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STRUCTURAL TRANSITION OF AMMONIUM ALUMINIUM ALUMS STUDIED BY E.P.R.

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Résumé. — Les résultats de spectroscopie R.P.E. de deux alums AlNH_4 et AlND_4 dopés avec des ions Cr^{3+} sont donnés. Ces alums subissent un changement de phase à 60 et 56 K. Les résultats obtenus pour $T > T_c$ sont qualitativement interprétés comme résultant de distorsions fluctuantes dues au changement de structure. L'alun AlNH_4 présentant des fractures internes après refroidissement, seule la phase basse température de l'alun AlND_4 a été étudiée. Elle dépend de la vitesse de refroidissement. La phase obtenue après un refroidissement lent appartient au système orthorhombique et trois types de domaines sont présents dans le cristal. Par contre, après un refroidissement rapide, les spectres compliqués obtenus n'ont été analysés que partiellement. Cette analyse suggère qu'ils sont dus soit à un certain désordre dans le cristal, soit à l'existence de nombreux domaines séparés par des parois épaisses.

Abstract. — EPR spectroscopy results for Cr^{3+} in two alums AlNH_4 and AlND_4 are reported. These alums undergo a phase transition at respectively 60 K and 56 K. The results for $T > T_c$ are qualitatively explained as resulting from fluctuations of distortions associated with the structural change. As AlNH_4 looks internally fractured after being cooled below T_c , only the low temperature phase of AlND_4 has been studied. The EPR spectra below T_c depend on the rate of cooling. After a slow cooling, the crystal contains three types of domains, each belonging to the orthorhombic system. After a fast cooling, complicated spectra are observed and partially analysed. The analysis suggests they are due either to some form of disorder or to the existence of many domains with large walls.

1. **Introduction.** — EPR is an excellent tool for studying the local symmetry of paramagnetic ions. Soon after its discovery, it was used to give complementary information on the structure of many solids, because the point symmetry at the site of the paramagnetic impurities observed can be deduced from the spectrum. It was also used for studying structural changes after the pioneering work of Muller [1] on SrTiO_3 in 1958. Recent experiments such as that of Muller *et al.* [2] show that this technique complements very well the other techniques used for studying details of the mechanism of the structural changes.

Alums have general formulae $(\text{SO}_4)_2 \text{TM}$, $12 \text{H}_2\text{O}$, where T is a trivalent metal and M a monovalent metal or a monovalent complex. (In this paper, we shall specify an alum by TM or by T(T') M when the metal T', paramagnetic, is an impurity in the TM alum.) They were studied by EPR as early as 1947

by Weiss *et al.* [3] and later by Bleaney [4] and Baguley and Griffiths [5] for determining the point symmetry of the site of the metal T. These experiments have shown the existence of a trigonal field in CrK, CrNH_4 , CrCs, CrRb and $\text{Cr}(\text{NH}_3\text{CH}_3)$, some of these trigonal fields being strongly temperature dependant. O'Reilly and Tung Tsang [6] have reported strong linewidth variation in $\text{Al}(\text{Cr})\text{NH}_3\text{CH}_3$, which becomes ferroelectric at low temperature, but not in $\text{Al}(\text{Cr})\text{K}$ which does not show a phase transition.

The structure of alums was first studied by Lipson [7]. Jona and Shirane reported in their book [8] a great number of published and unpublished works on alums, indicating those which become ferroelectric at low temperature. They were unable to draw any conclusion for AlNH_4 and AlND_4 . Refinement of the alum structures by X-ray and neutron diffraction made by Don Cromer, Kay and Larson [9] has brought new information on the high temperature structures. They pointed out that the space group Pa3 is only achieved statistically with ammonium alums,

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some of the sulfate groups being inverted along the threefold axis. The disorder could suggest a mechanism for the ferroelectric transition observed in some α ammonium alums (FeNH_4 , VNH_4 , InNH_4 for instance) and the unknown phase transition of AlNH_4 and AlND_4 .

Capiomont [10] has made dielectric measurements on AlNH_4 , but he has not been able to determine if the low temperature phase is ferroelectric.

The object of this work was to study the structural change of the two alums AlNH_4 and AlND_4 by EPR and to try to determine the nature of the low temperature phase. EPR experiments as a function of temperature have been made with Cr^{3+} doped crystals. After a description of the experimental conditions, we give the results obtained with the two alums above the transition temperature T_c . Below T_c , only AlND_4 can be studied. We describe the two sorts of spectra observed after either a fast or a slow cooling. The linewidth change above T_c and the nature of the spectra below T_c are then discussed in connection with the structural change.

2. Experimental details. — **2.1 SAMPLES.** — Monocrystals of $\text{Al}(\text{Cr})\text{NH}_4$ and $\text{Al}(\text{Cr})\text{ND}_4$ alums have been grown from solutions doped by 1% Cr^{3+} with respect to Al^{3+} (a few crystals have also been grown from solution at 0.1% Cr^{3+}). Chemical analysis of the crystals showed that the doping was only 0.12%. The deuteration was obtained after four growings in heavy water. To test the efficiency of the deuteration, we dissolved a crystal in heavy water and compared, by NMR, the number of protons present in the solution with the number of residual protons contained in the heavy water used. These measurements showed that 86% of the original water protons were replaced by deuterons. We assume the exchange $\text{H} \leftrightarrow \text{D}$ was the same for H_2O and NH_4 groups.

2.2 PROCEDURES FOR COOLING SAMPLES. — Two sorts of experiments have been done. In both cases, the sample was slowly cooled from room temperature to about 90 K. Then, in the first, this was followed by a fast cooling, i.e. in 10 or 15 min, to 20 K or 4.2 K. In the second, the rate of cooling was very slow (less than 5 K per hour) from 90 K till the transition temperature.

2.3 APPARATUS. — The first type of experiment described above was done at 9 300 MHz, with standard low temperature equipment permitting all magnetic field orientations with respect to crystallographic axes.

For the second type of experiment, made at 12 300 MHz, an apparatus was built to work at any temperature between 300 K and 12 K. The method used for varying and stabilizing the temperature is illustrated in figure 1. Two parameters are controlled: the flux of a cool gas (helium or hydrogen) for coarse regulation, and the power supplied to a heater

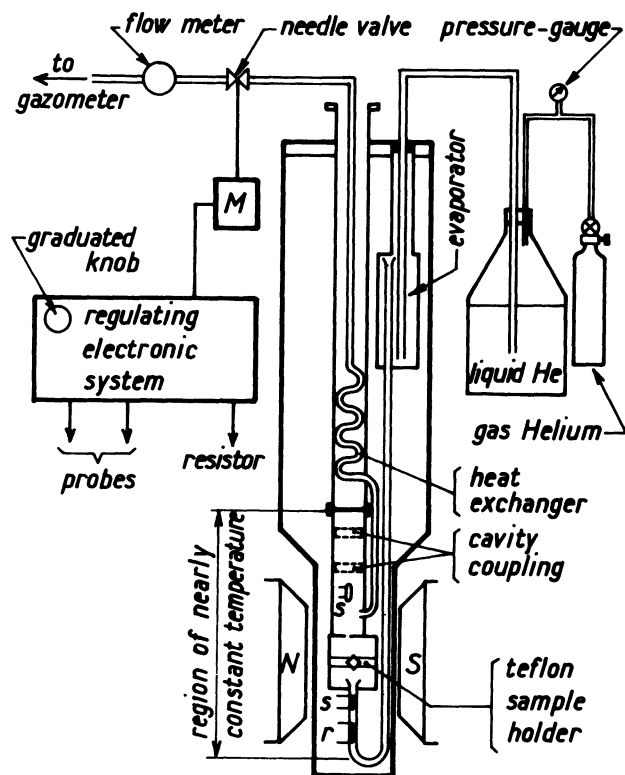


FIG. 1. — Block diagram of the temperature regulation system. M is the motor acting on the needle valve to change the flux of gas. r is the heating resistor, s are the platinum resistors.

resistor for fine regulation. The measuring bridge, powered by an oscillator, comprises a platinum resistor located near the sample and a precision potentiometer used for fixing the temperature. The error signal is phase detected and sent to a feed-back amplifier which delivers a current whose square contains a proportional and an integral term. That current is then sent to the heating resistor. In addition, a sequential device acting when ΔT (the difference between the desired temperature and the temperature of the probe) is too large changes the flow rate of the cryogenic gas. In this way, the heating power of the resistor is reduced to about 0.1 W and consumption of the cool gas is minimised. Another precision calibrated platinum resistor located 2 cm from the sample is used for measuring the temperature. The stabilization, in the critical region ($80 \text{ K} < T < 20 \text{ K}$) is better than 0.01 K. The consumption of the gas, expressed in litres per minute, varies from 1 (80 K) to 5 (20 K) with helium and from 0.5 (260 K) to 4.5 (40 K) with hydrogen.

