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The crystal fields in α-alums—A high pressure magnetic resonance study

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Abstract. The origin of the crystal field and its variation with temperature in several α-alums have been studied by NMR of ^{27}Al and EPR of Cr^{3+} at high hydrostatic pressures and low temperatures. The results lead to an explanation of the anomalous temperature variation of the axial crystal field at the trivalent ion site. The mechanism of the phase transition in ammonium alum is also explained. A correlation between the axial crystal field as determined by NMR (e^2qQ/h) and that determined by EPR (D) has been obtained.

Keywords.

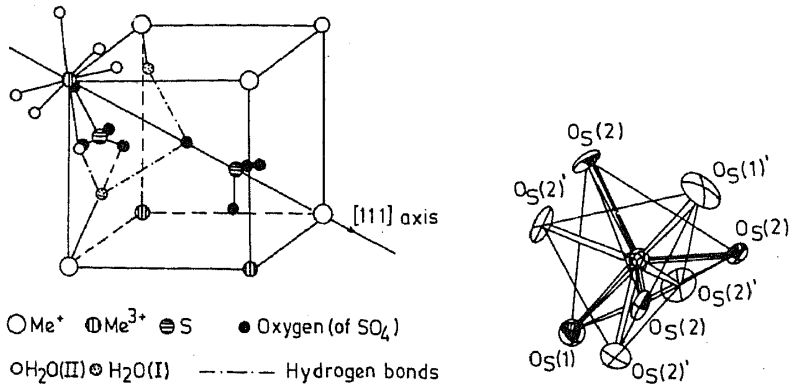
1. Introduction

The family of alums has been studied extensively, not only by a variety of magnetic resonance techniques but also by most other spectroscopic ones as well. The polymorphism of alums in α, β and γ-classes was first pointed out by Lipson and Beevers (1935), Lipson (1935a, b) and subsequently the study of their structures went through successive stages of refinement using both x-ray and neutron diffraction (Bacon and Gardner 1958; Cromer *et al* 1966, 1967; Larson and Cromer 1967; Cromer and Kay 1967; Ledsham and Steeple 1968a, b; Kay and Cromer 1970; Abdeen *et al* 1981).

The alums have the general formula $Me^+Me^{3+}(SO_4)_2 \cdot 12H_2O$, where combinations of different monovalent ions Me^+ and different trivalent ions Me^{3+} (together with the possibility of S being replaced by Se) give rise to a large number of members. All these compounds are cubic, with spacegroup $T_h^6 - Pa3$. There are four formula units ($Z = 4$) in each unit cell, with Me^+ and Me^{3+} arranged on alternate corners of a face-centred cube. Each of Me^+ and Me^{3+} are surrounded by an octahedron of water molecules. Also, in each octant of the unit cell, on the body diagonals, lie the SO_4^{2-} ions; the sulphur and one-special position oxygen, $O_s(1)$, lie on the (111) body-diagonal and the other three oxygens, $O_s(2)$, off the diagonals in general positions with axial symmetry (figure 1).

The interest in alums, on which most of these studies have concentrated, can be broadly classified into three groups: (i) the origin of the trigonal field at Me^{3+} and the contributions to its temperature variation, (ii) the status of the SO_4 group in α-alums, (iii) the phase transitions in alums. A brief description of these problems is given in order to define the motivation for the work reported in this paper.

The origin of the trigonal crystalline field at Me^{3+} had been speculated upon as early as 1929 by Van Vleck, who attributed it to three possible mechanisms: (i) a trigonal distortion of the first neighbour octahedron of water molecules, possibly by a Jahn-Teller type of mechanism, the distortion being much less than the resolution of x-ray



(a) (b)

Figure 1. (**a**) An octant of a unit cell of an α-alum, (with a sulphate group on one of the body diagonals). (**b**) The sulphate ion on (111) axis in α-alums. The special position oxygen $O_s(1)$ and general oxygen $O_s(2)$ are shown in the normal and reversed configurations.

studies, (ii) the "direct action" of ions in higher coordination spheres including the octahedron of SO_4^{2-} ions in the 2nd coordination and finally (iii) the "indirect action" of the same octahedron of SO_4^{2-} ions together with two SO_4's lying on the (111) axis in the 4th coordination sphere acting indirectly *via* the water octahedron. Subsequently Walsh (1959), O'Reilly and Tsang (1967) and Owens (1977a, b) attributed the trigonal field to the immediate neighbour water octahedron. Walsh, who had performed high pressure EPR experiments on NH_4Al alum (and hence could separate the implicit volume dependence from the explicit vibrational effects), could not account either for the isothermal volume dependence or isobaric temperature dependence of the zero-field splitting parameter D, assuming the above origin. He also stressed that explicit contributions from the thermal vibrations of the lattice might render calculations based on a static model (such as that of O'Reilly and Tsang (1967) somewhat naive. Similarly McGarvey (1964a, b), Danilov and Manoogian (1972a, b) and Danilov *et al* (1973), attributed a positive value of D at Me^{3+} site to an elongated water octahedron (as in NH_4Al alum) and a negative D value to a compressed one. On the other hand, Weiden and Weiss (1974, 1975, 1979) who carried out an exhaustive study on the crystalline field in alums using both NQR and quadrupolar perturbed NMR, compared their experimental results with calculated values on the basis of a model in which the SO_4 groups on the (111) axis were the cause of the trigonal field. They found very good agreement between the two not only for the α-alums but for the β-alums as well. They, however, conceded that complete self-consistent calculations, including higher multipole contributions could have changed the results qualitatively (although such calculations were not carried out because they would be prohibitively unwieldy).

The conclusion thus reached from a consideration of the calculations of other workers enumerated above is that an unambiguous picture attributing the origin of the trigonal field at the Me^{3+} site solely to either SO_4 groups or water dipoles cannot be constructed from static point charge calculations. Our experimental data of EPR at high pressures as well as low temperatures carried out on a series of alums provide the necessary basis for the resolution of the problem, viz. the origin of the trigonal field and its temperature dependence. For a more complete picture, we have also made an NMR study which would sense the electric quadrupolar coupling constant e^2qQ/h of the ^{27}Al nucleus. This would thus be another version of Burns' (1961) experiment in which the correlation between the EPR zero-field splitting parameter D and NMR quadrupolar constant is established, by parametrically eliminating the dependence of each on the change of interatomic distance. The latter was achieved by Burns by variation of temperature, while we achieved it by using pressure as the independent parameter. One further reason for carrying out the high pressure NMR experiment was the apparently contradictory signs of the slope of trigonal field dependence on interionic distance, obtained, on the one hand, by the high pressure EPR experiment (Walsh and ours) and on the other, by the NMR experiment of Weiden and Weiss. The latter obtained a variation of interionic distances by considering different isomorphic alums (containing Me^+ ions with different sizes), and obtained a positive coefficient, while our pressure experiments yielded a negative one.

As regards the status of the SO_4 groups, x-ray and neutron diffraction studies reveal, in α-alum, large thermal parameter associated with the sulphur atom (Bacon and Gardner 1958). It could not be unambiguously settled from such diffraction studies as to whether the SO_4 groups in α-alums were statically disordered in two possible configurations throughout the solid (Cromer and Larson 1967) or, time-wise fluctuating (Ledsham *et al* 1970). Weiden and Weiss (1974, 1975, 1979), from a consideration of the narrow line-widths of NMR transitions, of different quadrupolar nuclei, concluded in support of the time-wise fluctuations of the SO_4 groups distributed in two different configurations. Our studies, based on linewidth study of the EPR transitions, have shed new light on the disorder of SO_4 groups in α-alums, a preliminary report of which has been made in Sinha and Srinivasan (1982).

