\) variable (which we shall show to be the orientational ordering of one family of \(\text{NH}_4^+\) ions) and to describe its manifestations in Raman scattering experiments, performed at various temperatures.

Section 2 of this paper will be devoted to the experimental methods and results, which revealed the existence of a central peak in the \(B_{2g}\) representation. In section 3 we shall present first a brief summary, and a low temperature extension of the Landau-Yamada theory of linear coupling between a pseudo-spin variable and an elastic deformation. In the last part of this section we shall discuss the classical notion of relaxation time and show that below a phase transition, various contributions modify its thermal evolution. Finally, in section 4, the experimental results will be analysed and it will be shown that the anomalous thermal behaviour of the central peak can be correctly described when the various effects discussed in section 3 are taken into account.

2. Experimental methods and results.

2.1 CRystal GROWTHER. — Good optical quality single crystals have been obtained by a slow evaporation technique. 1.2 mole of oxalic acid \(\text{C}_2\text{O}_4\text{H}_2\), 2 \(\text{H}_2\text{O}\) is dissolved with 1 mole of ammonium oxalate \(\text{C}_2\text{O}_4(\text{NH}_4)_2\), \(\text{H}_2\text{O}\), in the amount of water just necessary for dissolution at \(b_0\) °C. Seeds obtained by cooling are brought into a solution with the same composition and just under saturation at 15 °C: the solution is then slowly evaporated at this temperature. Fully deuterated crystals (called Ammonium Deuterated Oxalate ADO) have been obtained by the same technique, dissolving in the same proportion in the heavy water, desiccated ammonium oxalate and oxalid acid. After two recrystallizations, the deuteration of the crystal, checked by I.R. absorption, was found to be better than 98% molar.

2.2 LOW FREQUENCY RAMAN SPECTRA.

2.2.1 Normal pressure experiments. — Low frequency Raman spectra were recorded in the six scattering geometries aa, bb, cc (\(A_{2g}\)), ab (\(B_{1g}\)), bc (\(B_{3g}\)) and ac (\(B_{2g}\)). It was found that above \(T_c\), no mode had an anomalous softening when decreasing the temperature, in any geometry, nor was hardening of any mode observed below \(T_c\). Conversely, a central peak, most intense close to \(T_c\), could be detected in the vicinity of the Rayleigh wing in a scattering geometry (tensor element ac) which is compatible with the detection of excitations which are of \(B_{2g}\) symmetry in phase I and of \(A_{2g}\) symmetry in phase II. A typical spectrum is shown in figure 2. It was found that both the intensity and the HWHM of this central peak vary with temperature and simple inspection shows that the former has its maximum at \(T_c\). Such a behaviour is clearly due to a relaxation mode involved in the
transition. In order to properly analyse this mode, its profile was recorded, as a function of temperature, from -90 cm\(^{-1}\) to 90 cm\(^{-1}\). Its intensity was monitored through the intensity of an internal mode at 880 cm\(^{-1}\), which was found to be insensitive to the phase transition. The existence of an external mode around 70 cm\(^{-1}\), of stray light in the vicinity of the Rayleigh wing, as well as of a parasitic light background, restricted the analysis of the central peak to the 6-36 cm\(^{-1}\) region between \(T_c - 40\) K and \(T_c + 80\) K. It was analysed with the assumption of a Lorentzian line shape which lead to an intensity, \(I_{\text{max}}\) at \(\omega = 0\), and a linewidth, \(W\), (HWHM) which were computed at each temperature. The result of this analysis is reported in figure 3 for AHO and figure 4 for ADO. Let us point out that, in the vicinity of \(T_c\), this procedure could lead to a systematic error: indeed, due to the softening of the elastic constant, internal strains, always present in any crystal, play a more important role (both static and dynamical) in the vicinity of \(T_c\). This may add a narrow central component, which, in the present analysis, would increase the value of \(I_{\text{max}}\), and decrease that of \(W\). This may explain some numerical discrepancies found in the analysis of these data (see 4.2). But, as the slope of the elastic constant \textit{versus} \(T\), below \(T_c\), is more than twice as large as above \(T_c\), such an artifact would lead to an abrupt increase of \(W\) below \(T_c\). This is the opposite of what is actually observed: While \(I_{\text{max}}\) has its maximum at \(T_c\), \(W(T)\) has a shallow minimum slightly below \(T_c\), and starts to increase again, approximately, only 15 degrees below \(T_c\). A much weaker central peak was also seen, above \(T_c\) in the ab geometry (B\(_{1g}\)), while no such peak exists in the other (aa or bc) geometries (Fig. 5). Its intensity was too small to be properly analysed.