3. Experimental results. — **3.1 GENERAL SURVEY.** — The two alums studied here, AlNH_4 and AlND_4 , are of α type and belong to the cubic space group Pa3 at room temperature. One can roughly describe the structure as follows: (Al, 6 H_2O) octahedra and NH_4 groups occupy the Na and Cl positions of a NaCl structure, the SO_4 groups and the other water molecules being located between, as described in reference [9].

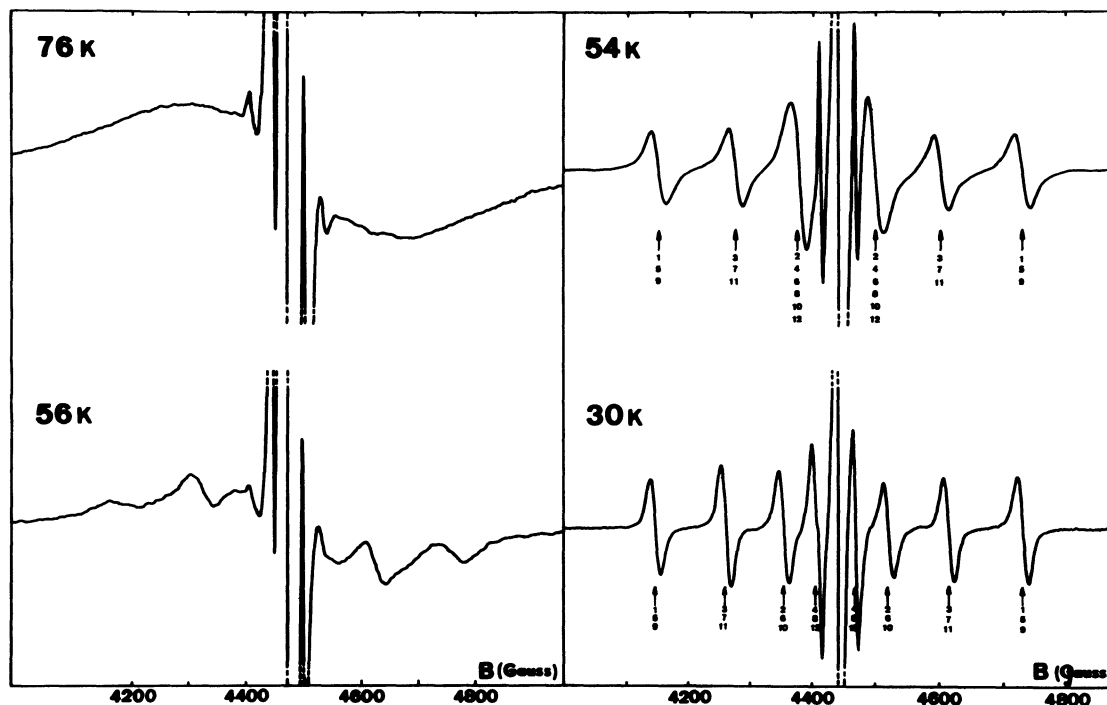


FIG. 2. — Spectra of Al(Cr)ND₄ alum for H along [111] at KU band for various temperatures. The spectra for T = 76 and 56 K and those for T = 54 and 30 K were obtained in different runs for which the resonant cavity frequencies were not equal. Sites 1, 2, 3, 4 are in one twin, 5, 6, 7, 8 in another and 9, 10, 11, 12 in the last. The two strong lateral lines are two hyperfine components of the strong central line.

For the two alums, at temperatures higher than 60 K, the EPR spectrum results from 4 equivalent Cr³⁺ at the Al³⁺ sites. These sites are trigonal, the axes being the four < 111 > directions.

When the temperature decreases, some lines are shifted, others are broadened. The behaviour of the two alums is, however, different. For the Al(Cr)NH₄, some new lines appear at about 60 K and their intensity increases till 50 K while the broad lines disappear. On heating the crystal, appreciable hysteresis is seen, the high temperature spectrum not being reestablished until above 70-75 K. The crystal then looks *broken* inside. Cooling again produces a low temperature spectrum which appears below 60 K and which is different from the previous one, the symmetry of the Al sites being lower.

For a deuterated alum cooled slowly (see 2.2), a new spectrum appears at 56 K as shown in figure 2. The intensity of its lines increases till 54 K, at which temperature the broad lines of the high temperature spectrum have disappeared. A slow heating of the crystal restores the high temperature spectrum with an hysteresis of less than 1 K; the crystal then appears as transparent as before the thermal cycle. The *transition* to the low temperature spectrum occurs again at 56 K during the following cooling. If the crystal is rapidly cooled either to 20 K or to 4.2 K (see 2.2), the spectrum observed is entirely different from the previous one as can be seen in figure 3.

We have studied in detail the changes in the high temperature spectra of the two alums but we have

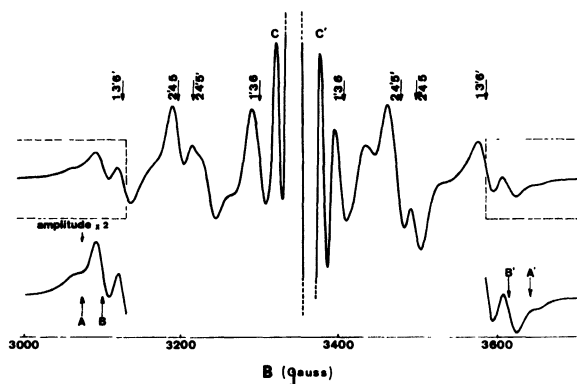


FIG. 3. — Spectrum of Al(Cr)ND₄ alum for H along [111] at X band after a fast cooling to 4.2 K. The numbered lines are those of the 12 completely identified sites. Lines B, B' belong to 12 other sites having z axes near the < 111 > directions. Lines A, A' belong to unidentified sites. Lines C, C' are hyperfine components of the strong central line.

analysed the low temperature spectra ($T \approx T_c$) only for the deuterated one. The apparently irreversible transition of the Al(Cr)NH₄ alum makes any spectroscopic analysis meaningless.

3.2 HIGH TEMPERATURE PHASES. — For the two alums, the spin Hamiltonian for each Cr³⁺ has the usual form :

$$\mathcal{H} = g\mu_B \mathbf{H} \cdot \mathbf{S} + \left[DS_z^2 - \frac{S(S+1)}{3} \right] \quad (1)$$

with $S = 3/2$, the z axis being the trigonal axis of the ion. The anisotropy of g is very small and the spectra are well explained with $g = 1.960 \pm 0.002$. The D value varies strongly with temperature (as usual, D will be expressed in gauss or in cm^{-1} , with the equivalence $10^4 \text{ G} \sim 0.915 \text{ cm}^{-1}$).

For studying this variation and that of the linewidth, we have chosen two magnetic field orientations, along [111] and [100]. With the former, the Hamiltonian (1) predicts 5 lines (we ignore the low intensity hyperfine lines of ^{53}Cr): a narrow central line due to the transitions $+1/2 \leftrightarrow -1/2$ of all ions and four lines due to the transitions $\pm 1/2 \leftrightarrow \pm 3/2$, two of them, at $\pm 2D$ from the central line, resulting from A ions whose axes are parallel to H (1/4 of the ions), the other two, at about $\pm 2D/3$ from the central line, resulting from B ions whose axes are at $70^\circ 33'$ to H (3/4 of the ions). We have plotted in figures 4, 5, 6 the variation of D and of some linewidths, with an indication for some of them of the ratio between the slopes at the centre and at the points of inflexion of the derivative of the lines, to illustrate the change of shape. This ratio is 2.2 for a Gaussian and 4 for a Lorentzian. For $T < 130 \text{ K}$, it becomes difficult to determine D and the width of the broad lines with precision because they are of the same order of magnitude. The width of the $\pm 1/2 \leftrightarrow \pm 3/2$ lines plotted for $55 < T < 80 \text{ K}$ is that of an apparently single broad line, centred on the narrow $-1/2 \leftrightarrow +1/2$ line, as if the average value of D were nearly zero. The intensity of this line is, however, low (due to its width) and it is not possible to be sure that $D \sim 0$.