Chicault and Buisson (1977) had studied in detail the phase transition in NH_4Al alum. They could not pinpoint any specific mechanism as the cause for the structural phase transition, but tentatively concluded that the same fluctuations which caused EPR line broadening were also the ones responsible for dielectric relaxation, but that these need not be the fluctuations of the primary order parameter. Manoogian and Leclerc (1976a, b) concluded that the phase transitions were caused by the D parameter going through zero, while Owens (1977a) attributed the cause of the phase transition to the onset of fluctuations of the water octahedron. Svare and Holt (1979) from proton T_1 measurement in NH_4Al alum, concluded that the phase transition is caused by the freezing of the motion of the NH_4 ion and consequent shifting of the centre of charge by 0·1 A along the (111) axis. Our use of pressure as an additional thermodynamic parameter allowed us to determine the specific mechanism causing the first order phase transition in NH_4 alums.

The experimental techniques used in the present study in order to examine the above issues, are those of high pressure and low temperature EPR of the Cr^{3+} ion and high pressure quadrupole perturbed NMR of ^{27}Al nucleus, in single crystals of the potassium and ammonium alums. The results thus obtained, after being duly corrected for different types of pressure relaxation, were analysed in terms of the equations of states in order to estimate the implicit and explicit contributions to the trigonal field, and subsequently to analyse the mechanism of the phase transition. In the following, a brief description of the experimental techniques is followed by the results and their analysis, each section being divided into parts dealing with EPR and NMR respectively.

2. Experimental techniques

2.1 *High pressure and low temperature* EPR

The Cr^{3+} ion ($S = 3/2$) has a ${}^4F$ ground state; a predominantly cubic crystalline field with a small trigonal distortion splits this level, to finally yield a splitting of the ground ${}^4A_2$ singlet into two Kramers doublets. The Hamiltonian in this spin manifold is:

$$\mathscr{H} = g\beta \mathbf{H}\cdot S + \mathbf{D}(S_z^2 - S(S+1)/3), \tag{1}$$

where D is the index of the trigonal component in the crystalline field. The principal component of this axial tensor lies along one of the body-diagonals such that in the unit cell of the alum there are four magnetically inequivalent Me^{3+}, each having its axis of distortion along one of the body diagonals. This produces a complex spectrum, for a general orientation of the (111) axis with respect to the magnetic field. It is simplified into a five-line spectrum when the crystal is rotated about its (110) axis, such that one of the (111) axes is parallel to the magnetic field, the distance between the outermost satellites giving directly the value of D.

Large single crystals of $KCr(SO_4)_2\cdot 12H_2O$, (abbreviated hereafter as KCr), $NH_4Cr(SO_4)_2\cdot 12H_2O$ (ACr), $KAl(SO_4)_2\cdot 12H_2O$ (KAl) and $NH_4Al(SO_4)_2\cdot 12H_2O$ (AAl), (the last two doped with 0·05% Cr^{3+}) were easily grown by slow evaporation at room temperature. In all the EPR experiments (both at ambient as well as at high pressure) the crystals were rotated about (110) axis. The ambient pressure, low temperature runs were carried out in a commercial Varian E109 spectrometer, the temperature being measured by a copper-constantan thermocouple, attached directly to the crystal inside the cavity.

The high pressure, low temperature studies were carried out using a Be-Cu, locknut-type high pressure cell, a complete description of which has been given elsewhere (Sinha and Srinivasan 1983). The high pressure cell was such that single crystal orientational studies could be carried out by rotating the magnet. The cell was immersed in a glass dewar having transfer-dewar attachments such that low temperature along with orientational study was simultaneously possible. Low temperatures were achieved by precooled nitrogen gas-flow, and the temperature was read off from a copper-constantan thermocouple attached to the cell. The large thermal capacity of the cell ensured good temperature stability (±1°C).

Considerable care was taken for the pressure calibration inside the cell, utilising the change of resistivity of manganin wire (described in detail by Sinha and Srinivasan 1983). The correct pressures, at room temperature, locked inside the pressure cell were first determined by the reading of the oil pressure gauge of hydraulic press used for pressurising. Next, the relaxation of this room temperature locked pressure with lowering of temperature was determined such that in the final analysis, only the correct value of pressure at any given low temperature was used. The upper limit of the error in pressure is estimated as the least count of the oil pressure gauge *i.e.* 200 bars.

2.2 *High pressure* NMR

The ${}^{27}Al$ nucleus ($I = 5/2$) was utilised to probe the crystalline field at the Me^{3+} site in KAl and AAl alums. The trigonal component of the field splits the nuclear levels into $I = \pm 5/2, \pm 3/2$ and $\pm 1/2$, which are further split into six levels by Zeeman interaction.

The splitting has an angular variation governed by the angle between the principal electric field gradient axis and the magnetic field H_0, and is given by the equation:

$$\Delta\nu_m = \left(\frac{3(2m-1)}{2I(2I-1)}\right)\left(\frac{e^2qQ}{h}\right)\left(\frac{3\cos^2\theta}{2}\right), \tag{2}$$

where $\Delta\nu_m$ refers to the separation of the transition $(m \leftrightarrow m-1)$ and $(-m \leftrightarrow -m+1)$. Even though the natural abundance of the ^{27}Al nucleus is 100%, the transitions between the quadrupolar split levels are hard to detect in single crystals of alum because of the large number of lines present in the case of a general orientation. However, by careful crystal orientation, a simplified five-line spectrum with a sufficiently high signal-to-noise ratio could be obtained. The axis of rotation chosen for the crystal for high pressure NMR study was the (110) axis. Angular orientation was carried out till the magnetic field direction in this plane was adjusted to make an angle of 35°16′ with one of the in-plane body-diagonals, indicated very accurately by a maximum S/N ratio. The lines in the simplified five-line spectra thus obtained were equally spaced, (in the first order), with the outermost lines corresponding to $\nu_{5/2}$: $\pm 5/2$ to $\pm 3/2$, the inner ones $\nu_{3/2}$: $\pm 3/2$ to $\pm 1/2$ while the central one was due to $\nu_{1/2}$: $\pm 1/2$ to $\mp 1/2$ transitions. Thus the splittings between these lines would yield directly the trigonal component or "*eq*" of the crystalline field. An exhaustive study of angular orientation in alums is given in the report by Weiden and Weiss (1974).

As far as the high pressure aspect of the NMR experiment was concerned, the same cell as the EPR was used. Details of this design, the actual experimental set-up as well as some of the ^{27}Al quadrupolar perturbed NMR signals are given in Sinha and Srinivasan (1983). In the NMR high-pressure experiment, there was no reduction in signal strength inside the cell as compared to that outside. The rest of the spectrometer remained the same as in the case of EPR (*i.e.* Varian E109) with only the microwave bridge being replaced by a Robinson oscillator. The magnetic field at the centre was 6300 Oe with frequency, 7·000 MHz and a scan range of 200 Oe (and in some cases 100 Oe) was used. A scan time of 1 hr with the maximum possible time constant of 30 sec was found to yield the best results. The error therefore arose only from the measurement of the magnetic field and was 4 kHz for e^2qQ/h determined from the outermost satellites and 8 kHz for that from the inner ones.

3. Results and analysis

3.1 *EPR*

In the present set of experiments, the temperature is varied continuously for different values of pressures P_{27}, clamped at room temperature (27°C). At each pressure, for each sample, at least two temperature runs were carried out in order to establish the reproducibility of the experimental data.

The D values thus obtained, as a function of temperature and pressure had to be 'reprocessed' at various stages. The 'raw' data is shown in figures 2a, b, c, d in the form of a variation of D as a function of temperature, for KAl, KCr, AAl and ACr alums respectively, at different room temperature clamped pressures, P_{27}, of 2·2, 4·2, 6·2, and 8·2 kb. These variations are labelled tentatively as "isobars" in order to emphasize that they are not actually isobars, since the pressure relaxes on lowering the temperature.