Fig. 3. — Temperature dependence of the linewidth \(W(T)\) and the maximum intensity \(I_{\text{max}}(T)\), of the central peak for the AHO. (The lines are only guides for the eye).
2.2.2 Pressure experiments. — Various Raman experiments have been performed between 80 K and 300 K at different pressures below 8 kbar and most of these results are analysed in a subsequent paper [6]. Let us just point out here that the same central peak was recorded at various pressures and showed, at the corresponding critical temperature, the same type of maximum, while the shallow character of the minimum of $W$ below $T_c$ was more pronounced with increasing pressure, $W$ showing no sign of an increase below $T_c$ above 1 kbar (Fig. 6).

Above 3 kb, another phase (phase III) was discovered, with a first order transition between phase II and phase III (see phase diagram in Fig. 7). At such pressures, on an isobar, $W(T)$ shows no sign of a change of slope at the phase I - phase III transition, but displays a discontinuity at the phase III - phase II transition (Fig. 8).

All these results make clear that the $B_{2g}$ central peak is related to the phase I - phase II transition, and is the « soft » degree of freedom, the existence of which was assumed in I. In order to interpret the results described above, we must, first, recall and slightly extend the pseudo-spin-phonon linear coupling theory of Landau-Yamada [7] and further analyse the various contributions to the thermal evolution of the relaxation time, a notion which is basic in the linear coupling theory. This is the purpose of section 3.

3. Pseudospin-phonon linear coupling theory.

3.1 INTRODUCTION. — The experimental results analysed in section 2, as well as the results of the Brillouin scattering experiments reported in I, or the Raman experiments related to an internal mode of $C_2O_4H^- [6]$ all agree on the second order character of the phase I - phase II transition. Furthermore, as in any ferroelastic transition [8], all the critical exponents are those expected in a mean field theory : $\gamma = 1$ for $C_{55} [5]$, and $\beta = 1/2$ for the elastic deformation $\epsilon [4]$. The ordering of the ammonium ion below $T_c [4]$ suggests, in view of the existence of two equivalent orientations above $T_c$ for the same ion [2], association of a pseudospin variable, $\sigma^i$, with the orientation of the (i, L) ammonium ion. In this formalism, i labels the four ammonium ions of the unit cell, and L labels the various lattice cells. Finally, for one given (i, L), $\sigma^i = +1$ ($-1$) is associated with one (or the other) NH$_4$ orientation, and the value of all the other pseudospin variables are deduced from that one by the operations of the $P_{mb}$ space group.

A pseudospin variable transforms itself as the $A^\pi$ irreducible representation of the $C_s$ point group.
of an individual NH$_4^+$ ion. This representation induces, in the crystal, for the $q = 0$ Fourier component, the four representations $B_{1g}$, $B_{2g}$, $A_u$ and $B_{3u}$, and, as expected, one of them is in the $B_{2g}$ representation, to which belong both the $e_s$ deformation and the central peak analysed in 2.2, while the $B_{1g}$ one corresponds to the weak central peak mentioned at the end of 2.2. We shall, thus, in the rest of this section, consider the coupling of this $B_{2g}$ component of the pseudo spin variable with the $e_s$ deformation.

3.2 EQUATIONS OF MOTION FOR THE PSEUDO-SPIN.

3.2.1 Free energy. — Let us write the relevant part of the free energy of the crystal as

$$F = F_0 + \frac{1}{2} (k_B T - J) Q^2 + \frac{b}{4} Q^4 + \gamma e_s Q +$$

$$+ \frac{1}{2} C_{55} e_s^2 + \sum \delta_i e_i Q^2 + \frac{3}{2} \sum C_{ij} e_i e_j . \tag{2}$$

In this expression ($^1$)

— $Q$ is a shorthand notation for the Fourier transform of the pseudospin variable belonging to the $B_{2g}$ ($q = 0$) irreducible representation ;

— $J = J_{B_{2g}}$ characterizes the pair interaction relative to $Q$, and defines the transition temperature for the uncoupled system of pseudo-spins by $J = k_B T_0$ ;

— the $\frac{1}{2} k_B TQ^2$ term represents the lowest term in $Q$ of the entropy of the spin system, while the $\frac{1}{4} bQ^4$ term describes the next order term, both of the entropy and of the energy contribution of the spins to the free energy ;

— $\gamma$ is a bilinear coupling constant between $Q$ and the $e_s$ deformation ;

— $C_{55}$ is the corresponding elastic constant ;

— $\delta_i$ are the lowest order coupling constants between $Q$ and the principal deformations $e_i$ and $C_{ij}$ are the corresponding elastic constants.