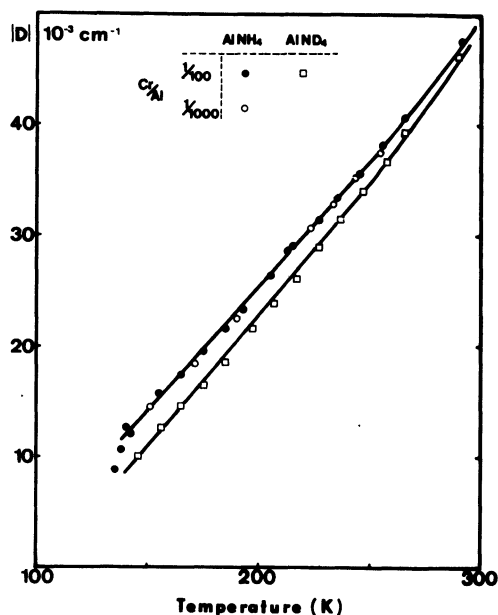


FIG. 4. — Variation of $|D|$ versus T for $\text{Al}(\text{Cr})\text{NH}_4$ and $\text{Al}(\text{Cr})\text{ND}_4$ deduced from [111] spectra. The precision is about $5 \times 10^{-4} \text{ cm}^{-1}$ for $T > 150$, less below that temperature.

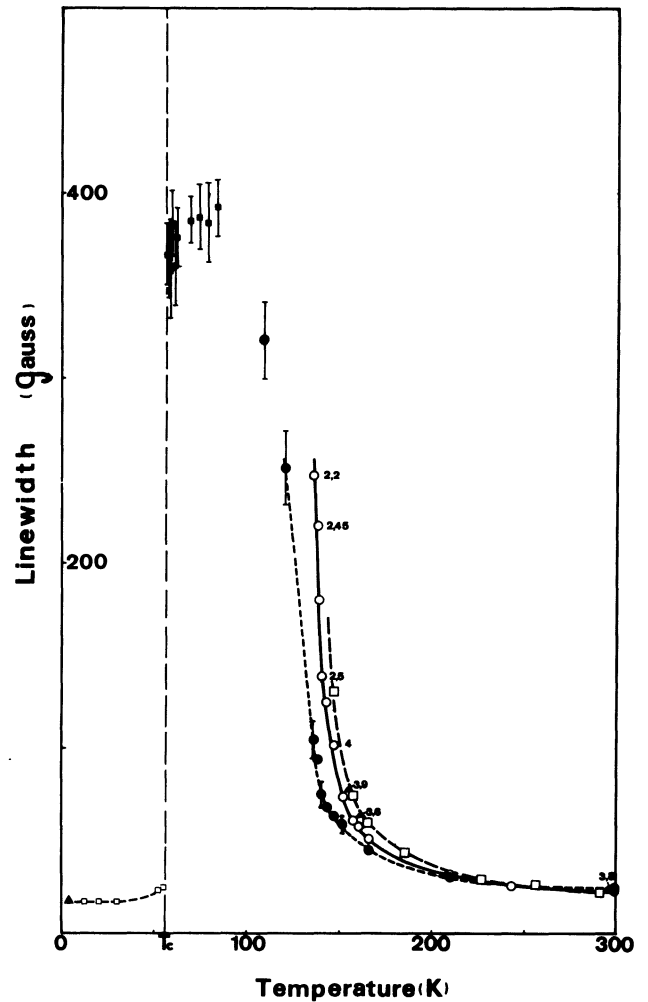


FIG. 5. — Linewidths variation of the $\pm 1/2 \leftrightarrow \pm 3/2$ transitions (peak to peak widths): \circ $\text{Al}(\text{Cr})\text{NH}_4$ H along [111]-sites A, $\theta = 0$; \bullet $\text{Al}(\text{Cr})\text{NH}_4$ H along [111]-sites B, $\theta = 70^\circ 33'$; \square $\text{Al}(\text{Cr})\text{ND}_4$ H along [111]-sites A, $\theta = 0$; \blacksquare $\text{Al}(\text{Cr})\text{ND}_4$ H along [111]-sites A and B; \square $\text{Al}(\text{Cr})\text{ND}_4$ H along [111]-after a slow cooling; \blacktriangle $\text{Al}(\text{Cr})\text{ND}_4$ H along [111]-after a fast cooling.

When the magnetic field is along [100], all the Cr^{3+} become equivalent and the spectrum shows only two lines, one due to $-1/2 \leftrightarrow +1/2$ transitions, the other due to $\pm 1/2 \leftrightarrow \pm 3/2$ transitions. As the temperature decreases, the splitting of these lines, equal to $7/3 D^2/g\mu_B H$, also decreases. Starting from room temperature, the two lines broaden but for $T < 150 \text{ K}$, the $-1/2 \leftrightarrow +1/2$ line narrows while the $\pm 1/2 \leftrightarrow \pm 3/2$ line continues to broaden.

For T below 120 K till the transition temperature, a structure appears on the broad lines. For H along [111], one small narrow line can be seen on both sides of the central $-1/2 \leftrightarrow +1/2$ line at about 60 G (see Fig. 2). Its intensity increases when T decreases. For H along [100], the $\pm 1/2 \leftrightarrow \pm 3/2$ line has an unusual shape for $T < 120 \text{ K}$ and seems to contain unresolved lines. The width of these lines decreases with T , but even just above T_c , it remains too great to permit resolution. Also for H along [100],

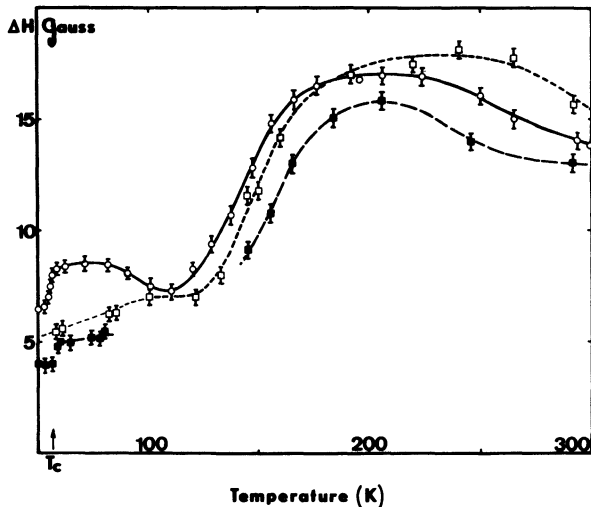


FIG. 6. — Linewidths variation of the $\pm 1/2 \leftrightarrow \pm 1/2$ transitions (peak to peak widths) : \circ Al(Cr)NH₄ H along [111]-first cooling; \blacksquare Al(Cr)ND₄ H along [111]; \square Al(Cr)ND₄ H along [100]. For T below 100 K, the line clearly shows an unresolved structure. The values plotted are the widths of the full line.

the narrow central line becomes more and more asymmetrical for decreasing temperature. Just below T_c , structure in this central line appears, resulting from the crystal structure change, while the broad line disappears.

3.3 COMPARISON WITH OTHER WORK. — Bleaney [4], using CrNH₄ alums, has observed a transition for $T_c \sim 81$ K. Capiomont [10], by means of dielectric measurements has observed for AlNH₄ alums :

- ϵ'_{\max} for $T = 63.2 \pm 0.3$ K at $f = 1\ 000$ Hz
- ϵ''_{\max} for $T = 59.8 \pm 0.2$ K at $f = 1\ 000$ Hz
- ϵ''_{\max} for $T = 58$ K at $f = 400$ Hz.