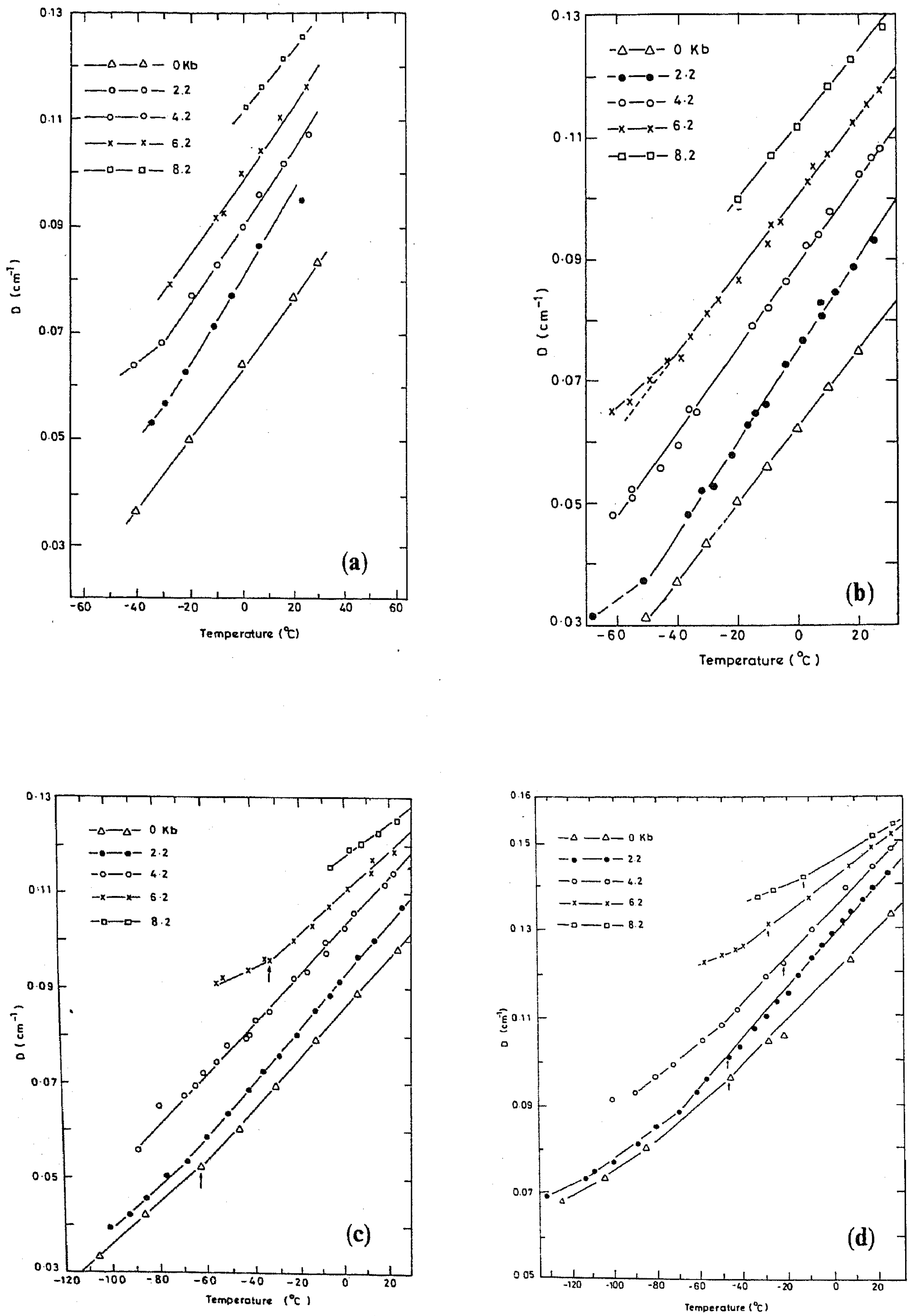


Figure 2. (**a**) "Isobars" of zero-field splitting *vs* temperature in KAl $(SO_4)_2 \cdot 12H_2O$, (Cr^{3+} doped). (**b**) "Isobars" of zero-field splitting *vs* temperature in $KCr(SO_4)_2 \cdot 12H_2O$. (**c**) "Isobars" of zero-field splitting *vs* temperature in $NH_4Al(SO_4)_2 \cdot 12H_2O$, ($Cr^{3+}$ doped). (**d**) "Isobars" of zero-field splitting *vs* temperature in $NH_4Cr(SO_4)_2 \cdot 12H_2O$.

This relaxation of P_{27} with temperature had been determined in a calibration experiment using a manganin resistance gauge, the details of which are described in Sinha and Srinivasan (1983). The pressure relaxed linearly with temperature, with the same slope, for all values of P_{27}, (small deviations from linearity being present only below 100°C), such that the pressure $P(T)$, in kb, at any temperature T (in °C) was given by:

$$P(T\,^\circ\mathrm{C}) = P_{27} + 0{\cdot}00156\,(T-27). \tag{3}$$

Having obtained the corrected pressure values in the above manner, the next step was to determine the fractional change in volume V/V_{24} of the crystal, compared with the initial volume V_{24} of the crystal at 24°C, on subjecting the crystal to an arbitrary pressure and temperature. (The choice of the volume at 24°C, V_{24} for comparison, is arbitrary). This necessitated the use of the equation of state of these crystals. One of the advantages of choosing the alums for high pressure study is the fact that most of the data necessary are available from previous studies.

The equation of state involves the derivatives of volume with respect to temperature and pressure as well as higher order derivatives. Such higher order derivatives have been used in our analysis where they were available. Thus, in Bridgman's (1952) work the compressibility had been expressed as:

$$V/V_0 = 1 + AP + BP^2. \tag{4}$$

The first and second order coefficients (A and B) had a further dependence on temperature, such that:

$$\begin{aligned} V/V_0 = 1 &+ [A_{24} + (\partial A/\partial T)_{24}\cdot(T-24)]\cdot P \\ &+ [B_{24} + (\partial B/\partial T)_{24}\cdot(T-24)]\cdot P^2, \end{aligned} \tag{5}$$

where the temperature dependences of compressibilities are assumed to be linear and expanded around 24°C. The same assumption is made for the temperature coefficient of volume which is assumed to be linear over the entire temperature range. Consideration of all the above factors yield the final form of the equation of state as:

$$\begin{aligned} V = V_0\{1 + (\partial V/\partial T)_{24}\cdot(T-24) &+ [A_{24} + (\partial A/\partial T)_{24}\cdot(T-24)]\,P \\ &+ [B_{24} + (\partial B/\partial T)_{24}\cdot(T-24)]\,P^2\}. \end{aligned} \tag{6}$$

The temperature coefficient of volume was taken from Klug and Alexander's (1942) data determined by x-ray methods and found to be linear over a temperature range of 19 to 52°C. (More recent data by Haussuhl (1961) could not be used, as all the details were not available. However, the new values confirm Klug and Alexander's to within 5%). The P values in the above equation were the values of pressure after having corrected for relaxation of pressure accompanying a decrease of temperature. There were certain parts of the data which were not available from Klug and Alexander (1942) and the assumptions made in their regard will be mentioned below.