3.2.2 Static regime. Transition temperature renormalization. — Minimization of (2) with respect to $Q$, $e_s$ and $e_i$ leads, after a straightforward but lengthy calculation, to a transition temperature

$$T_c = T_0 + \Delta T = T_0 + \frac{\gamma^2}{k_B C_{55}} \tag{3}$$

and to the equilibrium values

$$\langle Q \rangle = \langle e_s \rangle = \langle e_i \rangle = 0 \quad T > T_c \quad i = 1, 2, 3 \tag{4a}$$

$^1$ Notations have been chosen, here, to be as close as possible to those used in I. Nevertheless, in order to avoid confusion with the pseudospin variable we have changed $\sigma$ (used in I) into $\sigma$ (see Eqs. (1b) and (5a)) and we have also change $\beta$ into $b$, to keep, as usual, $\beta$ for the inverse of $k_B T$.

$$\langle e_s \rangle = -\frac{\gamma}{C_{55}} \langle Q \rangle \tag{4b}$$

$$\langle e_i \rangle = - \sum_j C_{ij} \delta_j \langle Q \rangle^2 \tag{4c}$$

$$T = T_c = \frac{k_B}{b} (T_c - T) \times$$

$$x \frac{1}{1 - \alpha} = B (T_c - T) \tag{4d}$$

with $\alpha = \frac{2}{b} \sum \delta_i C_{ij} \delta_j \tag{5a}$

and $B = \frac{k_B}{b} \frac{1}{1 - \alpha} \tag{5b}$

3.2.3 Fluctuations dynamics. — $Q$, $e_s$ or $e_i$ may fluctuate around their equilibrium values. Due to the minimization conditions, the fluctuating part of the free energy reads

$$F' = \frac{1}{2} \left( \frac{\partial^2 F}{\partial Q^2} \right) Q^2 + \left( \frac{\partial^2 F}{\partial Q \partial e_s} \right) Q' e'_s +$$

$$+ \sum \left( \frac{\partial^2 F}{\partial Q \partial e_i} \right) Q e'_i + \frac{1}{2} \left( \frac{\partial^2 F}{\partial e_s^2} \right) e'_s^2 +$$

$$+ \frac{1}{2} \sum \left( \frac{\partial^2 F}{\partial e_i \partial e_j} \right) e'_i e'_j \tag{6}$$

with $Q = \langle Q \rangle + Q'$ ; $e_s = \langle e_s \rangle + e'_s$ ; $e_i = \langle e_i \rangle + e'_i \tag{7}$

where all the second order derivatives are computed from (2) for the equilibrium values $\langle Q \rangle$, $\langle e_s \rangle$ and $\langle e_i \rangle$ given by (4).

$F'$ contains two types of variables.

a) The pseudospin variable $Q'$ the dynamical equation of which is [7]

$$- \frac{\delta F'}{\delta Q} = k_B T \tau \dot{Q}'(t) \tag{8}$$

with $Q'(t) = Q_0 \ e^{i(q \cdot r - \omega t)} \quad q \rightarrow 0$

where $\tau$ is a characteristic time which will be discussed in 3.3.

b) The elastic deformations, $e'_i (i = 1, 2, 3)$ to which corresponds a kinetic energy $\frac{1}{2} \rho u'^2$, where $u(q)$ is the displacement related to the acoustic mode, the corresponding elastic deformation being the $q \rightarrow 0$ limit of

$$e'_i = \frac{\partial u_i}{\partial x_i} + \frac{\partial u_3}{\partial x_1} \tag{9}$$

with $u = \sum u_i \hat{x}_i \ e^{i(q \cdot r - \omega t)} \tag{10}$

$\rho$ being the mass per unit volume and $\hat{x}_i$ a unit vector in the direction $\hat{x}$, $\hat{y}$ or $\hat{z}$.
Replacing $e_i$ and $e'_i$ by their expressions (9) and (10) and writing that

$$\frac{\partial F}{\partial u_i} = \rho (\mathbf{u} \cdot \mathbf{x}_i)$$  \hspace{1cm} (11)

lead, with the help of (8), to a set of four linear equations in $u_i$ ($i = 1, 2, 3$) and $Q_0$, for each value of $q$. These equations can be brought under the form of a $4 \times 4$ dynamical matrix, the exact expression of which is given in Appendix A. This matrix describes, for finite but small $|q|$, the four coupled acoustic-pseudospin modes which exist in the system for any $q$. The important point here is that, as $e_i$ and $e'_i$ are proportional to some components of $q$, the terms in

$$(\frac{\partial^2 F}{\partial e_i \partial e_i}) \quad \text{and} \quad (\frac{\partial^2 F}{\partial e'_i \partial e'_i})$$

of (6) are quadratic in the components of $q$, while those in

$$(\frac{\partial^2 F}{\partial Q \partial e_i}) \quad \text{and} \quad (\frac{\partial^2 F}{\partial Q \partial e'_i})$$

are linear in the same components. Thus, in the $|q| \to 0$ limit, but for finite $\omega$, this dynamical matrix (12) simply reads

$${\bar{G}}^{-1} = \begin{pmatrix}
-\rho \omega^2 \delta_{ii} & 0 \\
0 & \left(\frac{\partial^2 F}{\partial Q^2}\right) - ik_B T \tau \omega
\end{pmatrix}.$$  \hspace{1cm} (12)