The difference between our transition temperature (60 K) and that reported by Bleaney is the result of the substitution Al \rightarrow Cr. It can be recalled that the unit cell for the two alums AlNH₄ and CrNH₄ is slightly different, 12.24 Å and 12.27 Å respectively. There can be no direct comparison between our transition temperature (defined from the appearance of the EPR spectrum) and the various temperatures observed by Capiomont since they are defined differently. We can, however, point out that they are in qualitative agreement.

Our values of D are also different from that of Bleaney who found 0.068 cm^{-1} at 290 K and estimated 0.035 cm^{-1} at 90 K. Again, these differences may be due to the substitution Cr : Al, but they can also result from a reduced precision of the measurement for CrNH₄ alum due to the great dipolar broadening of the lines.

3.4 LOW TEMPERATURE PHASES OF DEUTERATED ALUM. — We describe in turn the spectra obtained after a fast cooling or after a slow cooling (see 2.2). As the spectra were identical for equivalent directions

of H (see however the end of section 3.4.1), we have used the cubic high temperature symmetries for analyzing these spectra. This is possible because the symmetry elements lost inside a cell of the low temperature structure relate the twins between them.

3.4.1 Fast cooling. — Below T_c , the symmetry of the Cr³⁺ sites is rhombic instead of axial. We then have to use the spin Hamiltonian adapted to this symmetry

$$\mathcal{H} = g\mu_B \mathbf{H} \cdot \mathbf{S} + D \left[S_z^2 - \frac{S(S+1)}{3} \right] + E(S_x^2 - S_y^2) \quad (2)$$

where D, E, x, y, z , are the eigenvalues and eigenaxes of the fine structure tensor. We keep for g the isotropic value 1.960.

Working at 20 K or 4.2 K, we have studied the very complicated spectra, which contain a great number of lines of width 7-13 G, using the following well known method. We search for a maximum for the distance between the central line ($-1/2 \leftrightarrow +1/2$ transitions) and a lateral line ($\pm 1/2 \leftrightarrow \pm 3/2$ transitions) by varying the magnetic field direction. We confirm that this maximum exists when the magnetic field is along equivalent directions. All these directions will be the z axes of the sites. We then try to find, in a plane perpendicular to one of these directions, another maximum whose distance to the central line is lower than the first which will indicate the y axis of the site. It is necessary, for this study, to get a large number of spectra because the orientation of H depends on two angles and also because the complexity of the spectra, due to the number of lines, requires a degree by degree analysis.

Preliminary results, published previously [11], have been completed by further experiments. The final conclusions are :

i) 12 sites are fully determined. The fine structure tensor axes are indicated on the Wolf diagram in figure 7. The sites, by pairs, have the same z axes but different y axes. They are numbered 1 to 6 and 1' to 6'. The fit between the theoretical angular variation of the line positions with $D = 136$ G and $3E = 98$ G and the experimental *pointé* of the lines is illustrated in figure 8 for H lying in the (001) plane. The theoretical positions of the lines are also indicated in figure 3 when H is along [111].

ii) 12 other sites are partly determined. Only the z axes orientations and the value of $D = 132$ G (a value definitely different from that of the previous sites) have been measured. The z axes, indicated in figure 7, are at about $(8 \pm 1)^\circ$ from the $\langle 111 \rangle$ directions. Some of the lines associated with these sites are located in figure 3 (lines B and B').

iii) An examination of figure 3 shows that other sites exist in the crystal : lines A and A' for instance

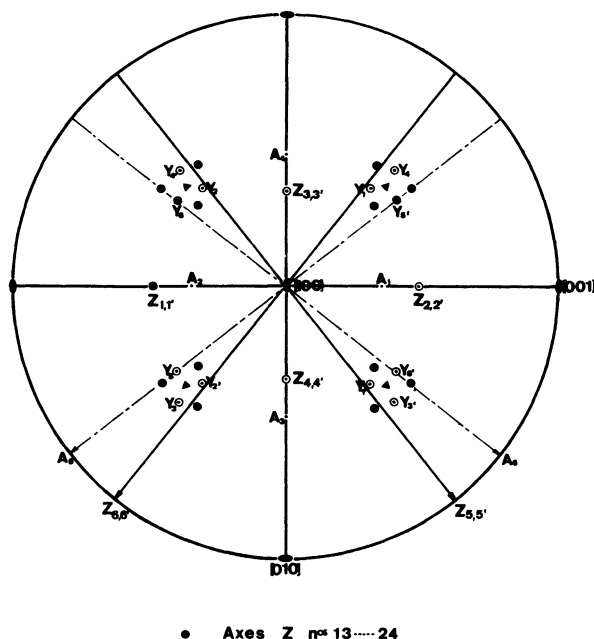


FIG. 7. — Wolf diagram showing the Z and Y axes of the 12 identified sites (numbered 1,1', ..., 6,6') and the Z axes of 12 other sites (numbered 13 ..., 24) for $\text{Al}(\text{Cr})\text{ND}_4$ after a fast cooling. Directions A_i are in the $\{100\}$ planes and perpendicular to Z_i axes. Y_i and Y_i' axes are perpendicular to Z_i and at 36° from A_i .

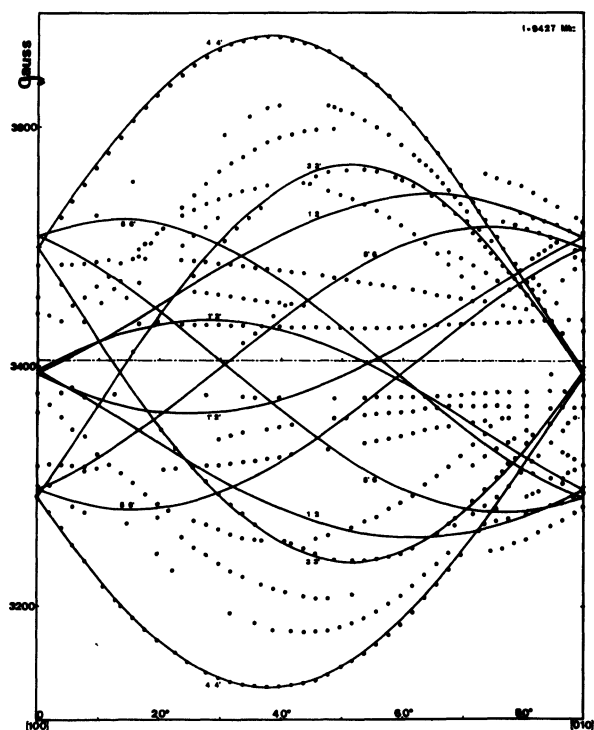


FIG. 8. — Angular dependence of the observed lines when H is in the (001) plane for $\text{Al}(\text{Cr})\text{ND}_4$ at 4.2 K. Points are experimental, lines show the calculated dependence for the 12 identified sites.

are not due to the 24 previous sites (lines C and C' are hyperfine components of the strong central $-1/2 \leftrightarrow +1/2$ line). That is corroborated by other

field orientations. It is difficult to specify their number, but we can say that the total number of sites is greater than 36. Thus, if the structure of the crystal was well defined (see 4.2), we could conclude, using the symmetry analysis of the appendix, that it belongs to the triclinic system.

As the spectra observed with equivalent magnetic field orientations are identical, including the line intensities, the various twins are probably of equal volume. We have however sometimes observed qualitatively equivalent spectra (lines at the same positions) for say [100] and [010] but with different relative intensities of the lines, indicating differences in volume of the twins.

3.4.2 *Slow cooling.* — After a slow cooling, the spectra of the deuterated alum, below T_c , are very much simpler. For H along [111], only six narrow lines, of width 25 G, appear at 56 K on the broad line (see Fig. 2). Their intensity increases till 54 K while the broad line disappears. At about 50 K the two lines which are nearer the central line, with an intensity twice that of the others, are split in two components of equal intensity (see Fig. 2). As the temperature decreases till 12 K, the lines shift slightly but there is no qualitative change of the spectrum.