Most of the compressibility coefficients A and B, as well as the higher order derivative with respect to temperature, $\partial A/\partial T$, $\partial B/\partial T$ had been determined by Bridgman (1952) (whose units of kg/cm^2 and (kg/cm^2)^2 first had to be converted to bars). These values had been determined with respect to the compressibility of iron, at

$$30^\circ\mathrm{C}:\ -\Delta V/V = 5{\cdot}76\times10^{-7}\,P - 2{\cdot}02\times10^{-12}\,P^2,$$

and

$$70^\circ\mathrm{C}:\ -\Delta V_0/V_0 = 5{\cdot}82\times10^{-7}\,P - 2{\cdot}02\times10^{-12}\,P^2. \tag{7}$$

More recent values of compressibility of iron as determined (at 30°C) by Vaidya and Kennedy (1970) have improved upon the values of Bridgman:

$$A = 5{\cdot}8441 \times 10^{-7}\ \text{bar}^{-1};\quad B = -1{\cdot}5008 \times 10^{-12}\ \text{bar}^{-1}. \tag{8}$$

Thus Bridgman's A and B values have to be corrected by the amounts:

$$\Delta A = +0{\cdot}08;\quad \Delta B = -0{\cdot}52. \tag{9}$$

All the values of A, B, $\partial A/\partial T$, $\partial B/\partial T$, and α were available for both KAl and AAl from Bridgman's and Klug-Alexander's data. However, for KCr alum, Bridgman could determine the A and B values only at 30°C since it dehydrated at higher temperature, while Klug and Alexander had not determined its thermal expansion coefficient. Bridgman had also been unable to determine the compressibility of ACr alum. The elastic compliance and stiffness coefficients were available from Landolt-Bornstein (1966), so that the bulk compressibility could be found from:

$$\beta = 3/(c_{11} + 2c_{12}) = 3(s_{11} + 2s_{12}), \tag{10}$$

(since the alums are cubic). However, the second order coefficients were not available in the form supplied by Bridgman. In order to fill these gaps the following assumptions were made:

(i) The temperature derivatives of A and B for KCr alum were assumed to be the same as that of KAl alum.

(ii) The (linear) thermal expansion coefficient was presumed to undergo the same change while going from KAl to KCr as in going from AAl to ACr alums *i.e.* from 9·5 to $10{\cdot}6 \times 10^{-6}$ giving a value of $12{\cdot}1 \times 10^{-6}$/K. The validity for this is borne out by Haussuhl's (1961) value of $12{\cdot}3 \times 10^{-6}$/K for KCr alum.

(iii) For the compressibility coefficients of ACr alum, the difference of A and B values of AAl and ACr was presumed to be the same as those for KAl and KCr (the corresponding potassium alums). The derivatives of A and B with respect to temperature in ACr were supposed to be the same as in the case of AAl alum.

Under all these conditions, the final values of the different coefficients appearing in the equation of state (equation (6)) that have been used, are listed in table 1.

Table 1. Values of coefficients in the equation of state for alums.

	KAl	KCr	AAl	ACr
α, $(\partial V/\partial T)_{24}$ (°K^{-1})	$3{\cdot}3 \times 10^{-5}$	$3{\cdot}6 \times 10^{-5}$*	$2{\cdot}85 \times 10^{-5}$	$3{\cdot}18 \times 10^{-5}$
A_{24} (bar^{-1})	$6{\cdot}284 \times 10^{-6}$	$6{\cdot}464 \times 10^{-6}$	$6{\cdot}259 \times 10^{-6}$	$6{\cdot}44 \times 10^{-6}$*
$(\partial A/\partial T)_{24}$ (bar^{-1} K^{-1})	$-0{\cdot}0159 \times 10^{-6}$	$-0{\cdot}0159 \times 10^{-6}$*	$-0{\cdot}0034 \times 10^{-6}$	$-0{\cdot}034 \times 10^{-7}$*
B_{24} (bar^{-2})	$114{\cdot}7 \times 10^{-12}$	$110{\cdot}7 \times 10^{-12}$	$98{\cdot}05 \times 10^{-12}$	$94{\cdot}05 \times 10^{-12}$*
$(B/T)_{24}$ (bar^{-2} K^{-1})	$-0{\cdot}5 \times 10^{-12}$	$-0{\cdot}5 \times 10^{-12}$*	$-0{\cdot}032 \times 10^{-12}$	$-0{\cdot}032 \times 10^{-12}$*

* The values in asterisk are not experimentally determined values. They have been derived following the procedure outlined in the text. The thermal expansion coefficients are from Klug and Alexander (1942), while the compressibility coefficients and their temperature derivative are from Bridgman (1952) subsequently corrected as mentioned in the text.

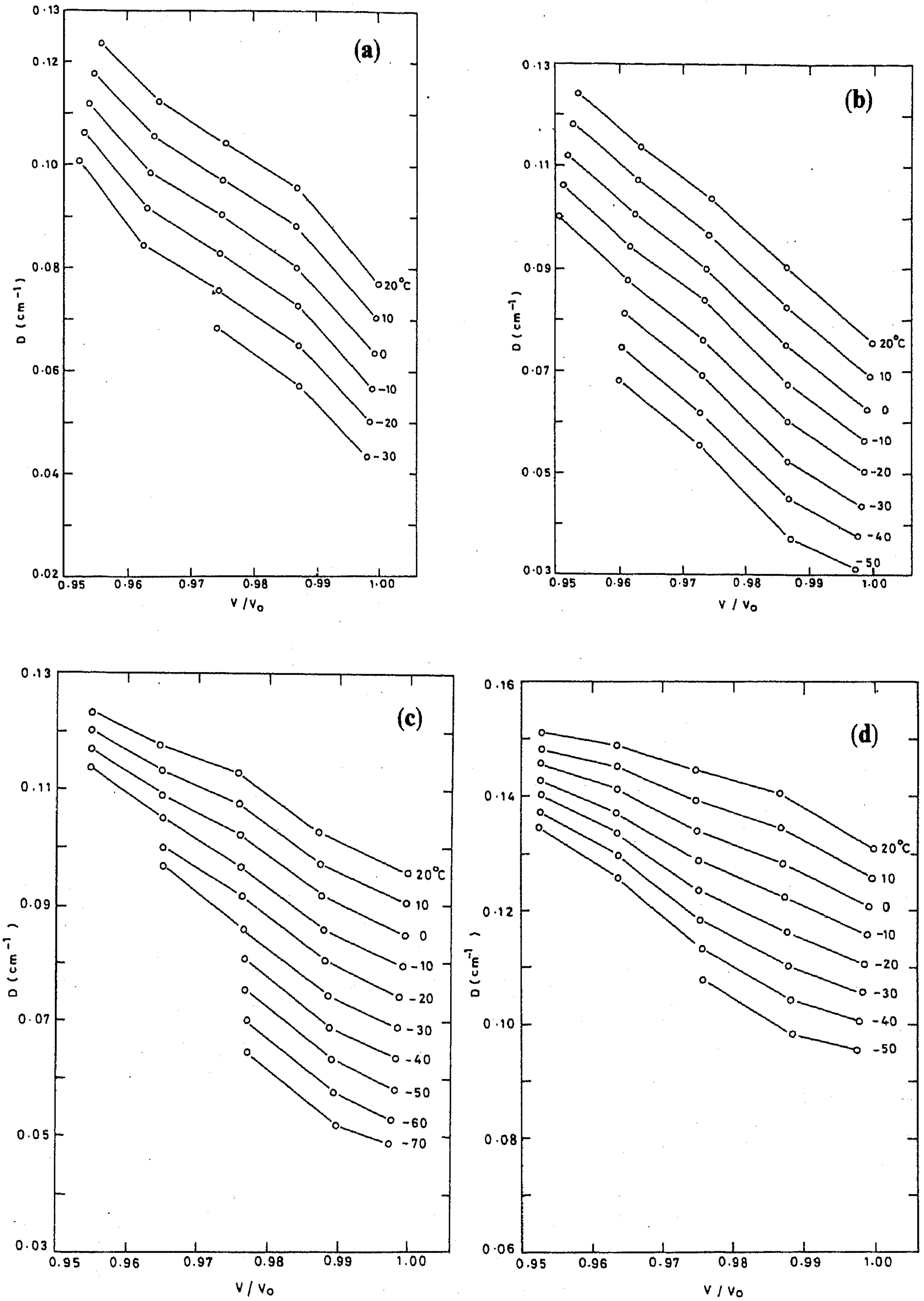


Figure 3. (**a**) Isothermal variation of zero field splitting with fractional volume in KAl alum, (Cr^{3+} doped). (**b**) Isothermal variation of zero field splitting with fractional volume in KCr alum. (**c**) Isothermal variation of zero field splitting with fractional volume in NH_4Al alum (Cr^{3+} doped). (**d**) Isothermal variation of zero field splitting with fractional volume in NH_4Cr alum.