With the help of the usual response function theorem, the Stokes Raman intensity of the pseudospin mode is then given by

$$I(\omega) = [R_{Q}^2(n(\omega) + 1) \text{Im}(G)_{QQ}(\omega)]$$  \hspace{1cm} (13)

where

$$R_{Q}^2 = \frac{\partial \mathbf{e}^{xz}}{\partial Q}$$  \hspace{1cm} (14)

is the Raman tensor associated with the pseudo-spin variable

- $n(\omega)$ is the Bose Einstein factor
- $G_{QQ}(\omega)$ is the $QQ$ component of $\bar{G}^{-1},$

$$(G)_{QQ}(\omega) = \frac{1}{\left(\frac{\partial^2 F}{\partial Q^2}\right) - ik_B T \tau \omega}.$$  \hspace{1cm} (15)

Taking the low frequency limit of $n(\omega)$ finally leads to

$$I(\omega) = \left[R_{Q}^2\right]^2 k_B T \frac{k_B T \tau}{\left(\frac{\partial^2 F}{\partial Q^2}\right)^2 + k_B T \omega^2}.$$  \hspace{1cm} (16)

(16) represents a central, Lorentzian peak, that we shall now analyse more precisely, above and below $T_c$.  

### 3.2.4 Analysis of the central peak.

a) $T > T_c$.

For $T > T_c$, following (2),

$$\left(\frac{\partial^2 F}{\partial Q^2}\right)_{Q=0} = k_B(T - T_0) = k_B(T - T_c) + k_B \Delta T.$$  \hspace{1cm} (17)

Then

$$I(\omega, T) = \left[R_{Q}^2\right]^2 \frac{1}{\tau} \left[\frac{1}{\left(\frac{T - T_c}{T} + \frac{\Delta T}{T}\right)}\right]^2 + \omega^2.$$  \hspace{1cm} (18)

which gives

$$W(T) = \frac{1}{\tau} \left[\frac{T - T_c}{T} + \frac{\Delta T}{T}\right].$$ \hspace{1cm} (19a)

$$I_{\text{max}}(T) = \left[R_{Q}^2\right]^2 \frac{1}{\tau W(T)^2}. \hspace{1cm} (19b)$$

b) $T < T_c$.

Using (2), (4) and (5) one easily gets:

$$\left(\frac{\partial^2 F}{\partial Q^2}\right)\langle q \rangle, \langle \mathbf{e} \rangle = \frac{2 k_B}{1 - \tilde{\alpha}} (T_c - T) + k_B \Delta T$$  \hspace{1cm} (20)

which gives

$$W(T) = \frac{1}{\tau} \left[\frac{2}{1 - \tilde{\alpha}} \frac{T_c - T}{T} + \frac{\Delta T}{T}\right].$$  \hspace{1cm} (21)

$I_{\text{max}}(T)$ being still related to $W(T)$ by (19b). Below $T_c$, these results just extend, those already obtained by Yamada et al. [7].

Equations (19a and b) and (21) show that, in every respect, the central peak plays, in the case of a pseudo-spin system, i.e. in the prototype case of an order-disorder phase transition, the same role as the soft mode for a displacive transition : in the absence of linear coupling with an elastic constant, the line width would behave as $(T - T_0)$ above $T_0$ and $\frac{2}{1 - \tilde{\alpha}} (T_0 - T)$ below it, as does the square of the frequency of the soft mode. The linear coupling shifts the transition to $T_c$, in both cases, preventing the soft degree of freedom from going to zero, but does not change its slope, either above or below $T_c$. This has to be expected as, in the free energy (2), $Q$ could be a pseudospin as well as a normal mode variable, the difference appearing only in the dynamical equation (8).
3.3 ROLE OF THE RELAXATION TIME $T$.

3.3.1 Relaxation time above $T_c$. — Up to now, we have not paid much attention to the physical meaning and the temperature dependence of the relaxation time, $\tau$, which appears in the r.h.s. of (8). This thermal evolution is usually not taken into account when using equations such as (19), because one limits oneself to the immediate vicinity of $T_c$. As we wish to study $W(T)$ and $I_{\text{max}}(T)$ both above and below $T_c$, and to study those quantities for not too small values of $\frac{|T-T_c|}{T_c}$, we have to be more careful.