We have analysed in detail the situations for $T = 54$ K and $T = 30$ K. The lines of the simple spectrum obtained at 54 K for H along [111] are split as H is rotated off this direction. The four extreme lines are each split into three components; the two more central lines are certainly split into six components, although we cannot observe them. Since each Cr^{3+} ion gives two lateral lines (transitions $\pm 1/2 \leftrightarrow \pm 3/2$) and one central line ($-1/2 \leftrightarrow +1/2$), we conclude that the crystal contains 12 different sites of rhombic symmetry. As there are 4 sites in a unit cell, we can say that there are three sets of twins, each one giving the same spectrum for H along [111]. These twins are thus related one from another by the threefold axis of the cubic symmetry. These conclusions are corroborated by the spectra obtained with H along [110]. They are in agreement with X-ray investigations on the AlNH_4 alum in which the threefold axes are lost in the low temperature structure [10]. The existence of only 12 sites permits one to say, using the symmetry analysis given in the appendix, that the crystal structure belongs to the orthorhombic system. It is impossible from EPR to determine the point group but we can obtain information on the *local* symmetry of the Cr^{3+} sites. The coincidence of two lines associated with different sites for H along [111] and the fact that the structure of each twin is orthorhombic lead to the following conclusions: if we call I, II, III the twins having their c axes along [001], [010] and [100], we can say that the four z axes of the twin I must be in the (110) and $(\bar{1}\bar{1}0)$ planes and the four y axes either along [110] and $[\bar{1}\bar{1}0]$ or in the (110) and $(\bar{1}\bar{1}0)$ planes. The orien-

tations for the twins II and III are easily obtained by rotation of $2\pi/3$ around the $\langle 111 \rangle$ directions. By a comparison between the two predicted anisotropies and the actual spectra, we take the second possibility. Further spectroscopic analysis shows that the z axes are at 5.5° from the $\langle 111 \rangle$ and that $D = 147 \pm 0.1$ G, $3E = 45 \pm 0.5$ G. The positions of the axes are given in figure 9.

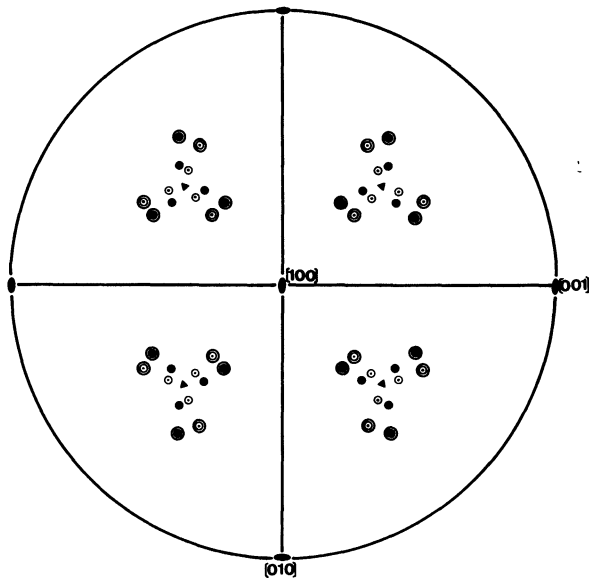


FIG. 9. — Wolf diagram showing the fine tensor principal axes for $\text{Al}(\text{Cr})\text{ND}_4$ after a slow cooling : \blacktriangle $\langle 111 \rangle$ directions; \circ Z axes at $T = 54$ K (at 5.5° from $\langle 111 \rangle$ in planes $\{110\}$); \odot Y axes at $T = 54$ K (in the planes $\{110\}$); \bullet Z axes at $T = 30$ K (at 7° from $\langle 111 \rangle$); \odot Y axes at $T = 30$ K.

At $T = 30$ K, the spectrum for H along $[111]$ remains simple (see Fig. 2) but the lateral lines of the four sites of each twin are resolved. The number of sites remains 12 and thus the structure remains orthorhombic. The spectroscopic analysis is less easy, because 5 parameters have to be determined (D , E , two angles for a z axis, one angle more for a y axis). We can however find that the z axes are at 7.0° from the $\langle 111 \rangle$ (see Fig. 9) and that $D = 149.8 \pm 0.1$ G and $3E = 58 \pm 0.5$ G.

In addition to the lines associated with these 12 sites, one can see lines of very low intensity located at the same field positions as some observed after a fast cooling. Their relative intensity with respect to the intense lines changes from one experiment to another; it shows that a small fraction of the Cr^{3+} ions occupy sites of low symmetry.

4. Discussion. — 4.1 LINEWIDTH IN THE HIGH TEMPERATURE PHASES. — 4.1.1 Origins of the width. — A great number of well-known mechanisms can

contribute to the EPR linewidth. In our case, we can say that the following are effective :

- i) Dipole-dipole coupling between Cr^{3+} ions (2nd moment of about 25 G^2);
- ii) Dipole-dipole coupling between Cr^{3+} ions and protons (2nd moment ranging from 0 to 70 G^2 depending on magnetic field orientations) or deuterons (2nd moment from 0 to 2 G^2);
- iii) Spin lattice relaxation (rough measurements of T_1 have shown that $T_1 \sim 7 \times 10^{-3}$ s at 4.2 K, 4×10^{-5} s at 59 K and 3×10^{-8} s at 200 K);
- iv) Random strains in the crystals (unknown).

A complete analysis of the linewidth and lineshape induced by the simultaneous effect of these mechanisms is impossible. We can only say that the mechanisms i), ii) and iv) are certainly responsible for the widths below the critical temperature. We can also say that the spin lattice relaxation certainly contributes to the width at room temperature. However, none of these four mechanisms can explain the strong width variations observed above T_c . O'Reilly and Tung Tsang [6] have reported analogous variations for the alum ($\text{Al}, \text{NH}_3\text{CH}_3$) but no variation for the alum (Al, K). The former, as the alums studied here, shows a structural change and the latter does not. We thus conclude that the variations in ΔH are the result of fluctuations connected to the structural change.

4.1.2 Effect of fluctuations on the linewidths. — Many observations of width variations near a critical temperature have been made. The case of SrTiO_3 has been very well studied and explained [12]. For T slightly above T_c , the fluctuations of the lattice connected with the structural change (a soft mode in this case) are slow; for EPR, they are quasi static and the inhomogeneous lines (generally Gaussian) reflect their continuous random distribution. For increasing T , the fluctuations become faster and faster and the lines are *motionally narrowed*, becoming Lorentzian.

For the (AlNH_4) and (AlND_4) alums, we do not have a physical model for the structural change and the order parameter is not known. Thus, in order to study the influence of the fluctuations we have made a semi-classical calculation, following that of O'Reilly and Tung Tsang [6]. We consider that in the Hamiltonian (2), the principal values D and E and the orientations of the principal axes of the fine structure tensor vary both in space and time, but that g is constant and isotropic. Taking as quantization axis the magnetic field direction, which makes the polar angles θ and ψ with respect to the principal axes of the fine tensor, we transform the one spin Hamiltonian (2) in :

$$\mathcal{H} = g\mu_B HS_z + \hbar \sum_q F^q(t) A \frac{1}{2}, \quad (q = 0, \pm 1, \pm 2)$$

where

$$A_2^0 = S_z^2 - \frac{S(S+1)}{3}, \quad A_2^{\pm 1} = S_z S_{\pm} + S_{\pm} S_z$$

$$A_2^{\pm 2} = S_{\pm}^2$$

$$F^0 = \frac{1}{2} [D(3 \cos^2 \theta - 1) + 3 E \sin^2 \theta \cos 2 \psi]$$

$$F^{\pm 1} = \frac{1}{4} [-D \sin 2 \theta + E \sin 2 \theta \cos 2 \psi \pm 2 i E \sin \theta \sin 2 \psi]$$

$$F^{\pm 2} = \frac{1}{4} [D \sin^2 \theta + E(1 + \cos^2 \theta) \cos 2 \psi \pm 2 i E \cos \theta \sin 2 \psi].$$

These equations may be used in two limiting cases. First, for the slow regime where the fluctuations are quasi-static, one can evaluate the shifts of the lines by simple perturbation calculation. One finds,

$$\Delta E = - \frac{24 |F^1|^2}{\hbar \omega} + \frac{12 |F^2|^2}{\hbar \omega}$$

for

$$- \frac{1}{2} \leftrightarrow + \frac{1}{2} \text{ line}$$

$$\Delta E = \pm 2 F^0 + \frac{24 |F^1|^2}{\hbar \omega}$$

for

$$\pm \frac{1}{2} \leftrightarrow \pm \frac{3}{2} \text{ lines.}$$

As D , E , θ , ψ do not have definite values, but random values these shifts are also random quantities. There results a line width, whose value is the RMS of the shifts. If we neglect second order terms, we find for the $\pm 1/2 \leftrightarrow \pm 3/2$ line a width

$$\delta \omega_s = 2 \sqrt{\overline{|F^0|^2}} \quad (3)$$

where the bar denotes a spatial average.