The corrected pressure values, $P(T)$ of (3), and $T(°C)$ were substituted in the above equation of state. The variation of the zero-field splitting could next be plotted in terms of change in volume fraction (V/V_0) and are shown in figures 3a, b, c and d for KAl, KCr, AAl, and ACr alums respectively. Now, if vertical lines are drawn in these diagrams they would represent constant volume lines (no thermal expansion) with temperature variation. The corresponding Y-coordinates of the intersection points with the isotherms would represent the variation of D with temperature at constant volume *i.e.* the explicit effect. V_0 is chosen arbitrarily as the volume at 24°C at different pressures. Further, the values of V/V_0 without pressure relaxation, with decreasing temperatures can be calculated from the above equation of state and the corresponding abscissae can be determined from the isotherms of D vs (V/V_0). Thus, D vs T can be replotted, representing the actual isobars with pressure remaining constant at the room temperature locked values. Both these values representing the summation of explicit and implicit contributions to the temperature effect, (without pressure relaxation), as well as the explicit contributions (*i.e.* at constant volumes) have been drawn in figures 4a, b, c and d in the same sequence as mentioned before. The difference between these two lines represent the implicit effects. Thus finally utilising (a) the raw data of D vs T at different pressures, (b) the equation for relaxation of pressure with temperature and (c) the equation of state one obtains: (i) the true D vs T isobars, (ii) the explicit contributions, (iii) the implicit contributions and (iv) the variations of D with V/V_0, fractional volume change at constant temperature.

3.2 *NMR*

The values obtained from our experiment for the pressure dependence of e^2qQ/h for both KAl and AAl alum are given in table 2 and shown in figure 5. The standard deviation for each point was less than the error bars of 8 kHz that are shown. The variation tends to level off at about 5 kbars for both KAl and AAl alum. The value of the slope $[\partial(e^2qQ/h)/\partial P]_{27°\mathrm{C}}$, of the nuclear quadrupolar coupling constant of ^{27}Al *vs* pressure was 21·04 kHz/kbars for KAl and 12 kHz/kbars for AAl alum. The last point at 6·2 kb was left out in both the cases and the coefficient of linear regression was better than 0·999. The values of $e^2qQ/h = 401 \pm 8$ kHz for KAl and 447 ± 8 kHz for AAl, at ambient pressure compare well with those of 400 ± 8 kHz and 446 ± 8 kHz as determined by Segleken and Torrey (1977) at room temperature.

Separation of the contributions of the explicit and implicit effects to the temperature variation of e^2qQ/h, is achieved by using the equation of state:

$$\left[\frac{\partial}{\partial T}\left(\frac{e^2qQ}{h}\right)\right]_v = \left[\frac{\partial}{\partial T}\left(\frac{e^2qQ}{h}\right)\right]_P - \frac{3\alpha}{\beta}\left[\frac{\partial}{\partial P}\left(\frac{e^2qQ}{h}\right)\right]_T. \tag{11}$$

The term on the left side is the temperature dependence at ambient pressure (containing both the explicit and implicit contributions). These had been determined by Segleken and Torrey (1977) and Burns (1960) and are quoted by Weiden and Weiss (1975) as +0·92 kHz/°K for KAl alum and +1·026 kHz/°K for AAl alum. The positive values of these coefficients are characteristic of the somewhat unusual behaviour of α-alums, in that they show an increase of e^2qQ/h of ^{27}Al with increasing temperature. Generally in ionic solids one expects that with increase of temperature ions should move out, thus decreasing the e.f.g. at the quadrupolar nuclear site.

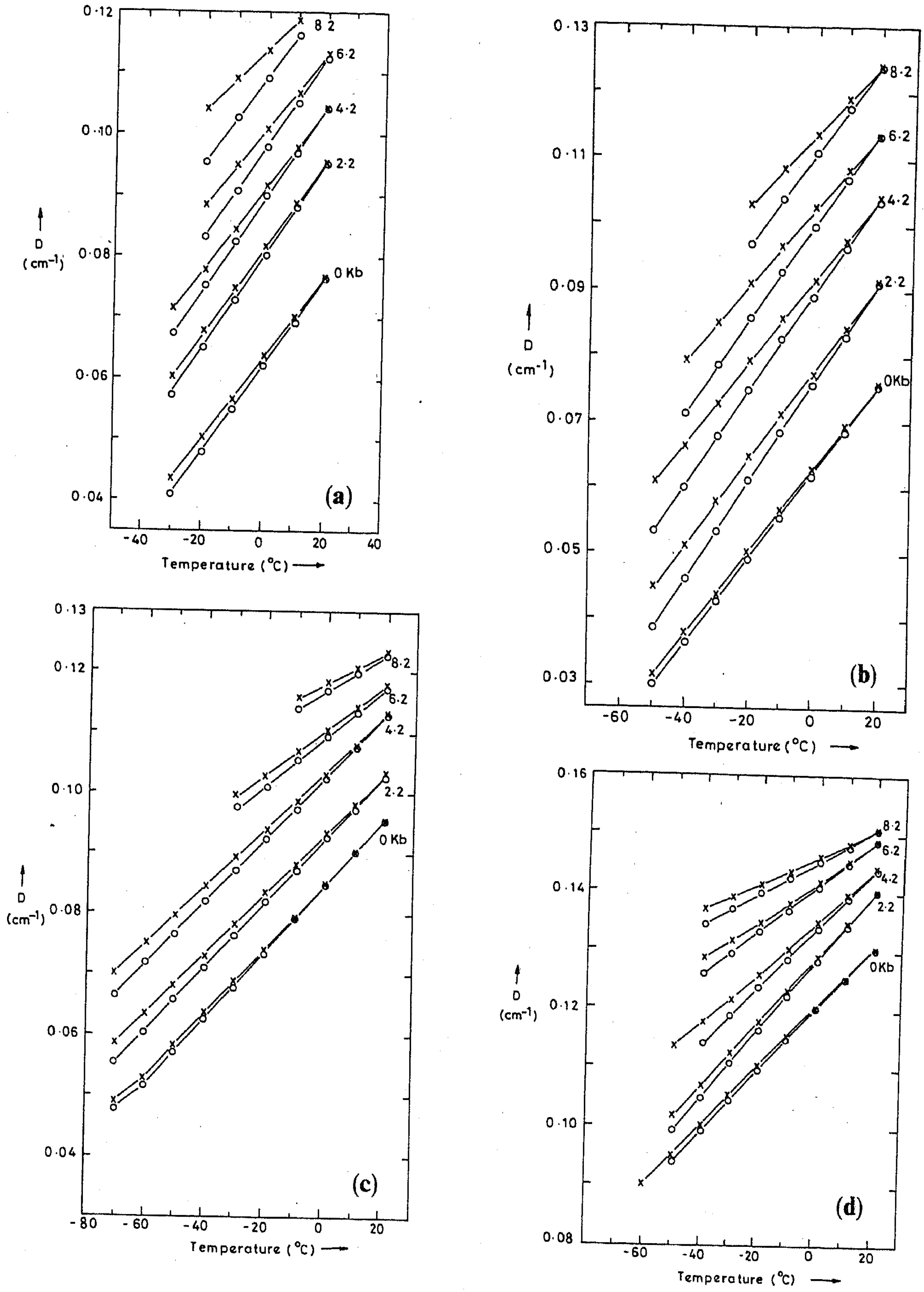


Figure 4. (**a**) Explicit (-x-x-) and sum of explicit and implicit (-o-o-) contribution to temperature dependence of zero-field splitting in KAl alum (Cr^{3+} doped). (**b**) Explicit (-x-x-) and sum of explicit and implicit (-o-o-) contribution to temperature dependence of zero-field splitting in KCr alum. (**c**) Explicit (-x-x-) and sum of explicit and implicit (-o-o-) contribution to temperature dependence of zero-field splitting in NH_4Al alum (Cr^{3+} doped). (**d**) Explicit (-x-x-) and sum of explicit and implicit (-o-o-) contribution to temperature dependence of zero-field splitting in NH_4Cr alum.

