

Nuclear Quadrupole Resonance and Electron Spin Resonance in $C(NH_2)_3Al(SO_4)_2 \cdot 6H_2O$ and Isomorphous Compounds*

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The temperature dependence of the nuclear quadrupole coupling parameters, eQq/h , of Al and Ga has been measured in the ferroelectric compound $C(NH_2)_3Al(SO_4)_2 \cdot 6H_2O$ (GAISH) and three other isomorphous compounds that result when Ga replaces Al and SeO_4 replaces SO_4 . Measurements were also made on deuterated GAISH. The temperature dependence of the electron spin resonance (ESR) of Cr^{3+} , substituted for Al or Ga in the above five compounds, was also measured. For the five compounds, eQq/h versus temperature for each compound was similar, small (~ 100 kc/sec), linear with temperature, and in some cases changed sign. Within the framework of the ionic model, eQq/h and $d(eQq/h)/dT$ have been calculated. It is found that the latter is fairly insensitive to the x-ray and charge distribution parameters and depends mainly on the large anisotropic thermal expansion coefficient. Using the theoretically calculated antishielding factor, there is agreement between the calculated and the measured $d(eQq/h)/dT$. The data also indicate that the ratio of the antishielding factors of Al^{3+} and Ga^{3+} are in approximate agreement with the calculated values.

The temperature dependence of the electron spin resonance of

Cr^{3+} in the five compounds is again similar to each other. The g values for the Al and Ga compounds are the same within experimental error. The zero-field splitting (D term in the spin-Hamiltonian) of the deuterated GAISH has a slightly larger variation with temperature than the undeuterated compound. By parametrically eliminating temperature, the relation between D and eQq/h is studied. The result is two parallel lines, one for the two different sites in the two Al compounds and the other for the Ga compounds. The lines are parallel only if the Ga nuclear quadrupole moment and antishielding factor are normalized to those of Al. Using simple crystal field theory, it is shown that D should be proportional to eQq/h . However, the data show that D and eQq/h are not simultaneously zero and that the slope is ten times larger than calculated. These two discrepancies are discussed. A calculation of the extra potential seen by the $3d$ electrons, due to the fact that the crystal field induces a quadrupole moment in the core electrons, is discussed. However it does not remove the discrepancy. It appears that the relation between D and the crystalline field is not firmly established.

INTRODUCTION

SINCE Pound¹ studied the quadrupole splitting of nuclear magnetic resonance (NMR) lines in solids and Dehmelt and Kruger² observed pure quadrupole resonance in solids, the techniques of quadrupole resonance have been used as a sensitive probe to study internal fields.³ Electron spin resonance has also been used fruitfully for similar purposes.⁴ In this paper the results of applying both of these techniques to a series of five isomorphous compounds are reported and discussed.

The isomorphous compounds studied are listed in Table I with the abbreviations that shall be used to identify them. All of these compounds are ferroelectric⁵ over the entire temperature range studied. Heating causes them to decompose rather than go into a paraelectric state. The temperature dependence of the nuclear quadrupole coupling constant, eQq/h , of Al and Ga has been measured. The electron spin resonance (ESR) has been measured by substituting small

amounts of Cr^{3+} in place of Al^{3+} or Ga^{3+} . This is easily done since $C(NH_2)_3Cr(SO_4)_2 \cdot 6H_2O$ is isomorphous with the compounds listed in Table I.

The temperature dependence of eQq/h and the electron spin resonance in general are similar for all these compounds. The quadrupole coupling constant is linear with temperature and for several compounds exhibits the unusual behavior of passing through zero. Without going into any detailed model, one can understand the difference in the slopes of eQq/h versus temperature for the Ga and Al compounds in terms of the difference in the nuclear quadrupole moments and antishielding factors. Then, using a model in which the highly anisotropic thermal expansion coefficients⁶ play an important role, the slope of eQq/h versus temperature can be calculated and compared with the experimental results.

The electron resonance results for Cr^{3+} indicate the cubic component of the crystalline field has the same value in both the Ga^{3+} and Al^{3+} compounds. However, the axial components differ (i.e., the D term in the spin Hamiltonian, which is a measure of the axial component of the crystalline field). By parametrically eliminating temperature, eQq/h of Al^{3+} or Ga^{3+} versus D of Cr^{3+} is considered. The result is two straight lines. One line for both sites in both Al compounds and the other for both Ga compounds. The two lines are parallel when normalized to the same Q and antishielding factor. Simple arguments are given to show why a linear relationship is expected, but detailed analysis indicates inadequacies in crystal field theories.

* A preliminary account of some of this work has appeared in Bull. Am. Phys. Soc. **3**, 371 (1958).

¹ R. V. Pound, Phys. Rev. **79**, 685 (1950).

² H. G. Dehmelt and H. Kruger, Naturwissenschaften **37**, 111 (1950).

³ For general references to the field of NQR see: M. H. Cohen and F. Reif, *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., N. Y., 1958), Vol. 5; and T. P. Das and E. L. Hahn, *ibid.*, Suppl. 1.

⁴ For general references to the field of ESR see: W. Low, *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York (1960) Suppl. 2; and B. Bleaney and K. W. H. Stevens, Repts. Progr. in Phys. **16**, 108 (1953).

⁵ A. N. Holden, W. J. Merz, J. P. Remeika, and B. T. Matthias, Phys. Rev. **101**, 962 (1956).

TABLE I. General summary of results of others, and resonance results reported here.

Compound	Abbr.	Unit cell ^b			Thermal exp. ^d (10^{-6} deg ⁻¹)		Site	eQq/h (kc/sec) 23°C	$d(eQq/h)/dT$ (kc/sec) deg ⁻¹	g at 24°C	D (cm ⁻¹) at 24°C	g at -196°C	D (cm ⁻¹) at -196°C
		a (Å)	c (Å)	c/a	α_c	α_a							
$C(NH_2)_3Al(SO_4)_3 \cdot 6H_2O$	GAISH	11.745	8.592	0.7622	92.80	10.05	(1)	± 23	0.575	1.978	0.0752	0.107 ^f	
							(2)	∓ 30	0.411	0.0593	0.0821 ^f		
$C(NH_2)_3Al(SeO_4)_3 \cdot 6H_2O$	GAlSeH	11.989	9.062	0.7560	83.89	10.16	(1)	± 300	0.525	1.977	0.143	1.976	0.185
							(2)	± 200	0.228	0.110	0.131		
$C(NH_2)_3Ga(SO_4)_3 \cdot 6H_2O$	GGaSH	11.761	9.051	0.7696	83.85	14.17	(1)	∓ 485 (∓ 253)	1.96(1.02)	1.976	0.0576	1.978	0.0866
							(2)	∓ 635 (∓ 331)	1.51(0.787)	0.0456	0.0664		
$C(NH_2)_3Ga(SeO_4)_3 \cdot 6H_2O$	GGaSeH	12.020	9.144	0.7607	71.16	12.07	(1)	± 78 (± 41)	2.29(1.19)	1.977	0.100	1.975	0.119
							(2)	∓ 197 (∓ 103)	1.13(0.589)	0.0774 ^e	0.114		
$C(ND_2)_3Al(SO_4)_3 \cdot 6D_2O^a$	GAISD	c	c	c	c	c	(1)	c	c	1.977 ^e	0.0610 ^e	0.0885	
							(2)	c	c	0.0610 ^e	0.0885		

^a By comparing the proton resonance in this sample with that obtained from GAISH, this compound is 85% deuterated. Since the samples used for the electron resonance were grown from 99.5% D₂O, this sample is probably deuterated by at least the same amount.

^b These are results of N. Stemple (private communication) and are in good agreement with other recent measurements. He also finds $c=9.026$ and $a=11.809$ for $C(NH_2)_3V(SO_4)_3 \cdot 6H_2O$.