The second limiting case corresponds to fast fluctuations. Using the Redfield theory, O'Reilly and Tung Tsang have found Lorentzian lines with half width given by

$$\frac{1}{T_2} = \delta \omega = 2 J_0(0) + 12 J_1(\omega_0)$$

for

$$\pm \frac{1}{2} \leftrightarrow \pm \frac{3}{2} \text{ lines} \quad (4a)$$

$$\frac{1}{T_2} = \delta \omega = 12 J_1(\omega_0)$$

for

$$- \frac{1}{2} \leftrightarrow + \frac{1}{2} \text{ line} \quad (4b)$$

where $J_q(\omega)$ is the spectral density of the random function $F^{(q)}(t)$, ω_0 the resonance frequency. These results are correct only if $T_2 > \tau_c$, τ_c being the correlation time of the fluctuations.

If we choose, as usual, the spectral densities as

$$J_q(\omega) = 2 \overline{|F^q|^2} \frac{\tau_c}{1 + \omega^2 \tau_c^2} \quad (5)$$

(we suppose of course that the spatial average and the time average of the F^q are identical), we can draw the following conclusions : i) from (4b), it is seen that the width of the $-1/2 \leftrightarrow 1/2$ line goes through a maximum when $\tau_c = \tau_{c1} = 1/\omega_0$; ii) as in (4a) the ratio between the second and the first term is

$$6 \frac{\overline{|F^1|^2}}{\overline{|F^0|^2}} \frac{1}{1 + \omega_0^2 \tau_c^2}$$

and thus $\ll 1$ for $\tau_c \gg 1/\omega_0$, we obtain from (3) the width of the $\pm 1/2 \leftrightarrow \pm 3/2$ lines

$$\delta \omega = 4 \overline{|F^0|^2} \tau_c = \delta \omega_s^2 \cdot \tau_c,$$

a well known result in motional narrowing theory ; iii) the change from the slow to the fast regime occurs when

$$\tau_c = \tau_{c2} \sim T_2 = \frac{1}{\delta \omega_s} (\tau_{c2} > \tau_{c1}).$$

For $\tau_c < \tau_{c2}$, the line is Lorentzian, for $\tau_c > \tau_{c2}$, the lineshape depends on the shape for the distributions of the random quantities D , E , θ , ψ .

4.1.3 *Comparison with our results.* — The temperature dependence of the widths and the shapes of the lines shown in figures 5 and 6 are in qualitative agreement with the model for $T > 100$ K. The temperature at which the width of the $-1/2 \leftrightarrow 1/2$ line reaches its maximum (~ 200 K) is higher than that for which the shape of the $\pm 1/2 \leftrightarrow \pm 3/2$ line changes from Gaussian to Lorentzian (~ 140 K). Since τ_c is a decreasing function of T , the inequality $\tau_{c2} > \tau_{c1}$ is verified.

As an attempt for quantitative comparison, we first compare the values of τ_c which can be deduced from our results with the values of the dielectric relaxation time τ . We must however keep in mind that our phenomenological τ_c and τ are not identical, the former resulting from local fluctuations around Cr^{3+} ions, the latter being for the whole crystal. This problem has been studied in detail for instance by Avogadro *et al.* [13] and by Rigamonti [14] for explaining NMR relaxation times in various compound and by Muller *et al.* [12] for discussing EPR results in SrTiO_3 . In our case, a detailed analysis cannot be very fruitful in so much as we do not know the physics of the structural change. If however we suppose an order-disorder transition (based on the observation that

the lattice constant is not doubled below T_c) we can use for instance the results of Rigamonti [14] which is an adaptation to the ferroelectric case of Suzuki and Kubo's calculations on an Ising system [15]. Taking an isotropic form for the dipolar interaction, one can show that the relaxation time of a mode \mathbf{k} goes as $\tau_{\mathbf{k}} = \tau(1 - \beta k^2)$ where β is positive for a ferroelectric transition and $\tau = \tau_{\mathbf{k}=0}$ is the dielectric relaxation time. The local relaxation time τ_c is approximately the average of $\tau_{\mathbf{k}}$ in the Brillouin zone. From the above expression, we deduce $\tau_c < \tau$. Thus, our phenomenological τ_c must be smaller than the dielectric relaxation time τ .

The variation of τ with the temperature for $(\text{AlNH}_4)_2$ alum is shown in figure 10 using the results obtained at low frequency by Capiomont [10], at high frequency by Guillien [16] and at very high frequency by Rolland

and Freymann [17] and by Griffiths and Powell [18]. Two measurements have also been made by the authors. For the evaluation of τ_c , we use the results of the model described in the previous section. As indicated above, for $T \sim 200$ K the width of the $-1/2 \leftrightarrow 1/2$ line is maximum and thus

$$\tau_c = \tau_{c1} = \frac{1}{\omega_0} = 1.3 \times 10^{-11} \text{ s.}$$

For $T \sim 140$ K the shape of the $\pm 1/2 \leftrightarrow \pm 3/2$ lines changes so that

$$\tau_c = \tau_{c2} = \frac{1}{\delta\omega_s} = 3 \times 10^{-10} \text{ s}$$

where $\delta\omega_s$ is the half width in the slow regime deduced from the 320 G width of the gaussian line at $T \sim 100$ K (see Fig. 5). Again from figure 5, we see that the $\pm 1/2 \leftrightarrow \pm 3/2$ line associated with A sites is Lorentzian between 145 K and room temperature. Thus, by simple subtraction of the room temperature width, we can extract the contribution $\delta\omega$ due to the distortions which is related to τ_c by $\delta\omega = \delta\omega_s^2 \cdot \tau_c$. This simple relation is, however, valid only when $\tau_c > \tau_{c1}$ i.e. when $T < 200$ K. We have plotted in figure 10 the values of τ_c deduced by this method for $145 < T < 200$ K as well the values of τ_{c1} and τ_{c2} . The use of the $\delta\omega_s$ value deduced from the width of the single line observed at $T \sim 100$ K is questionable since we cannot extract the slow regime widths associated with sites A and B (are these sites even distinguishable in that regime? see following paragraphs). Should that be possible, we would obtain far larger τ_c values.

In conclusion, we see that the values of τ_c deduced from EPR results seem to have the same temperature dependence as, but are greater than, τ (in the small range where the comparison is possible). From previous discussion, τ_c and τ must have the same temperature dependence but τ_c must be smaller than τ . Although the precision of the measurements does not permit us to draw a definite conclusion, the disagreement between the predicted and observed relative importance of τ_c and τ could be explained if the fluctuations most active in broadening the lines were different from those which are responsible for the dielectric relaxation time. Thus our results, as well the dielectric measurements of Capiomont [10] (which show a relatively weak dielectric anomaly near T_c as compared with the strong change of the EPR spectra), lead to the conclusion that the dielectric fluctuations are not fluctuations of the primary order parameter.

