

Paramagnetic Resonance Spectrum of Gadolinium in LaAlO_3 †

W. LOW AND A. ZUSMAN

Department of Physics, The Hebrew University, Jerusalem, Israel

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The resonance spectrum of Gd^{3+} in LaAlO_3 was investigated as a function of the temperature. It was found that the trigonal parameter b_2^0 changes smoothly from $67 \times 10^{-4} \text{ cm}^{-1}$ at 689°K to $491 \times 10^{-4} \text{ cm}^{-1}$ at 20°K . The transition to cubic phase is found by extrapolation to be at $720 \pm 15^\circ\text{K}$. The spin Hamiltonian appropriate to the trigonal phase is given by $H = g\beta\mathbf{H} \cdot \mathbf{S} + B_2^0 O_2^0 + B_4^0 O_4^0 + B_6^0 O_6^0 + B_4^2 O_4^2 + B_6^2 O_6^2 + B_6^4 O_6^4$. The evaluation of the magnitude of the various parameters B_m^n is presented.

INTRODUCTION

THE perovskite crystals of general formula ABO_3 have interesting properties. Some crystals such as BaTiO_3 are ferroelectric. They show several phase transitions at well-defined temperatures. Some crystals such as PbZrO_3 are antiferroelectric.¹ Other crystals such as SrTiO_3 do not show any ferroelectricity at temperatures near the phase transition. Paramagnetic impurities in this crystal system have been studied by a number of workers.²⁻⁴ Rubins and Low⁴ have shown that the paramagnetic resonance spectra show a continuous deformation from the cubic to the tetragonal spectrum. This change in deformation is very fast, but not sudden, near the transition temperature of 110°K .

The lanthanum aluminates do not show any sudden first-order phase transition.^{5,6} At relatively high temperatures, in the neighborhood of 700°K , they have the ideal cubic perovskite structure. As the temperature is lowered, the crystal shows a continuous deformation into a trigonal symmetry. So far no definitive evidence has been found for ferroelectric behavior.

The continuous change of the deformation suggest that this system would be interesting to be studied by means of paramagnetic resonance techniques. At the site of the lanthanum ion, different rare-earth ions or uranium group ions can be substituted and at the site of the aluminum ions other iron group elements. Gränicher and Müller⁶ have studied the paramagnetic resonance spectrum of powdered samples of $(\text{Gd-La})\text{AlO}_3$. They were able to show from their

measurements at 295, 195, 83, and 4.2°K that the resonance spectrum indicated no sudden phase transition in this temperature range. Since these authors worked on a powdered sample, they could not determine the value of the various parameters in the spin Hamiltonian, nor the dependence of these parameters on the temperature. Assuming that the main splitting arises from the presence of a trigonal crystal field, they concluded that the over-all initial splitting of the gadolinium spectrum is approximately proportional to the deformation angle.

We report here a detailed study of the paramagnetic resonance spectrum of gadolinium in single crystals of LaAlO_3 over a large temperature range.⁷ The transition temperature to the cubic phase is found to be at $720 \pm 15^\circ\text{K}$. Below this temperature there is a continuous change in the parameters of the spin Hamiltonian down to 4.2°K . The change in these parameters is very large and the over-all splitting of the ground state changes by an order of magnitude in the temperature range of 690 to 20°K , i.e., from 0.08 to 0.588 cm^{-1} . This property may be utilized as a secondary thermometer over a relatively large temperature range and possibly as means for temperature stabilization.

CRYSTAL STRUCTURE OF LaAlO_3

The class of rare-earth aluminates have a perovskite-like structure with a chemical formula of ABO_3 . The ideal cubic perovskite structure is shown in Fig. 1. In the center of the cube is the ion A (in this case lanthanum) and surrounded by eight cations B (in this case Al^{3+}). An A ion is, in addition, surrounded by twelve oxygen ions. The crystal-field potential set up by the aluminum ions and oxygen ions are of the

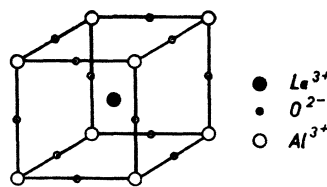


FIG. 1. The structure of the ideal cubic perovskite.

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¹ For a review of ferroelectricity and antiferroelectricity in perovskite structures, see W. Känzig, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957), Vol. 4, p. 1.

² K. A. Müller, in *Proceedings of the First International Conference on Paramagnetic Resonance* (Academic Press Inc., New York, 1963). This paper summarizes the findings in the iron group.

³ L. Rimai and G. A. de Mars, in *Proceedings of the First International Conference on Paramagnetic Resonance* (Academic Press Inc., New York, 1963).

⁴ R. Rubins and W. Low, in *Proceedings of the First International Conference on Paramagnetic Resonance* (Academic Press Inc., New York, 1963).

⁵ H. Gränicher and K. A. Müller, *Suppl. Nuovo Cimento* 6, Ser. X, 1216 (1957).

⁶ S. Geller and V. B. Bala, *Acta Cryst.* 9, 1019 (1956).

⁷ D. Kiro of this laboratory has also studied the spectrum of Cr^{3+} in this crystal. However, because of the many other impurities present, he could not study the spectrum over a large temperature range. The chromium spectrum seems to show similar characteristics as the gadolinium spectrum reported here.

opposite sign but very likely the potential caused by the oxygen ions is the larger. Each of the B ions is surrounded by six oxygen ions arranged in a perfect octahedron.