^c These results are the same as in GAISH.

^d These are results of Haussuhl and Trost. See reference 13.

^e This has been measured at 20° rather than 24°C.

^f This has been measured at -164° rather than -196°C.

CRYSTALLOGRAPHY

The crystal structure of GGaSH has been determined by Geller and Booth.⁶ Their results will be used in this paper. Other but less complete, results have also been published.⁷

The space group of this trigonal crystal is C_{3v}^2-P31m with three molecules per cell as shown in Fig. 1. The Ga³⁺ ions are on threefold axes and are surrounded by a somewhat distorted octahedra of waters. The guanidinium ions lie above and below the octahedra and are loosely bound indicating the possibility of disorder or rotation. Proton resonance measurements indicate this may be the case.^{8,9}

Of the three Ga ions per cell, two are equivalent to each other and called site 2 or (2). The other is called site 1 or (1).

The lattice parameters used are listed in Table I. They have been measured by Stemple¹⁰ of this laboratory and are in good agreement with those published recently by Haussuhl¹¹ and the values measured by Ezhkova *et al.*¹² for GAISH. Haussuhl and Trost¹³ have measured the coefficients of thermal expansion and they are listed in Table I for convenience. Their results are in good agreement with those obtained by Ezhkova *et al.*¹² for GAISH.

⁶ S. Geller and D. P. Booth, *Z. Krist.* **III**, 2 (1958). See also S. Geller, *Z. Krist.* **114**, 148 (1960).

⁷ L. A. Varfolomeeva, G. S. Zhdanov, and M. M. Umanskii, *Kristallografiya* **3**, 368 (1958) [Translation: *Soviet Phys.—Cryst.* **3**, 369 (1958)].

⁸ D. W. McCall, *J. Chem. Phys.* **26**, 706 (1957).

⁹ R. D. Spence and J. Muller, *J. Chem. Phys.* **26**, 706 (1957).

¹⁰ N. Stemple (private communication).

¹¹ S. Haussuhl, *Z. Krist.* **III**, 5 (1959).

¹² Z. I. Ezhkova, G. S. Zhdanov, and M. M. Umanskii, *Kristallografiya* **3**, 231 (1958) [Translation: *Soviet Phys.—Cryst.* **3**, 230 (1958)].

¹³ S. Haussuhl and F. Trost, *Z. Naturforsch.* **14a**, 437 (1959).

EXPERIMENTAL PART

The quadrupole coupling constants were small enough so that they could be found by measuring the splitting of the nuclear magnetic resonance line. A Pound-Knight-Watkins¹⁴ spectrometer with minor modifications and a 12-in. Varian magnet capable of rotating about the vertical axis were used. The work was done at fixed frequency (15.8 Mc/sec for Al²⁷) while the magnetic field was slowly swept through the resonances.

The temperature of the sample was accurately

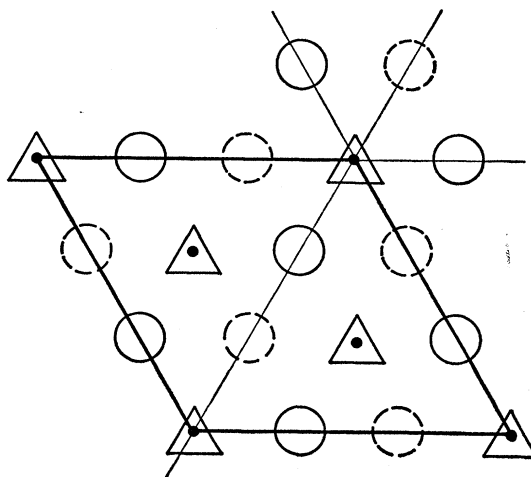


FIG. 1. A schematic diagram of a unit cell of GAISH looking down the c axis. The triangles represent threefold axes with Al ions in the plane of the paper and a guanidine ion above and below. Each Al ion is octahedrally surrounded by six waters. The circles represent SO_4^{-2} groups above the plane and the dotted ones below.

¹⁴ R. V. Pound and W. D. Knight, *Rev. Sci. Instr.* **21**, 219 (1950). R. V. Pound, *Progr. in Nuclear Phys.* **2**, 21 (1952).

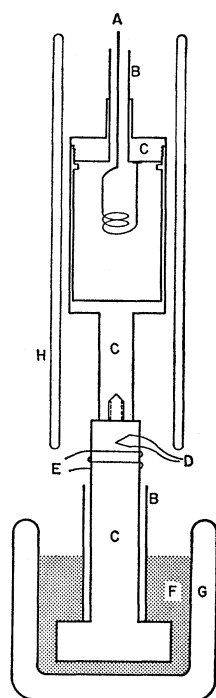


FIG. 2. A schematic diagram of the sample holder and cooling system. *A*—Silverplated, stainless steel rf lead. *B*—Thin-walled stainless steel. *C*—Copper. *D*—Control thermocouple. *E*—Heater. *F*—Coolant (liquid nitrogen, etc.). *G*—Dewar. *H*—Bottomless Dewar.

controlled by a proportional controller similar to that described by Gunther-Mohr and Triebwasser.¹⁵ The heater, noninductively wound constantan wire, was located on the copper rod that served to connect the sample container thermally to the coolant below. The control thermocouple was in the copper rod close to the heater. Another thermocouple in the sample container was used to measure the sample temperature. The arrangement can be seen in Fig. 2.

Most of the samples were grown at room temperature from water solutions. The Cr³⁺-doped samples were grown the same way with no difficulty.

The electron-spin resonance was observed in a Varian X-band spectrometer using a TE_{012} mode cavity. A small piece of DPPH ($g=2.0037$)¹⁶ was glued to the sample to determine the g of the resonance. The field at which resonance occurred was determined by measuring a proton resonance while sitting on the resonance line. Only the splitting between the lines is required to determine the coefficients in the spin-Hamiltonian.

RESULTS

The temperature dependence of eQq/h is shown in Fig. 3. The field gradient tensor has axial symmetry about the c axis (splitting of the lines $\propto (3 \cos^2\theta - 1)$, where θ is the angle between the c axis of the crystals and the external magnetic field), as would be expected from the x-ray work^{6,7} and from the previously reported

¹⁵ G. R. Gunther-Mohr and S. Triebwasser, IBM J. Research Develop. **1**, 84 (1957).

¹⁶ C. A. Hutchison and R. C. Pastor, Phys. Rev. **81**, 282 (1951).

electron spin resonance of Cr in GAISH.¹⁷ There are two curves for each compound. One set of observed lines had twice the intensity of the other. Thus the lines corresponded to site (2) and site (1), respectively.

The pattern obtained on the chart recorder sometimes was complicated (see Fig. 4) due to the small value of eQq/h and the fact that the quadrupole coupling constants of the two nonequivalent sites were equal or one was half of the other at certain temperatures. To remove possibilities of error, especially for GAISH, the temperature dependence was followed in some detail, as can be seen by the large number of data points for GAISH in Fig. 3.

The Ga results in Fig. 3 are those for Ga⁷¹. However, some of the points on the GGa⁷¹SH (2) line were obtained by observing the Ga⁶⁹ resonance and then converting it to Ga⁷¹ by using the accurately known ratio of the quadrupole moments ($Ga^{69}/Ga^{71}=1.5868$).¹⁸ The crystals that were used for Ga resonances were thin and in both cases a reasonable filling factor was obtained only by stacking. Fortunately, the good cleavage and growth plane perpendicular to the c axis enabled the stacking to be accomplished with minimum misalignment. However the satellites were broader than the Al lines. This, along with the fact that the natural abundance of Ga⁷¹ is $\sim 40\%$, made observations of the Ga resonances more difficult than the Al. Thus the temperature dependence of eQq/h could not be followed to as high a temperature as the Al resonances.