It is important to realize that $\tau$ is, in fact, a relaxation time which governs, for an individual ion, the stochastic process through which this ion has one or the other orientation. Indeed, the r.h.s. of (8) describes, basically, the relaxation process towards equilibrium of an individual ion, and it is written in a Fourier space language only because the r.h.s. of (8) is expressed in such a variable. The $\text{NH}_4^+$ ion acting here as a classical molecule, this process is itself governed by the height of the energy barrier the molecule has to overcome in order to go from one potential well to the other. One may thus write,

$$\tau = \tau_0 e^{\beta V} \beta = \frac{1}{k_B T}$$

(22)

where $\tau_0^{-1}$ is an attempt frequency and $V$ the potential barrier height.

3.4 THERMAL EVOLUTION OF $\tau$ BELOW $T_c$. — In the high temperature phase, the individual potential barrier height of the $(i,L)$ $\text{NH}_4^+$ ion does not depend on the value of $\sigma_i^L$. Thus, this barrier height transforms as the $A'$ (identity) representation of the $C_2h$ symmetry group of the site of the ammonium ion and as the $A_g$ representation, in the crystal group, for the $q=0$ wave vector. As the pseudospin variable $Q$ is in the $B_2g$ representation, the odd powers of $Q$ transform as the $B_2g$ representation, and the even powers as the $A_g$ representation. The only possible coupling between the pseudospin variable $Q$ and the mean potential barrier in the crystal must then be written as:

$$V(Q) = V_0 + V_2 Q^2 + V_4 Q^4 + \ldots$$

(23)

Above $T_c$, where $\langle Q \rangle = 0$ (23) leads to (22) with $V = V_0$, while, below $T_c$, the full expression (23), with $Q = \langle Q \rangle$, as given by (4d), must be used; in other words, the energy barrier is renormalized below $T_c$. Physically, this is the same kind of effect as that expressed by the cubic coupling $\delta_i \langle Q^2 \rangle e_i$ (or, alternatively, one can say that the barrier height is linearly coupled to the three $e_i$), and we have seen, in paper I, that, as in the similar case of LaP$_3$O$_{14}$, [9], this effect brings the non negligible correction in

$$\frac{1}{1 - \alpha}$$

which appeared, e.g., in (20) or (21).

The correction (23) is, nevertheless, not the only one which has to be taken into account. Below $T_c$, the equilibrium occupation of the two potential wells is given by

$$P_0^+ = \frac{1}{2} [1 + \langle Q \rangle], \quad P_0^- = 1 - P_0^+.$$

If $P^+(t) = \frac{1}{2} [1 + \sigma(t)]$ is the occupation, at time $t$, of a potential well labelled by $+$, and $\sigma(t)$ the corresponding value of the pseudo-spin variable attached to the site, ($\sigma(t)$ is the mean value of the spin over an ensemble of equivalent sites, in the statistical thermodynamics sense) the equation governing the relaxation of $P^+(t)$ towards equilibrium is:

$$\frac{d}{dt} [P^+ - P_0^+] = - \frac{P^+ - P_0^+}{\tau^+} + \frac{P^- - P_0^-}{\tau^-} = - \left[ \frac{1}{\tau^+} + \frac{1}{\tau^-} \right] (P^+ - P_0^+)$$

(24a)

which is equivalent to

$$\frac{d}{dt} [\sigma - \langle Q \rangle] = - [\sigma - \langle Q \rangle] \left[ \frac{1}{\tau^+} + \frac{1}{\tau^-} \right]$$

(24b)

This defines $\tau$ by

$$\frac{1}{\tau} = \frac{1}{\tau^+} + \frac{1}{\tau^-}$$

(25)

where, by hypothesis

$$\tau^+ = \tau_1 e^{\beta [V(\langle Q \rangle) + J(\langle Q \rangle)]}$$

$$\tau^- = \tau_1 e^{\beta [V(\langle Q \rangle) - J(\langle Q \rangle)]}$$

(26)

where $2J(\langle Q \rangle)$ is the difference of energy between the bottoms of the two potential wells.

One thus obtains

$$\tau = \frac{\tau_1}{2 \cosh \beta J(\langle Q \rangle)}$$

(27)

expression which is identical to (22) above $T_c$, provided that $\tau_1 = 2 \tau_0$.