Table 2. Variation of e^2qQ/h for ^{27}Al with pressure (at room temperature).

Pressures (kbar)	KAl alum		AAl alum	
	kHz	cm^{-1} (10^7)	kHz	cm^{-1} (10^7)
0	401	133·7	447	149·1
1·16	424	140·5	461	153·7
2·16	447	148·9	473	157·5
3·17	—	—	483	160·9
4·18	489	162·9	497	165·5
5·18	505	168·2	510	170·1
6·19	514	171·3	516	172·1

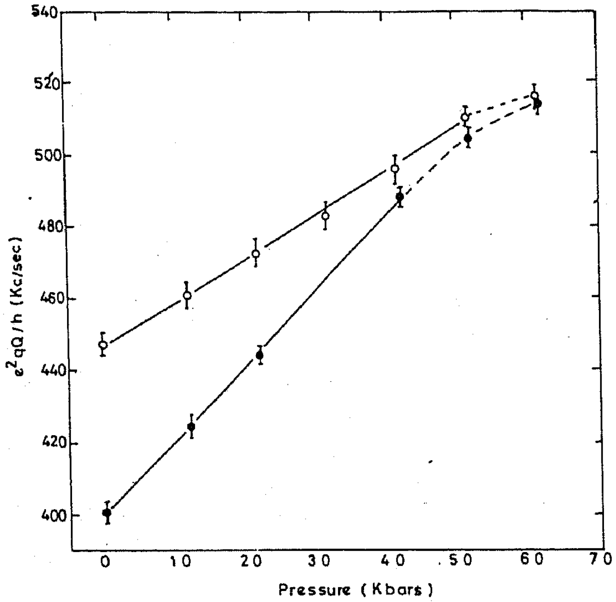


Figure 5. Variation with pressure of EFG at ^{27}Al site in (**a**) (–o–o–) KAl alum (**b**) (–o–o–) NH$_4$Al alum.

This "expected" behaviour of a negative coefficient arises out of the thermal expansion or implicit contributions. A positive coefficient therefore need not be "unexpected" if the contribution of the implicit effects is small when compared with that from the explicit effects (which may have either a positive or negative coefficient, depending on the nature of the contributing vibrations). Therefore, in order to determine the relative magnitudes of the implicit and explicit contributions a pressure experiment is necessary.

Our pressure experiment yielded the last term on the right side of (11) and has already been quoted before as the slope of the variation of e^2qQ/h with pressure. Combined with the values of α and β, this term gives the implicit contribution. The values of all the terms in the equation are given in table 3.

Thus it is seen that while the implicit contribution is indeed negative as expected, it is

Table 3. Values of the different coefficients in the equation of state (11).

	KAl alum	AAl alum
3α (°K^{-1}) Klug and Alexander (1942)	$3{\cdot}3\times10^{-5}$	$2{\cdot}85\times10^{-5}$
β (taken only to first order), bar^{-1} Bridgman (1952)	$-6{\cdot}189\times10^{-6}$	$-6{\cdot}239\times10^{-6}$
Temperature coefficient at ambient pressure, $\left[\frac{\partial}{\partial \mathrm{T}}\left(\frac{e^2qQ}{h}\right)\right]_P$ (kHz/K) Burns (1960)	$+0{\cdot}92$	$+1{\cdot}026$
Implicit contribution $\frac{3\alpha}{\beta}\left[\frac{\partial}{\partial P}\left(\frac{e^2qQ}{h}\right)\right]_T$ (kHz/K)	$-0{\cdot}11$	$-0{\cdot}055$
Explicit contribution $\left[\frac{\partial}{\partial T}\left(\frac{e^2qQ}{h}\right)\right]_V$ kHz/K	$+1{\cdot}03$	$+1{\cdot}081$

actually the large positive contribution of the explicit effect that results in a positive coefficient of the temperature variation of e^2qQ/h at constant pressure.

The explicit contribution is seen to be nearly 20 times the implicit one in the AAl alum as compared to only 9·3 times in the potassium alum. This is evident even from an examination of the dependence of EPR zero-field splitting D (which is proportional to e^2qQ/h) on temperature. The explicit and implicit contributions are given in figure 4a for KAl (:Cr) and figure 4c for AAl (:Cr) alum. The variation of D with change in volume fraction, shown in figures (3a) and (3c) also shows this clearly.

The conclusions from the above, concerning the field gradient at the trivalent ion site, can be summed up as follows:

(i) The change caused in field gradient by a change in volume is greater (twice) in potassium alum than in ammonium alum.

(ii) The change caused in the field gradient by a change of temperature at constant volume (*i.e.* the explicit contribution) is slightly smaller (about 0·95 times) in potassium alum than in the ammonium alum.

(iii) Therefore, since the explicit and implicit contributions act in opposite directions in both the cases, the temperature dependence of field gradient at constant pressure in ammonium alum is greater than that in potassium alum.

A possible reason for (ii) might be the motion of the ammonium group (over and above that of the sulphate) and is dealt with in detail in the next section.

4. Discussion

4.1 *Analysis of D and e^2qQ/h in α-alums*

The crystal field potential, limited to the fourth order term for the *d*-orbitals of the Cr^{3+} ion is given by Walsh (1959):

$$V(r) = Q_c[(10)^{1/2}(Y_4^3 - Y_4^{-3}) - (7)^{1/2}Y_4^0] + aY_2^0 + bY_4^0, \tag{12}$$

where Q_c reflects the cubic symmetry and *a*, *b*, the axial part. Both the EPR zero-field parameter *D* and the nuclear quadrupolar coupling constant, e^2qQ/h, are indicative of the axial crystalline field. *D* is proportional to the coefficients Q_c, *a* and *b*, *i.e.*

$$D = \frac{5}{4}(\Delta g/g)^2 \times \left(\frac{3}{2}\bar{a} + \frac{2}{3}\bar{b}\right), \tag{13}$$

where the deviation of the *g*-value from the free electron value g_0, is given as:

$$\Delta g = g - g_0 = (-4\lambda/15)\,(g_0/\bar{Q}_c), \tag{14}$$

where λ is the spin-orbit coupling and the bars over Q_c, *a* and *b* indicate radial averages over the *d*-orbitals. On the other hand, the quadrupolar nucleus also senses this field gradient, though by an amount smaller than the actual value, by the antishielding factor, γ_∞. Thus, there is a straightforward relationship between the *D* value of EPR and e^2qQ/h of the quadrupolar nucleus at the same site, as worked out by Burns (14):

$$D = \frac{-3}{112}(\Delta g/g_0)^2 \frac{\langle r\rangle^2 h}{(1-\gamma_\infty)Q}\left|\frac{e^2qQ}{h}\right|, \tag{15}$$

where the term involving *b* in the potential had been left out. He had tried to determine the variation of *D* with different values of e^2qQ/h, obtained by varying the temperature in $C(NH_2)_3Al(SO_4)_2 \cdot 6H_2O$ and isomorphous compounds. The assumption was that the effect of varying temperature would be solely implicit in character *i.e.* a change in the field gradient would occur solely due to thermal expansion effects, and indeed, in the particular cases of the compounds that he had studied this was the case.

However, in the case of α-alums, it has been definitely established (both by Walsh 1959 as well as our own observations) that the temperature effects are overwhelmingly explicit in character. Hence, the better way of obtaining different EFGs for different interionic distances (in order to correlate the corresponding *D* and e^2qQ/h values) would be through high pressure experiments where complications from explicit contributions do not arise. In this respect, our experiment is an improvement over Burns.