The results of electron spin resonances of Cr³⁺ in the five compounds are given in Table I. The resonances are fitted to the usual spin-Hamiltonian for Cr³⁺ in axial

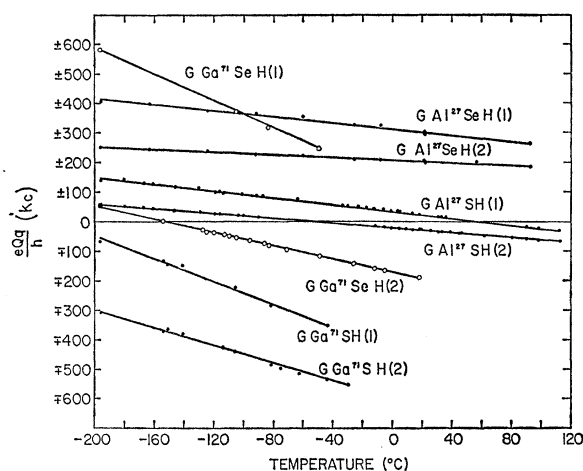


FIG. 3. eQq/h (in kc/sec) vs temperature for the two different sites in the five crystals studied. The line for GAISH also includes points obtained from the deuterated compound as no difference could be detected.

¹⁷ G. S. Bogle, J. R. Gabriel, and G. A. Bottomley, Trans. Faraday Soc. **53**, 1058 (1957). J. M. Daniels and H. Wesemeyer, Can. J. Phys. **36**, 144 (1958). E. G. Brock, E. I. Hormats, and F. C. Unterleitner, Bull. Am. Phys. Soc. **5**, 58 (1960).

¹⁸ G. E. Becker and P. Kusch, Phys. Rev. **73**, 584 (1948).

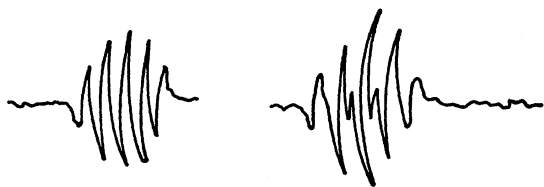


FIG. 4. Examples of the recorder traces for Al^{27} . In one trace both sites have the same quadrupole splitting. In the other, site 2 has twice the splitting of site 1.

symmetry

$$\mathfrak{H}c = g\beta\mathbf{H} \cdot \mathbf{S} + D[S_z^2 - 1/3S(S+1)], \quad (1)$$

where $S = \frac{3}{2}$ and g and D are obtained independently from the data. Angular measurements gave $g_{11} = g_{\perp}$ within experimental error.

The linewidths were 8 to 11 gauss peak to peak for the samples containing protons and 5 gauss peak to peak for the deuterated GAISD. The electron spin resonance in GAISH can be compared to three previously reported results in this compound.¹⁷ The D 's at 24°C are all close but there appears a definite concentration dependence. The D 's obtained from crystals with the widest lines were the smallest. Thus, D of the pure Cr compounds will probably be smaller than that of GAISH. The g 's obtained are in agreement with those previously reported. Here and elsewhere¹⁷ both sites have the same g while Bogle *et al.*¹⁷ find two different g 's at 17°C.

The optical absorption spectra of Cr^{3+} in $C(NH_2)_3-Cr(SO_4)_2 \cdot 6H_2O$ show absorptions at 17 500, 24 600 and 38 800 cm^{-1} . This is in good agreement with the spectra found in $KCr(SO_4)_2 \cdot 12H_2O$ ¹⁹ which is an alum. The absorption spectra were run on a model 14 Cary spectrometer at room temperature. The agreement is to be expected since the absorption spectra are a measure of the cubic part of the crystalline field which is expected to be very similar in the two substances since, in both, Cr^{3+} is surrounded by an octahedra of water molecules.

DISCUSSION

Before examining the electron spin resonance (ESR) data and its connection with the quadrupole data, the eQq/h results will be discussed in Secs. A-E. In Sec. F there will be a discussion of the effect of ferroelectricity on the eQq/h results. Finally, in the remaining sections the ESR results will be discussed.

A. Introduction

Within the framework of the ionic model the field gradient, q , at the Al^{+3} or Ga^{+3} nucleus should be

$$q = (1 - \gamma_{\infty}) \sum_i \left(\frac{3 \cos^2 \theta_i - 1}{r_i^3} \right) e_i \quad (2)$$

The sum is over all the other charges in the lattice where e_i is the charge of the i th ion a distance r_i away, θ_i is the angle between the z axis (c axis) and the vector to the i th charge, and γ_{∞} is the antishielding factor of the ion for which the quadrupole coupling constant is being calculated, i.e., Al^{3+} or Ga^{3+} in this paper. Thus the temperature dependence of eQq/h should come from the sum in Eq. (2), which depends on the positions of the charges in the lattice.

A short but probably ample review of the experimental confirmation of the validity of the concept of an antishielding factor, γ_{∞} , can be found in a recent publication.²⁰ The theoretical and experimental values of γ_{∞} for the alkali ions are in agreement. For the halide ions the poor agreement is probably associated with the fact that the outer electron shell of these negative ions is easily deformed.²¹ However only positive ions (Al^{3+} and Ga^{3+}) will be considered here.

Secs. B-E describe the quadrupole coupling data. First, the general behavior of eQq/h is discussed. Then it is shown how the theoretical ratio of $(1 - \gamma_{\infty})$ of Al^{3+} to Ga^{3+} is needed to make the data much more consistent. This is done without using any detailed model of the lattice. In the third section q is directly calculated, using Eq. (2) and the x-ray data. Then the sensitivity of q to the various uncertainties in the structural data is investigated. The temperature dependence of eQq/h is calculated and its sensitivity is investigated. In the fourth section the relationship of eQq/h among the compounds is analyzed.

B. General Behavior

In molecular crystals it has generally been observed that eQq/h usually increases with decreasing temperature while the slope of the curve decreases toward zero at very low temperature.³ As can be seen in Fig. 3, eQq/h is markedly linear with temperature, and in several cases changes sign. Of course, the sign of eQq/h has not been measured. Thus \pm and \mp are used in the figure, but it is quite apparent that eQq/h does go through zero. This is the first time this has been observed for quadrupole resonances.

One can also see in Fig. 3 that the general behavior of eQq/h is similar for the two nonequivalent sites in all the compounds studied. As mentioned before, some of the points on the $Ga^{71}SH$ (2) curve have been obtained by observing the Ga^{69} resonance and then converting it to the curve by multiplying by the known ratio of the quadrupole moments. There is no curve for GAISD because it was found the results are the same as for GAISH. Thus, the curves marked GAISH (1) and (2) contain values measured on both deuterated and undeuterated samples.

¹⁹ See D. S. McClure, *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1959), Vol. 9.

²⁰ G. Burns and E. G. Wikner, *Phys. Rev.* **121**, 155 (1961).

²¹ G. Burns, *Phys. Rev.* **115**, 357 (1959).

C. Antishielding

The effect of antishielding factors can be examined without considering any detailed model of the lattice.

As can be seen in Fig. 2 or in Table I $d(eQq/h)/dT$ for the gallium compounds is larger than the aluminum compounds. Since the nuclear quadrupole moment of Ga^{71} is smaller²² than that of Al^{27} , the temperature dependence of the field gradient itself, dq/dT , for the Ga compounds relative to Al compounds is even larger than that shown in Fig. 3.

One would expect the movement of the ions with temperature and thus the temperature dependence of the lattice sum in Eq. (2) to be similar for the Al and Ga compounds, since all these compounds are isomorphous and have very similar temperature dependent physical properties. Even the temperature dependence of the spontaneous polarizations is quite similar.⁵ Thus, without considering in detail how the lattice sum in Eq. (2) behaves with temperature, but only assuming its temperature dependence is similar for the Ga and Al compounds, normalized Ga $d(eQq/h)/dT$ results should approximately be the same as the corresponding Al results.