$J(\langle Q \rangle)$ may finally be determined by noticing that the equilibrium situation must satisfy the detailed balance equation

$$\frac{P_0^+}{\tau^+} = \frac{P_0^-}{\tau^-}$$

(28)

which, using the definition of $P_0^+, \ P_0^-, \ \tau^+$ and $\tau^-$ yields:

$$\langle Q \rangle = \tanh \beta J(\langle Q \rangle)$$

(29)
(29) may be used for expressing the denominator of
(27) as a function of \( \langle Q \rangle \) only. Before doing this, it
is worthwhile evaluating the role of this second
correction, and for this, one may solve (29) as a
function of \( T \), in a way which must be consistent with
(4d). As \( J (\langle Q \rangle) \) is odd in \( \langle Q \rangle \), writing
\[
J (\langle Q \rangle) = J_1 \langle Q \rangle + J_3 \langle Q \rangle^3
\]
one obtains, by identification (see Appendix B)
\[
J_1 = k_B T_c, \quad J_3 = \frac{k_B T_c}{3} - \beta (1 - \bar{\alpha}).
\] (31)

This calculation shows that, even at the lowest
order in \( \langle Q \rangle \) the effect of the effective asymmetry
between the two wells is important, as \( J_1 = k_B T_c \); \( J_1 \)
is thus different from \( J = k_B T_0 \) as could be thought from a naive inspection of (2). This is due to
the strong pseudospin-deformation coupling, which
also gives rise to the large value of \( \Delta T \).

For all practical purposes, it is, of course, easier to
directly express \( [\cosh \beta J (\langle Q \rangle)]^{-1} \) as a function of
\( \langle Q \rangle \) through (29), and to write
\[
\tau = \tau_0 \sqrt{1 - \langle Q \rangle^2} e^{\beta V (\langle Q \rangle)} \] (32)
where \( V (\langle Q \rangle) \) is expressed by (23) and \( \langle Q \rangle^2 \)
by (4d).

4. Discussion.

4.1 COMPARISON BETWEEN THEORY AND EXPERI-
MENT. — The intensity at \( \omega = 0 \), \( I_{\text{max}} (T) \), and
the line width \( W (T) \) determined in section 2 may now be
compared with the theoretical expressions obtained
in section 3. In principle, as \( T_c \) is known by the
maximum of \( I_{\text{max}} (T) \), and \( \Delta T \) has been obtained in
paper I, one could obtain \( V_0 \) (see (22)) from the
experiments above \( T_c \), then \( V_2 \) and \( V_4 \) from those
below \( T_c \), provided that the thermal dependence of
\( \langle Q \rangle \) is known.

Unfortunately, the experimental situation is less
simple. Firstly, the thermal evolution of \( \langle Q \rangle \) is not
known, even in the vicinity of \( T_c \) (i.e. we have no
measure of the coefficient \( b \)). Secondly, the uncertain-
ities in the values of \( W (T) \), the possible systematic
errors on their values close to \( T_c \) as well as the range
of temperature \( (T_c - 40 \text{ K} \text{ to } T_c + 100 \text{ K}) \) is not
large enough to allow for a precise fit by such a
procedure. Finally, \( \langle Q \rangle \) is given by (4d) only in the
vicinity of \( T_c \), and must have a negative curvature as
a function of \( T \), in order to be always smaller than 1.
It is thus inconsistent to use, at the same time, (23) to
describe the thermal evolution of the barrier
height, and (4d) for the thermal dependence of
\( \langle Q \rangle \) as the latter neglects higher terms in \( \langle T_c - T \rangle \).
After a few trial and error processes which have,
inter alia, convinced us that it was not possible to
neglect terms quadratic in \( T_c - T \), in \( V (\langle Q \rangle) \) we
have finally decided:

a) to keep \( \Delta T \) as a free parameter;

b) to fit, altogether, the data above and below
\( T_c \);

c) to express the barrier height as a function of
\( T_c - T \), writing
\[
V (\langle Q \rangle) = V' (T)
\] (32)
with
\[
V' (T) = V_0, \quad T > T_c \quad \quad \text{(33a)}
\]
\[
V' (T) = V_0 + U (T), \quad T < T_c \quad \quad \text{(33b)}
\]

In (33b), \( U (T) \) is such that \( V' (T) \) is continuous at
\( T_c \), while its first derivative is not. Furthermore, we
impose on \( U (T) \) a very weak variation at low \( T \) and a
uniform variation between 0 K and \( T_c \).

In order to keep the number of parameters as
small as possible, we have postulated
\[
U (T) = \frac{V_1 (T_c - T)}{T_1 + (T_c - T)}, \quad T_1 > 0 \] (34)

which in view of (4d) and (5b) means
\[
V_2 = \frac{b (1 - \bar{\alpha}) V_1}{k_B T_1} = \frac{V_1}{B} \] (35)

Finally, as our data do not extend below 100 K,
we found it unnecessary to use for \( \langle Q \rangle \) an ex-
pression similar to (32-34). We have simply used (4d), with \( B \) as a free parameter, and verified that,
with such an expression, \( \sqrt{1 - \langle Q \rangle^2} \) would diverge
at a value sufficiently far below 100 K (the lowest
temperature with precise enough data) that we need
not consider this error.