To go further in the comparison between the calculations of section 4.1.2 and our results, we need estimates of the amplitudes of the fluctuations of D , E , θ , ψ and of the correlation between them. That can be known in detail only when the mechanism of the structural change is established. We can

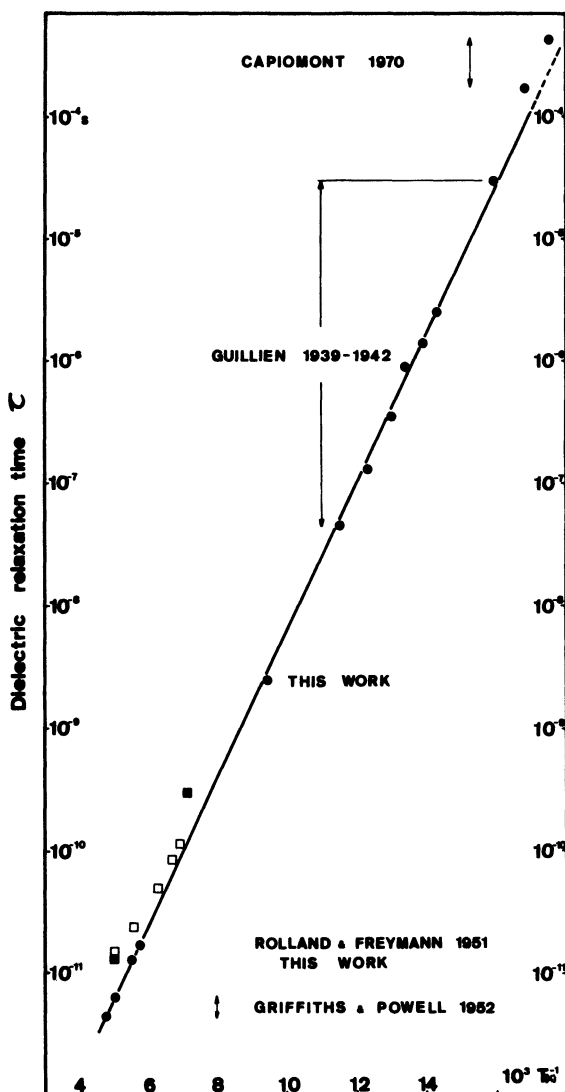


FIG. 10. — Dielectric relaxation time dependence on temperature for AlNH_4 : ● Values of τ measured by various authors; □ Values of τ_c deduced from the Lorentzian part of the $\pm 1/2 \leftrightarrow \pm 3/2$ lines of sites A for H along [111] (see Fig. 5) by the relation $\delta\omega = \delta\omega_s^2 \cdot \tau_c$; ■ Values of τ_{c1} and τ_{c2} (see text).

however test a particular model for these distortions by comparing its predictions with the results of the experiments. From the results of section 3.4, we see, i) that above T_c the four sites of each cell have an average axial symmetry pointing to the four $\{111\}$ directions, ii) that below T_c the z axes of these sites point near the four $\{111\}$ directions (see Fig. 9). Thus, one could think that the fluctuations do not much change the direction of the z axis of each site, i.e. the most important distortion of the water molecules octahedra remain in the same direction. From this model, δD could be equal to the low temperature D value, ~ 150 G and $\delta\theta$ would be only 5.5° . With these values, with $E \sim 15$ G, ψ uniformly distributed and ignoring correlation between the four random variables, we calculate $\sqrt{|F_0|^2}$ and $\sqrt{|F_1|^2}$ for $\bar{\theta} = 0,70^\circ 33'$ and $54^\circ 44'$. These cases correspond respectively to ions A and B for H along $[111]$ and all ions for H along $[100]$. Then, from eq. (4) we calculate the widths of the $\pm 1/2 \leftrightarrow \pm 3/2$ lines when

$$\tau_c = \frac{1}{\omega_0} = 1.3 \times 10^{-11} \text{ s.}$$

The results are shown in table I where we have also given the experimental widths at 200 K (see previous paragraphs). We have also calculated the widths in the slow regime from eq. (3) to compare the experimental value at 80 K. Even if we look only at the ratios of these values, the disagreement is total. A detailed analysis of the averaging shows that to explain a quasi isotropic width for $T \sim 80$ K, we must necessarily use much greater values for $\delta\theta$, i.e. the principal distortion of the water molecule's octahedra can take any orientation, whatever the average orientation they had at higher temperature. This point will be used in the next section for the interpretation of low temperature spectra observed after a fast cooling.

As a conclusion of this section, we would like to point out some differences between our results and those obtained with SrTiO_3 [12]. In our case, the broadening of the width begins at $T \sim 3 T_c$ while for SrTiO_3 it is observed only at $T \sim 1.4 T_c$. Although measurements are not easy between 56 and 100 K, it seems that the linewidth changes very little if at all, while for SrTiO_3 the broadening becomes stronger as $T \rightarrow T_c$. The width of the lines above T_c is much

larger for alums than for SrTiO_3 . Below T_c , the change in width is smaller for alums than for SrTiO_3 . These differences could be due to i) the difference in the nature of transition : order-disorder for alums, displacive for SrTiO_3 , ii) the difference in mobility of the H_2O , NH_4 , SO_4 groups in alums and of the oxygen ions in SrTiO_3 . This last point, for instance, could explain the very broad lines (great mobility) and the fact that the motional narrowing does not begin at T_c but at a higher temperature and finishes at a temperature far away from T_c . We suggest that in the alums studied here, which are more complicated (there are $48(\text{H}_2\text{O})$, $8(\text{SO}_4)$ and $4(\text{NH}_4)$ in one cell), the broadening of the EPR lines, the dielectric properties and the structural change could be due to different type of collective excitations, in contrast to what occurs in SrTiO_3 .

4.2 RESULTS FOR T LOWER THAN T_c . — In the previous section, we have seen that the variation of the linewidth for $T > 100$ K can be interpreted as resulting from fluctuations of the crystal field. For $T \lesssim T_c$, these fluctuations are slow for EPR and randomly distributed (i.e. not correlated) since we observe a broad line and not a spectrum of distinct lines. From this state of the crystal, we can get two situations below T_c depending on the cooling velocity. We discuss three plausible explanations : i) existence of three structural phases, ii) quenching of the high temperature disorder, iii) influence of the volume of the domains.

In the first, the three phases would be cubic, orthorhombic and triclinic with one of the two energy diagrams shown in figure 11. For case *a*), a fast cooling could lead to the triclinic metastable phase in partial agreement with our observations but a slow cooling could permit the observation of that triclinic phase between T_{c1} and T_{c3} contrary to what we have observed. Case *b*) is compatible with our results. In order to test that possibility, differential thermal analysis (DTA) experiments have been done by Lagnier and Bonjour of Centre d'Etudes Nucléaires de Grenoble. They have shown only one peak, of width 4 K, in increasing temperature experiments following either slow or fast cooling. We think that after a fast cooling, an *inverse* peak ought to have been observed at a temperature just below T_{c3} in case *a*) or near T_{c1} - T_{c2} in case *b*) during the heating, this peak being the

TABLE I

Values of the fast and slow regime linewidths within the hypothesis of $\delta\theta = 5.5^\circ$, $\delta D = 150$ G, $E = 15$ G and ψ equidistributed. $\bar{\theta}$ is the average value of the direction of the z axes of the site with respect to **H**

$\bar{\theta}$	$\sqrt{ F_0 ^2}$	$\sqrt{ F_1 ^2}$	$\Delta H = 4 F_0 ^2 \tau_c + 12 F_1 ^2 \tau_c$	ΔH exp. ($T = 200$ K)	$\Delta H = 2 F_0$	ΔH exp. ($T = 80$ K)
0	148	7	40	34	300	400
$70^\circ 33'$	52	24	8	32	100	
$54^\circ 44'$	23	35	8	22	46	

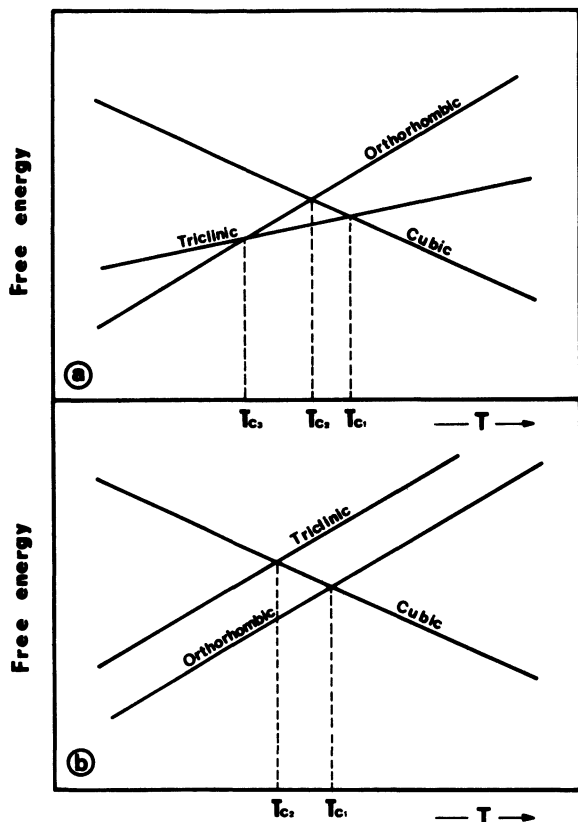


FIG. 11. — Possible free energy diagrams when three phases are permitted (straight lines have been drawn for simplicity).

result of jumps between the metastable to the stable phase. Thus, the explanation of our results with this model is impossible unless the intervals $T_{c3}-T_{c1}$ or $T_{c2}-T_{c1}$ are very small.