As already noted, normalizing $d(eQq/h)/dT$ to the same nuclear quadrupole moment makes the agreement between the Ga^{71} and Al^{27} results poorer. However, the use of the theoretically calculated antishielding factors make the results more sensible. To make the comparison, the values of the Ga^{71} eQq/h and its temperature dependence are multiplied by 0.521²³ and given in parentheses in Table I. These values would have been obtained if Ga^{71} had the same nuclear quadrupole moment as Al^{27} and if Ga^{3+} had the antishielding factor that one calculates Al^{3+} should have. The value 0.521 is obtained from the measured values of Q and calculated results of γ_∞ quoted in reference 23.

As can be seen in Table I, there is only very rough agreement. However it is very much better than one would obtain if only the nuclear quadrupole moments were normalized.

Independent and better agreement of the ratio of $(1-\gamma_\infty)$ Ga^{3+} to Al^{3+} has been observed in the NH_4 alums.²⁴ Thus, it is seen that the theoretically calculated γ_∞ 's are required to understand the temperature dependence of eQq/h , and the ratio of the Al^{3+} to Ga^{3+} $(1-\gamma_\infty)$'s are at least approximately verified.

²² For a list of values of nuclear quadrupole moments and references to the original work see: C. H. Townes, *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, Germany, 1958).

²³ The values used for Q of Ga^{71} and Al^{27} , were 0.12×10^{-24} and 0.15×10^{-24} cm² respectively (see reference 22). The values used for γ_∞ were those calculated from Hartree-Fock wave functions and are -6.94 for Ga^{3+} (reference 20) and -2.32 for Al^{3+} [G. Burns, *J. Chem. Phys.* **31**, 1253 (1959)]. Then to normalize the Ga^{71} eQq/h data to Al^{27} , eQq/h of Ga^{71} was multiplied by $(0.15)/(3.32)/(0.12)/(7.94) = 0.521$.

²⁴ G. Burns (to be published). In the NH_4 alum case the measured $[d(eQq/h)]/dT$ of Al^{27} is just 0.5 times the Ga^{71} measurements. See also G. Burns, *J. Chem. Phys.* **32**, 1585 (1960).

D. Calculation of q

In this section the field gradient q at the Ga^{3+} nucleus is explicitly calculated using the x-ray data of Geller and Booth.⁶ This is done by performing the lattice sum in Eq. 2. The sum was calculated on an IBM 704 using a program developed by Bersohn.²⁵

In calculating q and its temperature dependence, one is immediately faced with three problems: (1) The positions of the hydrogens must be ascertained; (2) the charge must be distributed (i.e., explicitly where is the charge in SO^{-2} ?); (3) the positions of the ions at low temperature must be ascertained if dq/dT is to be calculated. Of course, the sensitivity of the results to the educated guesses must be investigated. These three problems will be discussed in appropriately marked paragraphs below.

One cannot hope for very good agreement between the calculated value of eQq/h and the measured value. As originally emphasized by Bersohn,²⁵ the lattice sum is often sensitive to the x-ray parameters, even in simpler lattices than considered here. This sensitivity has been noticed elsewhere²⁶ and is of some importance.²⁰ Also, as will be seen, q is sensitive to some charge distribution parameters. However, even though the absolute magnitude of q cannot be determined accurately $d(eQq/h)/dT$ is found to be much less sensitive to the charge distribution and x-ray parameters. Thus more reliability will be placed on this latter quantity. The insensitivity of $d(eQq/h)/dT$ to position and charge parameters may occur in other crystals than those considered here. If this is the case the conclusions drawn should be more reliable than those drawn from comparing q at a single temperature.

(1) The x-ray data do not tell where the hydrogens are, so one must estimate their positions. Since there is hydrogen bonding between the oxygen of the waters of hydration and the oxygens on the SO_4^{-2} group the hydrogens were placed²⁷ 1.02 Å from the water oxygen along the line joining the two oxygens. The calculation was also done for a distance of 0.96 Å. The change in q was about 2% and thus not important. In the original x-ray work the internuclear distances in the SO_4^{-2} tetrahedra and guanidinium ion were assumed to be those usually found for these ions. These distances were used in the lattice sum. Although this approximation made in the x-ray work is quite reasonable, it again shows why good agreement cannot be expected between the value of q calculated from Eq. (2) and the measured value, if q is sensitive to the x-ray data.

(2) The guanidine ion has a net charge of +1. In order to use Eq. (2), the location of the charge must be known. The calculation was done assuming the

²⁵ R. Bersohn, *J. Chem. Phys.* **29**, 326 (1958).

²⁶ R. A. Bernheim and H. S. Gutowsky, *J. Chem. Phys.* **32**, 1072 (1960).

²⁷ This is the distance found in an alum by neutron diffraction. G. E. Bacon and W. E. Gardner, *Proc. Roy. Soc. (London)* **246**, 78 (1958).

TABLE II. Values of q for the two Ga sites at two values of c/a . The numbers must be multiplied by e/a^3 to get q in the usual units. To find the approximate value of eQq/h in kc/sec, normalized to Al^{27} , multiply by 10.

Ions contributing to q	q at Ga(1)		q at Ga(2)	
	$c/a=0.77242$ (high temp.)	$c/a=0.75383$ (low temp.)	$c/a=0.77242$ (high temp.)	$c/a=0.75383$ (low temp.)
Ga^{3+}	-55.615	-53.105	-57.058	-54.013
Guanidine ion ⁺ ; +1 charge on H (+1 charge on N)	+37.518 (+52.531)	+39.876 (+54.064)	+42.590 (+52.348)	+43.809 (+55.082)
Waters; charge on the oxygens = $-\eta = -0.6$	-9.207 $\eta = -5.525$	+9.994 $\eta = +5.996$	+68.964 $\eta = +41.378$	+91.490 $\eta = +54.894$
SO_4^{-2} groups; charge on oxygen = $-z = -\frac{1}{2}$	14.895 $z + 3.513 = +10.961$	11.918 $z + 3.513 = +13.436$	-32.789 $z + 5.150 = -11.245$	-28.974 $z + 9.325 = -5.152$
Sum for q (in esu/cm ²)	-7.802 = -2.269×10^{12}	+11.041 = $+3.240 \times 10^{12}$	+18.035 = $+5.245 \times 10^{12}$	+42.287 = $+12.671 \times 10^{12}$
eQq/h (in kc/sec) [normalized to Al^{27} ; i.e., $Q = 0.15 \times 10^{-24}$ cm ² , $(1 - \gamma_\infty) = 3.311$]	-81.70	+116.7	+188.9	+456.3
$\Delta(eQq/h)$ (normalized to Al^{27})		-1.067 $\times 10^4$ kc/sec		-1.438 $\times 10^{+4}$ kc/sec
$\Delta(c/a)$				
$\Delta(eQq/h)$ (normalized to Al^{27})		-0.5607 (kc/sec) (deg ⁻¹)		-0.7556 (kc/sec) (deg ⁻¹)
ΔT				

charge to be first on the nitrogens and then on the hydrogens. Both results are listed in Table II. For purposes of obtaining a total q the charge was assumed to be on the hydrogens, the more likely situation from an electrostatic point of view.²⁸ The difference in the q 's for the two cases is large. However as will be seen, the temperature dependence of eQq/h is not sensitive to the placing of this charge.