In summary, apart from scaling factors \( (\tau_0, \text{and}
R^2) \), we have used four arbitrary parameters
\( V_0, V_1, T_1, \text{and } B \), as well as a possible flexibility to
\( T_0 = T_c - \Delta T \) (instead of forcing \( T_0 = 4 \text{ K} \pm 10 \text{ K}, \)
as obtained in I).

4.2 NUMERICAL DISCUSSION. — Keeping the 5
parameters (plus 2 scaling factors) free, the best
result was obtained for \( T_0 = 70 \text{ K} \), but the fit was
very little altered when choosing \( T_0 = 40 \text{ K}, \)
the temperature for which we shall discuss our results.
The result so obtained is shown in figure 9 with the
fitting parameters given in Table I. The most import-
ant aspects of our data, namely the maximum of
\( I_{\text{max}} (T) \) at \( T_c \), the existence of a minimum of
\( W (T) \) below \( T_c \), as well as the very small increase of
this width below the minimum, are well reproduced.

In fact, we have found during the fitting procedure
that our overall agreement is the result of two
complementary factors. In the close vicinity of
\( T_c \), the only important role is played by the variation
of \( V (T) \). Its immediate increase below \( T_c \) (see
Fig. 9. — Best fit obtained for both $W(T)$ and $I_{\text{max}}(T)$ with $T_0$ fixed at 40 K (plain line) ; calculated $W(T)$ and $I_{\text{max}}(T)$ for $T_0 = 40$ K with $V_1 = B = 0$ (dotted line), (see Table I).

Table I. — Fitting parameters for the data at normal pressure.

<table>
<thead>
<tr>
<th>$V_0$</th>
<th>$V_1$</th>
<th>$T_1$</th>
<th>$B$</th>
<th>$T_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>230</td>
<td>120.5</td>
<td>19</td>
<td>0,0175</td>
<td>40</td>
</tr>
<tr>
<td>230</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>40</td>
</tr>
<tr>
<td>268</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>40</td>
</tr>
</tbody>
</table>

$V_0$ and $V_1$ are given in degree kelvin Units.

Fig. 10. — Best fit for both $W(T)$ and $I_{\text{max}}(T)$ for $T_0 = 40$ K, with $V_1 = B = 0$.

The $\beta$ term in $e^{\beta V(T)}$ starts to increase $\tau$ rapidly. This should result in a second decrease of $W(T)$, would not the $\sqrt{1 - \langle Q \rangle^2}$ factor of (32) play a role : its decrease counterbalances the effect of the Arrhenius term and keeps increasing $W(T)$ down to 100 K and less.

The overall role of the two factors introduced in sub-section 3.3 is shown (dotted curve) in figure 9 where we have drawn the result which would be obtained in our fit putting $V_1 = B = 0$, i.e. neglecting at the same time the renormalization of the barrier height and the asymmetry of the two wells. As expected, the dotted curve does not at all reproduce the experimental results ; we have further substantiated the role of these two corrections by looking for the best fit with $V_1 = B = 0$. The result is reproduced in figure 10, which, again, shows that the existence of a minimum of $W(T)$ for $T = T_0 - 15$ K cannot be reproduced without taking these effects into account.

4.3 COMPARISON WITH OTHER RESULTS. — The value of $T_0$ (40 K) that gives a reasonable fit to our data does not agree with that obtained in I (4 K $\pm$ 10 K). The origin of the possible experimental errors have been discussed in section 2, and presumably explains the most important part of our discrepancies. We have found it more convenient to express them by an artificial change in $T_0$, rather than giving a lower weight to the values of $W(T)$ and $I_{\text{max}}(T)$ close to $T_0$. as this is the region where the effect of the variation of the barrier height has its most dramatic effect. Let us remark that this is obtained by not a too dramatic change in the potential barrier, as is shown in figure 11, which represents the barrier height as a function of $T$.

As can be seen in figure 4, the dispersion of the data for ADO is larger than for AHO. Furthermore, no Brillouin or ultrasonic data are available, which would give a reasonable starting point for $T_0$. We
can thus simply point out that the same two effects invoked in section 3 are necessary to explain our results on the deuterated sample at normal pressure.

Finally, let us note that the pressure experiments, briefly described at the end of section 2, also agree with the overall picture discussed here. The phase diagram given in figure 7 suggests the existence of a tricritical point around 1 kbar, the phase I - phase II transition being first order between 1 kb and 3 kb. A tricritical point is characterized by the disappearance of the coefficient b of (2), which leads to \( \langle Q \rangle = (T_c - T)^{1/4} \), and thus to a stronger renormalization of the potential below \( T_c \), i.e. a more important effect on \( W(T) \). This is indeed what appears in figure 6, where there is no increase of \( W(T) \) down to 80 K, the lowest attainable temperature with our pressure equipment.