Using the results of the dependence of *D* on pressure (described in §3.1) and combining it with the dependence of e^2qQ/h on pressure (§3.2), one can parametrically eliminate pressure and obtain the dependence of *D* on e^2qQ/h. Table 4 gives such a comparison between *D* and e^2qQ/h for both KAl and AAl alums, and is shown graphically in figure 6. The slope thus obtained (of *D* vs e^2qQ/h) for KAl alum was $3{\cdot}1 \times 10^{-4}$ cm^{-1}/kHz or $9{\cdot}4 \times 10^3$ cm^{-1}/cm^{-1}, while the intercept on the *D* axis was $-0{\cdot}0498$ cm^{-1}. Similar figures of slope for the AAl was $3{\cdot}13 \times 10^{-4}$ cm^{-1}/kHz (or $9{\cdot}49 \times 10^3$ cm^{-1}/cm^{-1}) while the *y*-intercept was $-0{\cdot}045$ cm^{-1}. Comparison of the two figures for the two different alums obviously yields very good agreement. Considering that this comparison involved two different lattices and used two different

Table 4. Comparison of D and e^2qQ/h in KAl and AAl alums.

	KAl alum		AAl alum	
Pressure (kb)	e^2qQ/h kHz ($cm^{-1} \times 10^7$)	D cm^{-1}	e^2qQ/h kHz ($cm^{-1} \times 10^7$)	D cm^{-1}
0	401 (134)	0·0770	447 (149)	0·0953
1·2	424 (141)	0·0831	461 (154)	0·0991
2·2	447 (149)	0·0893	473 (158)	0·1028
3·2		—	483 (161)	0·1065
4·2	489 (163)	0·1019	497 (165)	0·1102
5·2	505 (168)	0·1076	510 (170)	0·1139
6·2	514 (171)	0·1137	516 (172)	0·1176

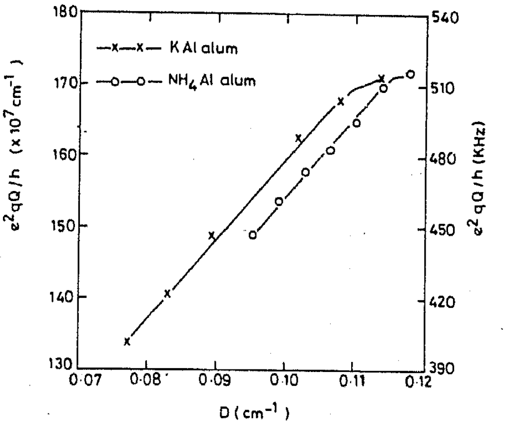


Figure 6. Comparison of field gradient at Me^{3+} site, as sensed by EPR (D parameter) and NMR (e^2qQ/h).

spectroscopic techniques, the agreement serves as a good proof of the consistency of the experiment and Burns' ideas. The value of the slope, $3{\cdot}13 \times 10^{-4}$ cm^{-1}/kHz, also agrees reasonably well with the figure of $2{\cdot}6 \times 10^{-4}$ cm^{-1}/kHz, obtained by Burns (1961) for the system: $C(NH_2)_3 \cdot Al(SO_4)_2 \cdot 6H_2O$ and isomorphous compounds.

Like Burns (1961) our value of the slope is larger than the theoretically expected value by an order of magnitude. This discrepancy is best attributed to (i) the shortcomings of the point charge approximation. A plot of the Hartree-Fock wavefunction of the $3d^3$

electron of Cr^{3+} revealed a considerable overlap with the nearest neighbour point dipole of the water molecule, thus making such approximations as the above equation (equation (15)) unreliable, (ii) the dependence of the EPR spin Hamiltonian parameter D on the crystalline field potential terms (Y_2^0, Y_4^0) assumed by Burns (originally developed by Becquerel and Opechowski (1932) are to some degree approximate. More rigorous calculations (Klein *et al* 1977) yielded contributions from anisotropic spin-orbit coupling as well as higher order admixing of excited levels into the ground state $^4A_2$ of Cr^{3+}. Considering these approximations, the discrepancy of the value of the slope is not surprising. (iii) In spite of the above two reasons, we feel the main shortcoming in Burns' derivation lies in the assumption that the source of the trigonal field is the distorted water octahedra. This was also assumed by Walsh (1959) in the derivation for D in $NiSiF_6 \cdot 6H_2O$, upon which work Burns' derivation was based. Our belief is that it is caused by the SO_4^{2-} ions on the (111) axis. (iv) One further possibility pointed out by Kruczynski and Pietrzak (1982) was the contribution of the higher order derivative of the crystal field potential (the term bY_4^0 in (12)) to the value of D. These were not considered by Burns.

The negative value of the intercept for both the cases of K and NH_4 alum indicates that the EPR parameter D goes through zero for a finite value of e^2qQ/h. This fact seems to be a result of the discrepancy in size of the Cr^{3+} ion (0·63Å) as compared with the host ion Al^{3+} (0·51Å). The discrepancy of the local compressibility value around the impurity ion Cr^{3+} as compared with the bulk value which is applicable for the ^{27}Al nucleus is not predictable, though some attempts have been made (Rimai *et al* 1964; Blum 1967).

4.2 *Origin of the crystalline field at the trivalent ion site and its temperature dependence*

The alum unit cell, containing four formula units of $Me^+ \; Me^{3+}(SO_4)_2 \cdot 12H_2O$ becomes complicated, in spite of its cubic symmetry, because of the close proximity of a large number of ions. The situation is made more complex in the α-alums because of the disorder of the SO_4 groups. Because of this, as already pointed out in §1, correlation between experiment and theory has not been able to unambiguously settle for any one model. We believe our investigation of the dependence of the crystalline field on both the thermodynamic parameters, temperature and pressure, monitored through EPR and NMR clarifies the situation to a certain extent. In the following, the origin of the static component of the crystalline field at Me^{3+} site will be discussed first and then its explicit characteristics will be considered.

We start by considering the point of contradiction between our results and those of Weiden and Weiss (1974, 1975, 1979) (already pointed out in §1). Weiss *et al* found a linear relation between $1/d^3$ (where d is the distance Me^{3+} sulphur atom on the three-fold axis) and the EFG at the Me^{3+} site, when considering the series of K, NH_4 and Rb aluminium alums. They, however, found that the slope was the reverse of the expected one and presumed as a working hypothesis, that an increase of d somehow decreased the symmetry of the field caused by the SO_4 groups. We feel that such arguments about the origin of the EFG refer specifically to its implicit (static) part and that an initial separation of the implicit and explicit contributions becomes necessary. Our experimental data on the variation of the EFG with pressure allow us to establish that the explicit contribution to the EFG is much larger (~10 times in the case of KAl and 20 in

NH_4 alum) than the implicit one. Therefore, Weiss' comparison of their theoretically derived value of the essentially, static component of the EFG with the experimentally determined value, which included both static and explicit components (which differ from system to system) is wrong. Now, our experiments yield the implicit contribution to the temperature variation as $-0{\cdot}55$ kHz/K in the case of the NH_4 alum and $-0{\cdot}11$ kHz/K in the case of K-alum. It should be noted that these figures are derivatives and not actual EFGs. Firstly, the negative sign for both the alums correctly implies that with increasing temperature, EFG decreases, as expected from thermal expansion effects in ionic solids. This also implies that Weiss' working hypothesis (referred to above) was unphysical because he compared the sum total of implicit and explicit contributions in the different alums. Secondly, the amount by which EFG changes due to a certain amount of thermal expansion in the NH_4 alum is half of that by which it changes in the potassium alums. This is consistent with the fact that d ($Me^{3+} \leftrightarrow S$) is larger in the NH_4-alum than in the K-alum, and hence, a change in S position would cause a smaller change ($1/d^n$) in the trigonal field at Me^{3+} in the NH_4-alum than in the K-alum. This would be true only under the assumption that the trigonal field is caused solely by the SO_4 groups.