For the SO_4^{-2} group, a charge of $-z$ was assumed to be on each oxygen with the remaining charge $4z-2$ on the sulfur. One would expect $z = \frac{1}{2}$,^{28a} i.e., all the charge on the oxygens, but again the slope of q is found insensitive to z . The waters of hydration have no total charge but a large dipole moment. The calculation was done assuming a charge of $-\eta$ on the oxygen and a charge of $+\eta/2$ on each hydrogen. A value of $\eta = 0.6$ is found for gaseous H_2O .²⁹ This might be larger in the solid because the electric fields due to the surrounding ions polarize the H_2O molecules. For want of better information $\eta = 0.6$ was used. The experimental O—H distance of 1.02 Å found in solids,²⁷ which is larger than the 0.96 Å found in the gas, possibly accounts for the polarization.

The results for the lattice sum for Ga at site 1 and 2 for $c/a = 0.77242$ are in Table II. This c/a ratio corresponds to the room temperature values measured by Geller and Booth.⁶ q , at the Ga site, due to each ionic group in the lattice is listed in terms of the charge distribution parameter. Then, using the above discussed value of the distribution parameter, a value of q is given. Also the calculated value of eQq/h (normalized to Al^{27}) is in Table II. As can be seen, the results are sensitive to the placement of charge in the guanidine ion and, to a smaller extent, on the parameters η and z

which describe the charge distribution on the H_2O and SO_4^{-2} groups respectively. Thus, it is not too surprising that while eQq/h is the right order of magnitude, it is not in detailed agreement with the measured value.

(3) To calculate $d(eQq/h)/dT$, the lattice sum must be evaluated at some low temperature. Since a low temperature x-ray structure has not been published, it must be estimated. The most attractive way to do this is to let all of the internal distances contract an amount proportional to the contraction of the macroscopic a and c axis. (This is called homogeneous contraction.) Thus, using the measured coefficients of thermal expansion,¹⁸ one can calculate the positions of the ions at some convenient low temperature and again perform the lattice sum. It should be pointed out that since the thermal expansion is so highly anisotropic, the z components of the positions of the ions in the lattice will be caused to decrease much more rapidly than the x components as the temperature is lowered. Using the coordinates of the ions thus obtained, the lattice sum was again evaluated for Ga at site 1 and 2 for $c/a = 0.75383$ (low temperature). The results are in Table II.

While the homogeneous contraction of the SO_4^{-2} group with respect to the guanidine group seems reasonable, one might expect the interval coordinates of a particular ionic group, i.e., SO_4^{-2} or $C(NH_2)_3$ to change less than the macroscopic contraction. Keeping some of the interval coordinates of the separate groups independent of temperature has little effect on q . For example, the C—N distance in the guanidine ion at $c/a = 0.7538$ (low temperature) was kept the same as it was at $c/a = 0.7724$ (high temperature). The result for site 1 was +53.987 instead of +54.064. A similar calculation for H_2O gives +6.651 instead of 6.557 as listed in Table II for the low-temperature q . For site 2 these same small effects were observed. Thus, the resultant q is not sensitive to the details of how the crystal contracts. The result depends mostly on the fact that the c axis contracts much more rapidly than

²⁸ L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1945) Sec. 25e.

^{28a} L. Pauling, reference 28, Sec. 30; J. H. Van Vleck, *J. Chem. Phys.* **7**, 61 (1939). Especially p. 65.

²⁹ See J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954), Chap. 13.

the a axis. This tends to flatten out the unit cell as the temperature is lowered, causing the contributions to q from all the ions to become more positive as can be seen in Table II.

Since Q of Al^{27} is positive,²² the calculation predicts that eQq/h becomes more positive as the temperature is lowered. Thus, the upper sign in Fig. 2 should apply.

When $\Delta(eQq/h)/\Delta(c/a)$ is considered rather than eQq/h , it is noticed that the result is much less sensitive to the x-ray and charge distribution parameters. For example, if the $+1$ charge of the guanidine ion is considered to reside on the nitrogen instead of the hydrogen, eQq/h is ~ 120 kc/sec more positive, which is a large fraction of the total. When $\Delta(eQq/h)/\Delta(c/a)$ is considered, the position of the charge on the guanidine ion causes the result to change by only 6%. Also, as already pointed out, q at low temperatures is insensitive to whether or not the C—N and H_2O bond distances vary with temperature, so $\Delta(eQq/h)/\Delta(c/a)$ will also be insensitive to the quantities. Then the slope of eQq/h versus temperature can be obtained from the calculated values by

$$\Delta(eQq/h)/\Delta T = \Delta(eQq/h)/\Delta(c/a) \times \Delta(c/a)/\Delta T. \quad (3)$$

This assumes that $\Delta(eQq/h)/\Delta T$ depends on temperature only through the c/a geometrical effect. The values are on the bottom of Table II. The agreement for site 2 is good (see Table I) and for site 1 within a factor of 2. The calculations predict a larger temperature dependence for site 2 than site 1. Experimentally, the opposite is found. This may be related to the fact that site 2 has a lower symmetry than site 1. Thus there is more chance for an error in the surrounding ion's coordinates and for them to contract inhomogeneously.

Since the structures of all the isomorphous compounds are quite similar the calculated values of $\Delta(eQq/h)/\Delta(c/a)$ should be close. The $\Delta(c/a)/\Delta T$ are also similar. Thus, the values of $\Delta(eQq/h)/\Delta T$ for all the compounds should be close to the values in Table II. Since these calculated values are in reasonable agreement with all the measured slopes of eQq/h versus temperature, the model is considered adequate. The next section shows how this same homogeneous contraction leads to a further understanding of the data.

E. Relationships Among the Compounds

Since the compounds are isomorphous and have very similar behavior, it is reasonable to ask why, at a given temperature, one compound should have a larger q than another. If, at any temperature, one plots eQq/h versus c/a for both sites of the four compounds on a single graph, the points fall roughly on a line with slope -2×10^4 kc/sec (assuming the upper sign in Fig. 2 and normalization to Al^{27}). This is in agreement with the results shown in Table II for $\Delta(eQq/h)/\Delta(c/a)$. Thus, the results from the two different sites in the four

different compounds can be fitted approximately by a single line that relates q to c/a .

F. Ferroelectricity

As mentioned before, these crystals are ferroelectric. However, they decompose before reaching a Curie point so eQq/h cannot be followed through the Curie point. The spontaneous polarization, P_s , $0.3 \mu\text{coul}/\text{cm}^2$ at room temperature and increases to $0.6 \mu\text{coul}/\text{cm}^2$ at liquid nitrogen temperature.³⁰ To correlate nuclear quadrupole resonance data with the spontaneous polarization change, it is necessary to assume a model for the origin of P_s . This has been somewhat successful in the case of KNbO_3 .³¹ In the case of GAlSH , it is not apparent by looking at the structure what moves in the unit cell to cause P_s to change or what the cell would look like if the crystals were paraelectric. One attractive possibility for the causes of the ferroelectric properties is that the guanidine ion is nonplanar. This possibility allows one to understand how the dipole moment would be reversible without causing large groups of ions to move. A calculation was made to see how this model would affect the quadrupole coupling data. The hydrogen atoms of a single guanidine ion must move down 0.41 Å in order for this model to yield the observed spontaneous polarization. The change in eQq/h that would result from this movement is 4 kc/sec. If all three guanidine ions move, the effect will be $\frac{1}{3}$ as much. Thus, if the nonplanarity of the guanidine ion is the cause of ferroelectricity, the change in P_s would not show up to any extent in these measurements.

To see if the application of dc fields could affect the coupling constant, fields up to 3500 volts/cm were applied parallel to the a and c axes in GAlSH and GAlSeH . No measurable change in eQq/h could be seen.

In summary, it appears that one can understand qualitatively and semiquantitatively the temperature dependence of eQq/h for these isomorphous compounds and the interrelationship among the compounds at a given temperature. This was done within the framework of the ionic model so that the appropriate antishielding factors were used. Homogeneous contraction was used to calculate $d(eQq/h)/dT$. The results were not sensitive to the details of the contraction and were in reasonable agreement with experiment.