### 4.4 CONCLUSION.

The analysis of the central peak which appears in the high temperature \( B_{2g} \) geometry makes clear the fact that the phase I - phase II transition which takes place in AHO or ADO at normal pressure is driven by a purely order-disorder phenomenon. The ordering of \( \text{NH}_2^- \) ions is very presumably the driving force of the transition.

The dynamics of the spin fluctuation shows unusual features that we have tentatively related to the thermal evolution of the pseudospin relaxation time. This effect, which is usually very weak, manifests itself rather clearly here, due to the fact that in AHO, the pseudospin are strongly coupled to the principal deformations \( e_i \) \((i = 1, 2, 3)\). The role of their coupling to \( e_3 \), i.e. the role of the asymmetry of the potential well below \( T_c \) is less apparent at first sight. The numerical analysis shows that its effect is fundamental to keep the HWHM increasing below its minimum.

### Acknowledgments.

It is a pleasure to thank Prof. R. M. Pick for various suggestions and fruitful discussions on the dynamics of the central peak.

### Appendix A.

Form of the dynamical acoustic phonon-spin matrix.

Replacing in (6)

\[
\begin{align*}
\frac{\partial u_i}{\partial x_i} & \quad \text{with} \quad i = 1, 2, 3 \\
\frac{\partial u_1}{\partial x_2} + \frac{\partial u_2}{\partial x_1} & \\
\end{align*}
\]

where

\[
\begin{align*}
u & = \sum_{i=1}^{3} u_i^0 \tilde{e}_i \exp(i \cdot \mathbf{r} - \omega t)
\end{align*}
\]

the \( 4 \times 4 \) dynamical matrix expressed on the basis \( u_i^0 \) \((i = 1, 2, 3)\) and \( Q' \) is easily found to have the following elements.

\[
\begin{align*}
G_{ij}^{-1}(\omega) & = \left( \frac{\partial^2 F}{\partial e_i \partial e_j} \right) q_i q_j + \delta_{ij} \left( \frac{\partial^2 F}{\partial e_i^2} \right) \\
& \times (\delta_1 \delta_{11} q_1^2 + \delta_3 \delta_{13} q_1 q_3 - \rho \omega^2) \quad (A.1) \\
G_{ij Q}^{-1}(\omega) & = \left( \frac{\partial^2 F}{\partial e_i \partial Q} \right) q_i + \left( \frac{\partial^2 F}{\partial e_j \partial Q} \right) q_j \\
& \times (\delta_1 \delta_{11} q_3 + \delta_3 \delta_{13} q_1) = G_{ij Q}^{-1}(\omega) \quad (A.2) \\
G_{ii Q}^{-1}(\omega) & = \left( \frac{\partial^2 F}{\partial Q^2} \right) - i k_B T \omega \tau \quad (A.3)
\end{align*}
\]

where \( \delta_{ij} \) is a Kronecker symbol while \( \delta_1 \) and \( \delta_3 \) are defined through (2). One sees that, in the \( q \to 0 \) limite, and for finite \( \omega \)

\[
\begin{align*}
G_{ii Q}^{-1}(\omega) & = G_{ij Q}^{-1}(\omega) = 0 \quad (A.4) \\
G_{ij}^{-1}(\omega) & = - \delta_{ij} \rho \omega^2 \quad (A.5)
\end{align*}
\]

### Appendix B.

Self consistent solution for the effective potential well. The equation for the effective potential seen by a pseudospin is (Eq. (29))

\[
\langle Q \rangle = \tanh \beta J(\langle Q \rangle) \quad (B.1)
\]

where \( J(\langle Q \rangle) \) is given by

\[
J(\langle Q \rangle) = J_1 \langle Q \rangle + J_3 \langle Q \rangle^3 \quad (B.2)
\]

Expanding the r.h.s. of (B.1) up to third order in \( \langle Q \rangle \) gives, after dividing by \( \langle Q \rangle \)

\[
\begin{align*}
\frac{1}{\beta} J_1 + \langle Q \rangle^2 \left[ J_3 - \frac{\beta^2 J_1^3}{3} \right] & \\
\Leftrightarrow \langle Q \rangle^2 = \frac{J_1 - k_B T}{\beta^2 J_1^3 - J_3} & \\
= k_B (T_c - T) \frac{1}{b(1 - \tilde{a})}.
\end{align*}
\]

Identification of the denominators yields

\[
J_1 = k_B T_c \quad (B.5)
\]

Replacing \( J_1 \) in the denominator by this value and \( \beta \) by \( k_B T_c \), in the vicinity of \( T_c \) one gets

\[
\begin{align*}
k_B T_c / 3 - J_3 & = b(1 - \tilde{a}) \\
\Leftrightarrow J_3 & = k_B T_c / 3 - b(1 - \tilde{a}) \quad (B.6)
\end{align*}
\]
References