We feel that the model approaches the correct picture and confirms Weiss' conclusions with certain essential modifications. In an attempt to locate the origins of the trigonal field at Me^{3+} it would be more fruitful to consider the derivatives with respect to temperature rather than the actual magnitudes of the zero-field splitting D, or the quadrupolar coupling eq^2Q/h. Such a comparison of the temperature dependence of the EFG in various alums is provided by table 2 in Weiden and Weiss (1975). It is immediately obvious from the table that only those alums show a large temperature dependence of their EFG in which the SO_4 groups are associated with a large thermal disorder, namely, the α-alums. In comparison, the β-alums do not show such large temperature dependence of either the nuclear coupling constant or the EPR D parameter.

The importance of the role of the sulphate group has already been made clear in Sinha and Srinivasan (1982). The rate of the fluctuations of the sulphate group between the two configurations on the (111) axis coincides with the timescale of the EPR experiment. The role of the SO_4 disorder in determining the temperature derivative, in the α-alums, has already been established by a comparison of its temperature variation of D with that in the β-alum, $CsAl(SO_4)_2{\cdot}12H_2O$ (which does not show a large dependence of either D or linewidth on temperature, consistent with the fact that there is no sulphate disorder in β-alum).

Weiden and Weiss (1975) made an extensive experimental study of the temperature variation of the EFG along with a comparison with theoretical models. However, we feel that there was a basic flaw in their model. In estimating the effects of the lattice vibrations, they calculated the variation in the EFG experienced by the Me^{3+} ion, as with increasing temperature, it increased its amplitude of motion along the (111) axis. The explicit character was incorporated only in the increased amplitude of the Me^{3+} vibrations. However, this approach did not account for the explicit contributions from the sources themselves, namely the SO_4^2 and H_2O ions. We feel it is the highly temperature sensitive motion of the SO_4 group which causes the large temperature dependence of the trigonal field at the Me^{3+} itself.

Thus, the sulphate group plays a very important role in creating the trigonal field, as well as the latter's dependence on temperature. However, the sulphate groups acting

Table 5. Thermal parameters (A)^2.

	α-alum (KCr) Bacon and Gardner (1958)	β-alum (CsAl) Cromer *et al* (1966)
Sulphate groups		
S	2·2	1·5
$O_s(1)$	8·0*	2·5
$O_s(2)$	6·9*	2·2
H_2O (2) molecule		
$O_W(2)$	2·5	1·9
$H_W(2)$	2·5	1·6
$H_W(2)$	4·1	2·7

directly on Me^{3+} site cannot be considered to be the sole origin of the trigonal field. The point charge calculations of Walsh (1959) as well as of O'Reilly and Tsang (1967) and finally the fact that Weiden and Weiss (1975, 1979) had to include the contribution of the H_2O molecules to get qualitative agreement with experiment, strongly imply that the water octahedron also makes a partial contribution. All the water molecules in the octahedron are hydrogen-bonded to at least one sulphate group. Thus the disorder of the sulphate group can be easily conceived to be transmitted to an equivalent disorder or motion of the H_2O molecules. This is also proved when a comparison is made of the thermal parameters of the atoms in the SO_4 groups and the H_2O (2) in the two cases of the α and β-alums (table 5). The comparison readily reveals that the large disorder of the sulphate oxygens $O_s(1)$ and $O_s(2)$ in the α-alums (in comparison to the β-alums) seems to be carried over to the disorder in the corresponding water molecules around Me^{3+} in the α-alum in contrast to the lower disorder in the β-alum.

In the following, certain aspects of our experimental results are given which lend support to the model described above.

(i) The change in the trigonal field at Me^{3+}, accompanying a change of interatomic distance is greater in the potassium alum than in the corresponding ammonium alum. This is illustrated by (a) the slope of D vs V/V_0 is much greater for KAl as well as KCr alum in figures 3a and 3b when compared with the same for AAl and ACr in figures 3c and 3d. (b) The implicit contribution to the D dependence on temperature as shown in figures 4a and 4b for KAl and KCr (in the form of the difference between the explicit contribution and ambient pressure temperature variation) is greater than the same in the NH_4 alum as shown in figures 4c and 4d. (c) Further the implicit contribution to e^2qQ/h in KAl alum is twice that in NH_4 alum as shown in §3.2. All these three facts can be explained on the basis of the fact that the distance d ($Me^{3+} \leftrightarrow SO_4$ on trigonal axis) is 6·475 Å in the KAl alum as compared with 6·551 Å in the AAl alum. Thus, a small atomic displacement of the SO_4 on the (111) axis, as would accompany a thermal expansion process, is likely to cause a much greater change in the KAl alum where it is nearer the Me^{3+} as compared with the AAl alum.

(ii) Walsh (1959) considered the variation of zero field splitting

$$D \propto (a/Q_c^2)$$

with volume. He assumed both Q_c, the cubic field component ($\alpha\, 1/d'^6$) as well as, a, the axial field component ($\alpha\, 1/d'^4$) were caused by the immediate octahedron of water molecules, where d' is the distance between Me^{3+} and H_2O (2). Thus, the variation of D with volume that he obtained was,

$$\frac{\partial \ln D}{\partial \ln V} = \frac{1}{3}\frac{\partial \ln D}{\partial \ln (d')} \simeq 8/3.$$

The implication of the above is somewhat surprising in that it implies D increases with increasing volume. One of the reasons for this is that Walsh assumed *both* the cubic and the axial field to be produced by the water octahedron. On the other hand, according to our conclusion, the cubic part is caused predominantly by the water octahedron, while the trigonal part primarily by the two sulphate groups on the (111) axis. A uniform compression would yield a (d') (Danilov *et al* 1973) dependence of D due to the first mechanism and a $(d')^{-3}$ or $1/V$ dependence due to the second. Depending on the relative compressibility of the water octahedron and the SO_4 cage, the dependence of D would vary between V^n, $(n \simeq 4)$ and V^{-1}. The actual dependence is of a linear type, $(1-KV)$, with K dependent on temperature. Hence, we find it more plausible to conclude that the trigonality is caused mainly by the SO_4 ions. At higher pressures, *i.e.* low values of V/V_0, the levelling of D vs V/V_0, might qualitatively be explained as being due to the compression of water octahedron, *i.e.* V^n mechanism taking over.

(iii) The explicit contribution to the temperature variation is found to be slightly larger in the NH_4 alum than in the potassium alum. This extra contribution may be expected to be due to the disorder of the NH_4 ions. The other aspect of the negative slope of D vs $1/d^3$ for the three alums of Rb, NH_4 and K, respectively can only be attributed to explicit contributions, since a positive slope of D vs $1/d^3$ has been verified in (i) above.

(iv) The last point concerns the second derivatives of the isobars of D vs T. At the outset it must be mentioned that our experiments as well as the values of the coefficient in the equation of state are not accurate enough to justify quantitative estimates. However, it is found in all the isobars (figures 3a, b, c and d) that the slope of the explicit contribution decreases with increasing pressure (*i.e.* $(\partial/\partial P)$ $(\partial D/\partial T_V) < 0$. This can be qualitatively attributed to the effect of pressure increasing the potential barrier between the two configurations of the SO_4 group. Similarly, the implicit contribution to the temperature variation is seen to increase with increase of pressure, at the same temperature *i.e.*

$$\frac{\partial}{\partial P}\left(\frac{\partial D}{\partial V}\times\frac{\partial V}{\partial T}\right) > 0,$$

and that this coefficient is greater in the K alum than in the NH_4 alum. This is because, with increasing pressure, the SO_4 moves closer to the Me^{3+}, and in this new position, a change in the SO_4 position due to (implicit) thermal expansion effects cause a greater change in the field gradient than in the lower pressure situation. All these conclusions are subject to the dependence of the thermal expansion and compressibility on the variation of temperature and pressure.

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