G. Electronspin Resonance Results, General

The results of the temperature dependence of the Cr^{3+} resonance in the five isomorphous compounds are discussed here. See Table I for the measured values.

There are no large differences in the spin-Hamiltonian parameters for Cr^{3+} in the Ga^{3+} or Al^{3+} compounds measured here. The ionic radius of Cr^{3+} is 0.64 Å, while Al^{3+} and Ga^{3+} have ionic radii of 0.50 Å and 0.62 Å,

³⁰ A. G. Chynoweth, Phys. Rev. **102**, 1021 (1956).

³¹ R. R. Hewitt, Phys. Rev. **121**, 45 (1961).

respectively.³² One might expect the cubic field splitting (which is a measure of the cubic component of the crystalline potential = $15\bar{Q}$) in the Al^{3+} compounds to be larger than in the Ga^{3+} compounds since the misfit is larger. In the electrostatic theory, the cubic field splitting increases rapidly as the $Cr^{3+}-H_2O$ distance decreases. This type of reasoning has been used to explain the concentration-dependent color changes that occur in ruby.³³ Changes in $15\bar{Q}$ should show up as changes in the spin-Hamiltonian parameter g , since⁴

$$g = g_f [1 - 4\lambda/15\bar{Q}]. \quad (4)$$

g_f is the free-electron g value (2.0023) and λ is the spin orbit coupling parameter. However, g values from the Al^{3+} and Ga^{3+} compounds are the same within experimental error, while from the above type of reasoning a noticeable difference should be seen. Probably in this open type of hydrogen bonded lattice, the ionic groups and the water dipole can move easily to relieve the strain caused by the Cr^{3+} ion. In the ruby lattice the strain cannot be relieved by shortening or twisting hydrogen bonds, so one sees the effects.³³ In the alums, which are hydrogen bonded, again no change in g is seen for Cr^{3+} replacing Al, Ga, and In.²⁴

As can be seen in Table I, the D term [which is a measure of the axial component of the crystalline field, see Eq. (1)] in $GAlSD$ is larger than in $GAlSH$ at room temperature and the difference increases as the temperature is lowered. Bleaney and Bowers³⁴ have observed that in $KAl(SeO_4)_2 \cdot 12H_2O$ the deuterated alum has a larger D than in the undeuterated alum. The opposite has been observed by Wang in $AlCl_3 \cdot 6H_2O$.³⁵ In this compound, as the temperature is lowered, D of the undeuterated compound increases much faster than in the deuterated sample. There appears to be no published theoretical discussion of these effects although consideration of them might be helpful in understanding some of the fine points in the origin of D and might be useful as a tool for studying the hydrogen bond.

As mentioned in the section on results, the effects of concentration on D can be seen even though the electron spin resonance is measured in what would be normally called dilute systems.

H. D vs eQq/h

The temperature dependence of eQq/h for Al and Ga, and of D for small amounts of Cr in the isomorphous compounds has been measured. One can eliminate

³² See tables of Pauling's values in C. Kittel, *Introduction to Solid-State Physics* (John Wiley & Sons, Inc., New York, 1956), 2nd ed., p. 82.

³³ L. E. Orgel, *Nature* **179**, 1348 (1957). However, the experimental work that Orgel's discussion is based on has recently been questioned. See J. Graham, *J. Phys. Chem. Solids* **17**, 18 (1960).

³⁴ B. Bleaney and K. D. Bowers, *Proc. Phys. Soc. (London)* **A64**, 1135 (1951).

³⁵ E. Y. Wong, *J. Chem. Phys.* **32**, 598 (1960). See also R. H. Hoskins, R. C. Pastor, and K. R. Trigger, *J. Chem. Phys.* **30**, 601 (1958).

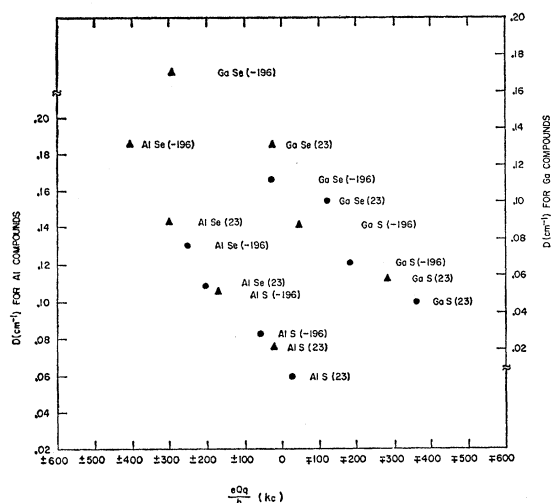


FIG. 5. D vs eQq/h . This is eQq/h (in kc/sec) for Al or Ga versus D of Cr. The abbreviation describing the particular points is obvious (i.e., $AlSe = GAlSeH$) the number in parentheses is the temperature in degrees centigrade. The circles and triangles represent results from sites (2) and (1), respectively. The eQq/h for Ga^{71} has been multiplied by 0.521 to normalize it to Al^{27} nuclear quadrupole moment and antishielding factor.

temperature and study the relationship between D and eQq/h . This has been done and the results can be seen in Fig. 5. In this figure each point corresponds to the D of Cr^{3+} when small amounts of Cr are substituted in the crystal as discussed previously, and eQq/h of Al (or Ga normalized to Al) at the same temperature. The temperature is given in brackets. The fact that D versus eQq/h is linear for a particular site in a particular crystal is not surprising. However, from the figure there is a single linear relation between D and eQq/h for both sites in the two different Al compounds. The Ga compounds behave similarly with a bit more scatter. Note that eQq/h for Ga compounds are the reduced values. That is they have been multiplied by 0.521 to normalize Q and $(1-\gamma_\infty)$ to Al^{27} . If the reduced values of eQq/h had not been used the two lines would not be approximately parallel. This is a further indication of the validity of the ratio of the antishielding factors. This linear relationship has also been observed in the alums.²⁴

The field gradient, q , is a measure of the departure of the crystal field from cubic symmetry. The second derivative of the electrostatic potential along the $z(\mathbf{c})$ axis evaluated at the nucleus, is $\partial^2 V / \partial z^2$. [See Eq. (2)]. The sum in Eq. (2) is q , due to all the ions in the lattice, provided the Al^{3+} ion has perfect spherical symmetry. Actually, the axial component of the crystalline potential distorts the spherical electron cloud of the Al^{3+} ion. Using first order perturbation theory,³⁶ one can write q as $(1-\gamma_\infty)$ times the sum. This is how it appears in Eq. (2).

³⁶ H. M. Foley, R. M. Sternheimer, and D. Tycko, *Phys. Rev.* **93**, 734 (1954); R. M. Sternheimer and H. M. Foley, *ibid.* **102**, 731 (1956).

The coefficient D in the spin Hamiltonian, Eq. (1), is also a measure of the departure of the crystal field from spherical symmetry. One can write the crystal field as the sum of a cubic part and an axial part.⁴

$$V = Q[(10)^{\frac{1}{2}}(Y_4^3 - Y_4^{-3}) - (7)^{\frac{1}{2}}Y_4^0] + Ar^2Y_2^0. \quad (5)$$

The first bracketed term is the cubic term and the second is the axial part. Y_n^m is a normalized spherical harmonic and Q and A are determined by the arrangement of the ions in the lattice. In the crystal-field approximation, one assumes the cubic part is much larger than the axial part which is borne out.⁴ Actually, there is also a $Br^4Y_4^0$ term in the axial part of Eq. (5). According to Walsh,³⁷ it is about 25% of the $Ar^2Y_2^0$ term in $\text{NiSiF}_6 \cdot 6\text{H}_2\text{O}$ and a smaller percent in Al_2O_3 .³⁸ No higher terms need be considered for Cr^{3+} since d electrons have an orbital angular momentum of two.⁴

One can relate the parameters in Eq. (5) to measured parameters g and D by Eqs. (4) and (6).^{37,39,40}

$$D = 30 \left(\frac{\lambda}{15\bar{Q}} \right)^2 \bar{A} = \frac{15}{8} \left(\frac{\Delta g}{g_f} \right)^2 \bar{A}, \quad (6)$$

where

$$\bar{Q} = -\frac{e}{14} \left(\frac{7}{\pi} \right)^{\frac{1}{2}} \langle r^4 \rangle Q, \quad (7)$$

and

$$\bar{A} = -\frac{e}{14(5\pi)^{\frac{1}{2}}} \langle r^2 \rangle A. \quad (8)$$

$\Delta g = g - g_f$, and $\langle r^n \rangle$ is the expectation value of r^n over the $3d$ electron wave function. Actually one can also measure $15\bar{Q}$ by optical absorption methods and this has been done in $\text{C}(\text{NH}_2)_3\text{Cr}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ as discussed in the section on results.