The second explanation is based on a *quenching* of the high temperature situation by a fast cooling. We have seen, in section 4.1.3 that the linewidths can be explained only if the distortions of the octahedra can have orientations far away from their average orientation along the $\{111\}$ directions. During a slow cooling, the distortion of each site is coordinated with that of the neighbouring sites leading to the structure described in section 3.4.2 in which the principal distortions of the four sites of each cell, point near the four $\langle 111 \rangle$ directions. After a fast cooling, on the contrary, the uncorrelated distortions which are present above T_c are *quenched*. However, some of them are too unstable and a partial coordination leaves only a finite number of Cr^{3+} sites (we have counted at least 36 sites). The fact that the maximum splitting of the $\pm 1/2 \leftrightarrow \pm 3/2$ lines after a fast cooling is 540 and 240 G for H respectively in $[111]$ and $[100]$ direction (as compared to 600 and 32 after a slow cooling) can also be used as a qualitative proof of this model since these splittings reflect the linewidth for $T > T_c$ (400 and 300 G respectively for the two magnetic field orientations). It is however rather surprising that among the very great number of

possible distortions, only a few (but at least 36) would be sufficiently stable to be present after a fast cooling. The presence of low intensity lines in the spectra after a slow cooling at the same positions as some lines of the spectra obtained after a fast cooling (see the end of section 3.4.2) is compatible with this model. These lines could be due to ions located in regions near the surface of the crystal and thus cooled faster than the central region.

For the third explanation, the volume of the domains following different cooling could be different. After a fast cooling, the domains would be small and most of the Cr^{3+} ions should be in the walls or near the walls, having thus a distorted surrounding. Again, one must suppose that these distortions are not completely random since we observe a spectrum of lines. In order to test that possibility, we have observed the domains, in collaboration with J. Bornarel and P. Bastie of this laboratory, after coolings at different velocity. Although they look different, they do not seem to have very different dimensions, few microns in all cases. However, the fastest cooling possible with the apparatus was perhaps not fast enough.

Thus, none of these three possibilities can be ruled out although none is very attractive. Complementary experiments on the observation of the domains and X-ray studies are planned.

4.3 INFORMATION ON THE STRUCTURAL CHANGE. — As EPR gives only the point symmetry of the Cr^{3+} site, the information on the structural change can be only qualitative and partial. It concerns only the immediate surroundings of the Cr^{3+} ions i.e. the water molecules' octahedra. The effects of the modifications of these octahedra on the rest of the structure cannot be determined without the help of other techniques.

At room temperature, the $Al(Cr)ND_4$ alum is of α type i.e. the water molecules' octahedra are extended along a trigonal axis [19]. Spatio-temporal distortions in the crystal change the shape of these octahedra but EPR only feels the *average* shape at high temperature. When temperature decreases, the average extension is reduced and the fluctuations are slowed. We cannot say if the average extension (characterized by \bar{D}) disappears between 110 K and 56 K but certainly it is comparable to the width of the fluctuations (characterized by δD). The results obtained in that temperature range do not permit one to draw definite conclusions. Distortions are always present since the linewidth is great but the unresolved structure for H along $[100]$ and the two narrow lines for H along $[111]$ indicate that these distortions are not randomly distributed. Also, the change in shape of the

$$-\frac{1}{2} \leftrightarrow +\frac{1}{2}$$

line shows a continuous modification of the Cr^{3+} site symmetry.

The first state of the low temperature structure at 54 K shows that the random distortions have disappeared and that the octahedra have a definite shape. Their rhombicity ($3E/D$) is small and their z axes are near the $\langle 111 \rangle$ directions. Thus, the octahedra still have a pseudo-trigonal axis near the trigonal axis they had at high temperature. We do not know if they are still extended, since the sign of \bar{D} is not determined. It is not unrealistic to think that in the temperature range 56-100 K the sign of \bar{D} has changed and that the octahedra are now compressed. When T decreases below 54 K, the shape of the octahedra is slightly modified but the orientations of their principal distortion clearly change. Thus below T_c , as well above T_c , there are continuous modifications in the positions of the water molecules and probably in the positions of the other molecules as well.

5. Conclusion. — We have reported here results of EPR spectroscopy on two alums $\text{Al}(\text{Cr})\text{NH}_4$ and $\text{Al}(\text{Cr})\text{ND}_4$ which undergo a phase transition at respectively 60 and 56 K. The high temperature spectra of the two systems look very similar : a reduction of the average D value together with a broadening of the $\pm 1/2 \leftrightarrow \pm 3/2$ lines when lowering the temperature from room value to T_c . That can be qualitatively interpreted as due to distortions of the Cr^{3+} site associated with the structural change. These distortions broaden the lines above T_c . When the temperature increases further, the fluctuations of these distortions motionally narrow the lines. Although this behaviour has some features common to those observed in other systems, it differs in the order of magnitude of the distortions and in the temperature range in which motional narrowing is effective. These differences could be due to the relatively greater mobility of the water molecules as compared to that of more tightly bound ions in other compounds.

Below T_c , we have only studied the deuterated system because the AlNH_4 crystals look internally fractured after a cooling below T_c . AlND_4 crystals,

on the contrary, are not damaged even after a great number of transitions. Two different sorts of spectra were observed depending on the cooling velocity. After a fast cooling, they are complicated, although reproducible. They show that Cr^{3+} ions are located in more than 36 sites, indicating that the structure is of very low symmetry (triclinic) or that there is some form of disorder. After a slow cooling, the spectra are simple with only 12 sites for Cr^{3+} . A symmetry analysis shows that the crystal then contains 3 types of domains, each one belonging to the orthorhombic system. The directions of the principal distortions of the water molecules' octahedra surrounding Cr^{3+} ions are determined. It is then possible to describe the *history* of these octahedra during the cooling from room temperature.

While we have proved that the stable low temperature phase is orthorhombic, we do not have a clear description of the crystal after a fast cooling. The results obtained from other techniques (differential thermal analysis, direct domain observation) have not allowed us to validate or invalidate some hypotheses we had proposed. Nor do we know if these alums are ferroelectric at low temperature. Experiments using other techniques will be necessary to answer these questions.

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Appendix : Symmetry analysis. — The $m3$ point group associated to the $\text{Pa}3$ space group of the alums at high temperature has 24 degrees of symmetry. X-ray investigations of Y. Capiomont [10] on AlNH_4 as other experiments made in collaboration with F.

TABLE II

System	Point group	Ferro-electricity	Inversion	d^0 of symmetry	Nb of twins	Max nb of spectra
Orthorhombic	$m\ m\ m$	no	yes	8	3	12
	$m\ m\ 2$	yes	no	4	6	12
	$2\ 2\ 2$	no	no	4	6	12
Monoclinic	$\frac{2}{m}$	no	yes	4	6	24
	m	yes	no	2	12	24
	2	no	no	2	12	24
Triclinic	$\bar{1}$	no	yes	2	12	48
	1	yes	no	1	24	48

Sayet at on $\text{Al}(\text{Cr})\text{ND}_4$ have shown that, in the low temperature phase : i) the threefold axes are lost ; ii) the lattice constants are not doubled with respect to the cubic value and are very near. The subgroups of $m3$ which have no 3-axis are those of the orthorhombic, monoclinic and triclinic systems. It is easy, by counting the number of degrees of symmetry of each one of these groups to find the number of twins which are possible in a crystal. The results are shown in table II where we have also indicated the groups which permit ferroelectricity [20].

Since there are 4Cr^{3+} sites in a cell, we ought to observe $4 \times n$ distinct spectra, when n is the number of twins. However, EPR cannot distinguish two rhombic sites if they are connected by i) inversion ; ii) a 2-axis parallel to one of the principal axes of the sites ; iii) a mirror parallel to one of the principal planes of the sites. Only the first situation occurs for the alums, when inversion is lost in the low temperature phase. In that case the number of distinct spectra is only $(4 \times n)/2$. The results for all the groups are given in the last column of table II.

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