From Eq. (5) one can also calculate the field gradient q ,

$$\partial^2 V / \partial z^2 = (5/\pi)^{\frac{1}{2}} A. \quad (9)$$

The question immediately arises, is this the field gradient due to the lattice as if the Al^{3+} has spherical symmetry, or is it the actual field gradient at the nucleus, (i.e., including the distortion of the almost spherical electron cloud that gives rise to γ_∞)? Since it arises from the potential due to the ions of the lattice around the Al^{3+} site, it is the former so it does not as yet contain the antishielding effects.

Combining Eqs. (6), (8), and (9), one obtains

$$D = -\frac{3}{112} \left(\frac{\Delta g}{g_f} \right)^2 e \langle r^2 \rangle q_u. \quad (10)$$

The subscript u is just a reminder that this is the unshielded field gradient. The relation between D and

eQq/h is

$$D = -\frac{3}{112} \left(\frac{\Delta g}{g_f} \right)^2 \frac{\langle r^2 \rangle h}{(1 - \gamma_\infty) Q} (eQq/h). \quad (11)$$

Using the values $Q = 0.15 \times 10^{-24}$ cm², $(1 - \gamma_\infty) = 3.32$,²³ and $\langle r^2 \rangle = 0.405 \times 10^{-16}$ cm²,⁴¹ one obtains⁴² -2.3×10^{-5} cm⁻¹ (kc/sec)⁻¹ for the slope of D versus eQq/h . Therefore, from fairly general reasoning, one expects D to be proportional to eQq/h with the constant of proportionality as given above. The measurements show that D and eQq/h are indeed linearly related, but $D \neq 0$ when $q = 0$ and the slope from the curve is 2.6×10^{-4} cm⁻¹ (kc/sec)⁻¹, i.e., an order of magnitude larger than the calculated value. The result for D versus eQq/h for the Ga compounds is the same as for the Al compounds but the line is displaced 0.04 cm⁻¹ in D .

One can qualitatively understand why D and eQq/h might not be simultaneously zero by remembering that the Cr^{3+} ion will not be a perfect fit in an Al^{3+} site. Thus the introduction of Cr^{3+} will result in a distortion in the lattice immediately around it. This could give a finite D even though the rest of the Al sites might have zero q . However the ionic radius of Cr^{3+} is much closer to Ga^{3+} than to Al^{3+} , so the D value at zero eQq/h should be smaller in the Ga compounds than in the Al compounds. The opposite is observed. Das and Bersohn⁴³ have pointed out that overlap effects can lead to the equivalent of a shift of the curve in the D direction, but again one would expect less of a shift in the Ga compounds. Thus the reason for the different intercepts for the Al and Ga data is not clear.

There are a number of possible reasons for the lack of agreement between measured slope of D vs eQq/h and that calculated from Eq. (11).

1. In Eq. (5), the axial component of the crystalline potential seen by Al^{3+} or Cr^{3+} is written as $\propto r^2$. This is correct if the charges producing the potential are outside the region of the ion that is being measured, which is within the framework of the ionic model. Actually some overlap must exist. It might be expected to affect D more than eQq/h since D is more dependent on the outer part of the wave function. Phillips⁴⁴ has shown in the case of calculations of the cubic crystal field splitting, $15\bar{Q}$, that to a first approximation, the effects of the finite distribution of charge of the neighbors cancel, and the estimates of $15\bar{Q}$ based on point charges is justified. If the same arguments are approximately applicable to D , then Eq. (5) is reasonable and one must look elsewhere to understand why the experi-

⁴¹ Calculated from wave functions computed by R. E. Watson, Phys. Rev. **118**, 1036 (1960).

⁴² To obtain the numerical value -2.3×10^{-5} cm⁻¹ (kc/sec)⁻¹, the value obtained from Eq. (11) was multiplied by approximately 2, since P. H. E. Meijer and H. J. Gerritsen, Phys. Rev. **100**, 742 (1955), show that Eq. (6) should be changed by this numerical value.

⁴³ T. P. Das and R. Bersohn (private communication).

⁴⁴ J. C. Phillips, J. Phys. Chem. Solids **11**, 226 (1959).

³⁷ W. M. Walsh, Jr., Phys. Rev. **114**, 1473 (1959).

³⁸ T. S. Piper and R. L. Carlin, J. Chem. Phys. **33**, 1208 (1960).

³⁹ J. Becquerel and W. Opechowski, Physica **6**, 1039 (1939).

⁴⁰ J. H. Van Vleck, J. Chem. Phys. **7**, 1039 (1939).

mental slope of D versus eQq/h is ten times larger than the calculated one.

2. Pryce⁴⁵ has pointed out that the magnetic spin-spin interaction between pairs of electrons within the Cr^{3+} ion gives a contribution to D . However this contribution should be independent of temperature. Thus it cannot affect the slope. It might on the other hand contribute to D not being zero when q is. It also might be a cause for the displacement of the D versus eQq/h for Ga^{3+} with respect to the Al^{3+} line, since the contribution from the spin interaction to D is sensitive to the wave function of the $3d$ electron. However this cause for the displacement is unlikely, since the difference in the contraction of the Cr^{3+} $3d$ wave functions in the Ga^{3+} and Al^{3+} compounds that is large enough to shift the D versus eQq/h curve, would also cause a change in $15Q$ large enough to show up in the measurements of g . [See Eq. (4).]

3. Another possible cause of the disagreement between the slope of D versus eQq/h calculated from Eq. (11), and the measured value could be the following: The Cr^{3+} electrons not only see the potential due to other external ions as in Eq. (5), but also see the potential due to any distortions in the ion core itself. Thus the axial part of the potential in Eq. (5) induces a quadrupole moment in the electron distribution of the Cr^{3+} ion. Then the $3d$ electrons on this ion see the potential due to the axial term in Eq. (5) plus this additional potential. Of course this extra potential has just the right symmetry to contribute to Eq. (6). It is this sort of reasoning that leads to shielding or antishielding³⁶ effects in calculating g . However the averaging here will be different.

Thus $A r^2 Y_2^0$ is considered as a perturbation on the electrons in the ion under consideration. This perturbation will have nonzero matrix elements with certain excited state wave functions. The resultant new wave function will produce a potential that can be written as⁴⁶

$$V(r, \theta) = A Y_2^0 W \left[\frac{1}{r^3} \int_0^r u_0 r_1^2 u_1 dr_1 + r^2 \int_r^\infty \frac{u_0 u_1}{r_1^3} dr_1 \right], \quad (12)$$

where u_0 is the radial part of the ground state wave function, u_1 the radial part of the particular excited state wave function that is connected to u_0 by the perturbation, and W is a number that arises from the angular integrations of the angular part associated with the wave functions u_0 and u_1 .⁴⁷ The quadrupole type perturbation ($A r^2 Y_2^0$) connects s states to d , p states to p and f , and d states to s , d , and g . To compare

the effects of this extra potential with the lattice potential $A r^2 Y_2^0$, one need only compare the radial part of the expectation value of $V(r, \theta)$ over the $3d$ electron wave function to $\langle r^2 \rangle$, the $A Y_2^0$ being necessarily common to both.

To do this calculation, good estimates of the excited wave function, u_1 , must be known to use the Eq. (12). Detailed calculations were carried out using the u_1 's calculated by Sternheimer⁴⁸ for the case of Cu^+ since it has $3d$ electrons. The sum of radial expectation values of $V(r, \theta)$ over the $3d$ electrons was ten times smaller than $\langle r^2 \rangle$ for the $3d$ electrons and less detailed calculations indicate the same small effect will occur in Cr^{3+} . Thus this approach does not seem fruitful.

4. Another possible source of understanding the discrepancy in slope, stems from calculations of Sugano and Tanabe.⁴⁹ They re-evaluated D in terms of the crystal field parameter and obtained for D the term listed in Eq. (6) plus two others. These two new terms arise from dropping the assumption that the spin orbit coupling is isotropic. They relate the anisotropic spin orbit coupling parameter to the anisotropic g factor. Unfortunately one must be able to measure a difference between g_{11} and g_{\perp} to apply the equations. For Cr^{3+} this difference is very small and usually not measurable,⁴ as is the case here. If it is measurable, the errors in g_{11} and g_{\perp} are close to $g_{11} - g_{\perp}$. Besides Al_2O_3 , the equations of Sugano and Tanabe⁴⁹ can be applied to the recently measured values of Cr^{3+} in $MgAl_2O_4$.⁵⁰ The agreement is reasonable, but it is also in agreement with the older theories that assume an isotropic spin orbit coupling. However optical measurements could distinguish between the two. An understanding of the anisotropic spin orbit coupling and its dependence on the crystalline fields would make this theory more useful. Recently, Sugano and Peter⁵¹ have calculated D in Al_2O_3 by an entirely different approach, where configuration mixing and covalency play a dominant role. Again, agreement is obtained.

SUMMARY

1. The temperature dependence of eQq/h for the two different sites in the four different compounds is similar. However, the large value of $[d(eQq/h)]/dT$ for the Ga compounds with respect to the Al compounds is shown to be evidence for an antishielding factor in agreement with the calculated value.

2. By using the structural data, thermal expansion coefficients, and reasonable estimates as to the charge distribution parameters, both q and dq/dT are calculated. The latter is found to be fairly insensitive to the

⁴⁵ M. H. L. Pryce, Phys. Rev. **80**, 1107 (1950).

⁴⁶ See for example reference 29, Chap. 12.

⁴⁷ Values for the angular integrals, W , are one-half times the angular integration values calculated by Sternheimer, Phys. Rev. **95**, 736 (1954). Thus, for the $s \rightarrow d$, $p \rightarrow p$, $p \rightarrow f$, $d \rightarrow s$, $d \rightarrow d$, and $d \rightarrow g$ contributions, W is 4/5, 24/25, 36/25, 4/5, 8/7, and 72/35, respectively.

⁴⁸ R. M. Sternheimer, Document No. 6044-ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C.

⁴⁹ S. Sugano and Y. Tanabe, J. Phys. Soc. Japan **13**, 880 (1958).

⁵⁰ R. Stahl-Brada and W. Low, Phys. Rev. **116**, 561 (1959).

⁵¹ S. Sugano and M. Peter, Bull. Am. Phys. Soc. **5**, 415 (1960).

structural data and to the charge distribution parameters. When it is multiplied by the known Q and the calculated $(1-\gamma_\infty)$, then it is in agreement with the values measured for $d(eQq/h)/dT$. The value calculated for eQq/h is of the right order of magnitude (within several hundred kc/sec of zero), but sensitive to the charge distribution parameters. The calculations also show the relationship of eQq/h among the compounds at a given temperature.

3. In an attempt to study the ferroelectricity of these crystals a simple model is proposed. However, the ion movements that are necessary to account for the large temperature dependence of the spontaneous polarization produce very small changes in eQq/h . These smaller changes would be masked by the other much larger changes in eQq/h with temperature as discussed here. Therefore they would not be seen.

4. The temperature dependence of the ESR of Cr^{3+} substituted for Al and Ga in two different sites of four compounds has been measured. Again the results are generally similar. The g value for the Ga and Al compounds is equal within experimental error. Thus "squeezing" of the Cr ions is not seen. The D term in the spin-Hamiltonian of the deuterated compound (GAISD) has a different value than in the undeuterated compound (GAISH) and the temperature dependence is slightly different. However no difference was seen for the Al nuclear quadrupole resonance in these two compounds.

5. By parametrically eliminating temperature, the relation between D and eQq/h is studied. The result is two parallel but displaced lines, one for the two sites in the two Al compounds, and the other for the two Ga compounds. The lines are parallel only if the normalized eQq/h values are used. Using the general results from the literature describing the connection between the crystal potential and the spin-Hamiltonian parameters, a relation is derived that shows D should be proportional to eQq/h . However the experimental data show that D and eQq/h are not simultaneously zero. Perhaps this is not too surprising since it is expected that the Cr ion distorts its immediate neighbors. Thus a finite D is possible, while the rest of the Al ions see zero q . However, the fact that the line for the Al compounds is displaced from the line for Ga compounds (the latter being the further from the origin) seems to be in disagreement with present understanding.

6. The measured value for the slope of the D versus eQq/h curve as discussed above is ten times larger than the calculated value. The origin of this difference is not known. One possible reason is investigated. The $3d$ electrons see not only the potential due to the crystalline field, but they also see the induced potentials of the core electrons. However this effect proves to be small.

Thus, using the general crystalline potential relations, an equation relating D to eQq/h is found. However, agreement with the experimental measurements is not satisfactory. Since the nuclear quadrupole resonance data are fairly well understood and the theoretical relation found between D and eQq/h should be general, it is concluded that detailed understanding of the zero-field splitting (D term) is lacking.

Note added in proof.—The variation of D with uniaxial stress was measured in GAISH. This was done to further check the variation of D with geometry of the unit cell. As discussed in the paper, one can understand the temperature dependence of eQq/h in terms of changes of the geometry of the unit cell. In particular, lowering the temperature causes the c axis to contract much faster than the a axis. This causes the contributions to q from all the ions to become more positive as the temperature is lowered, as can be seen in Table II. The calculated temperature dependence of eQq/h is in agreement with the measurements. Also, the variation of eQq/h with c/a from one compound to the other at one temperature is in agreement with the calculations. To explicitly check the dependence of D on the geometry of the unit cell, $[\partial D/\partial(c/a)]_T$ was measured at room temperature in GAISH by applying uniaxial pressure along the c direction. The general techniques used for this measurement were similar to those used by Walsh.³⁷ The elastic constants which are needed to find the variation of c/a with stress have been published.¹¹ The result is $(1/D)[\partial D/\partial(c/a)]_T = -21$. This can be compared to the variation of D with c/a at constant pressure (i.e., vary the temperature) $(1/D)[\partial D/\partial(c/a)]_P = -33$. Thus, changes in D appear to come mainly from changes of the distribution of the ions in the unit cell as determined by c/a . This is not always the case. For example, in $\text{NiSiF}_6 \cdot 6\text{H}_2\text{O}$ the D of Ni^{+2} is affected strongly by lattice vibrations³⁷ and the two derivatives have different signs, e.g., $(1/D)[\partial D/\partial(c/a)]_T = -120$ while $(1/D)[\partial D/\partial(c/a)]_P = +60$. It should be noted that the relationship between D and q should not be affected by the actual cause of the temperature dependence as long as the cause can be written in terms of the usual crystal field potential.

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