The actual crystal structure of LaAlO₃ is not an ideal perovskite structure but rhombohedral. It probably belongs to the space-group $R\bar{3}m$.

The primitive unit cell contains two molecules of LaAlO₃, while the ideal cubic perovskite contains one molecule. The distortion from cubic symmetry can be briefly described as follows: The cubic cell is stretched along one of the body diagonals. There are, in addition, slight changes in the coordinates of the three ions, in particular of the oxygen ions.

The crystal structure has been studied by Gränicher and Müller⁵ and more in detail by Geller and Bala.⁶ The latter followed the change in the volume of one

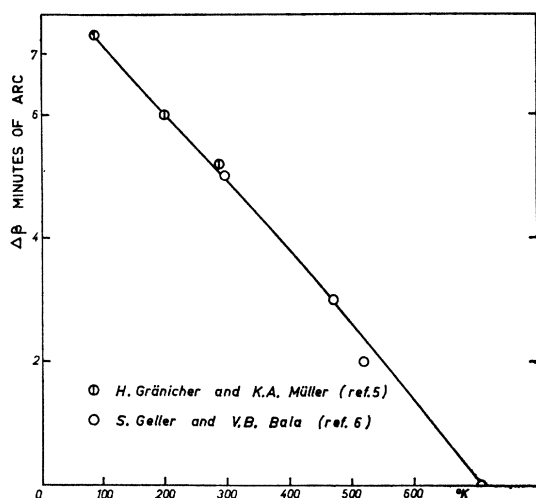


FIG. 2. Change of the deformation angle $\Delta\beta = \beta - 90^\circ$ as a function of temperature. The angle is measured in minutes of arc. The data denoted by an open circle \circ are from Geller and Bala (reference 6) and those denoted by \odot from Gränicher and Müller (reference 5).

molecule of LaAlO₃ as a function of the temperature from room temperature into the cubic phase. The data of Gränicher and Müller and those of Geller and Bala are not quite consistent with one another. They confirm, however, the following conclusions: (A) There is a continuous change in the deformation of the cube as the temperature is lowered. This is shown in Fig. 2. The data are taken from the results of the above authors. (B) There seems to be no sudden change in the structure near the transition temperature. (C) At the temperature of about $708 \pm 25^\circ\text{K}$ the structure is that of an ideal perovskite lattice.

The crystals were obtained from E. Warekois, Lincoln Laboratory. Presumably these were grown by the flame-fusion method. Later, we obtained crystals from E. P. Remeika, Bell Telephone Laboratories, which were grown by a flux method. However, in these

TABLE I. Measured paramagnetic transitions of gadolinium in LaAlO₃. Temperature = 273°K .

Transition	Parallel to trigonal axis $H \parallel z$ (in gauss)	Perpendicular to trigonal axis, $H \perp z$ (in G)	
		$\alpha = 0$	$\alpha = 30^\circ$
$7/2 \rightarrow 5/2$	730.9	4666.9	
$5/2 \rightarrow 3/2$	1779.5	4107.5	...
$3/2 \rightarrow 1/2$	2590.3	3604.4	3589.4
$1/2 \rightarrow -1/2$	3351.2	3151.6	3142.7
$-1/2 \rightarrow -3/2$	4109.1	2798.4	2816.0
$-3/2 \rightarrow -5/2$	4919.8	2553.9	2545.6
$-5/2 \rightarrow -7/2$	5970.8
DPPH marker	3330.1		3328.9

crystals the electron spin resonance (ESR) lines were considerably broader. Preliminary experiments show that by proper heat treatment the linewidth can be made narrower.

PARAMAGNETIC RESONANCE SPECTRUM

The resonance spectrum was measured with a conventional ESR spectrometer at X-band frequencies and in the temperature range from 4 to 700°K at fixed temperatures. One of the difficulties experienced was the necessity to keep the temperature constant since the spectrum was very sensitive to temperature variations. At temperatures above room temperature, a special cavity was built which permitted the heating of the sample up to 800°K . However, at temperatures above 600°K it became very difficult to measure the spectrum accurately for two reasons. First, we could not keep the temperature constant for sufficient long times so as to complete the measurement of all 7 lines. Secondly, above this temperature the lines tend to broaden appreciably presumably because of spin-lattice relaxation effects. At 690°K , we were still able to make a reliable measurement on some of the fine-structure lines.

A representative set of measured magnetic fields for the seven fine-structure components is given in Table I. The evaluation of the spin Hamiltonian is given below. Figure 3 shows the angular variation of the ESR in the plane of the trigonal axis. This measurement was made at 296°K . Figure 4 shows the angular variation of the fine-structure lines in a plane perpendicular to the trigonal axis.

EVALUATION OF PARAMETERS OF THE SPIN HAMILTONIAN

The spin Hamiltonian for gadolinium corresponding to a trigonal symmetry, C_{3v} , and with the z axis parallel to the trigonal axis can be written as

$$H = g\beta\mathbf{H} \cdot \mathbf{S} + B_2^0 O_2^0 + B_4^0 O_4^0 + B_6^0 O_6^0 + B_4^3 O_4^3 + B_6^3 O_6^3 + B_6^6 O_6^6. \quad (1)$$

The constants B_m^n are empirical parameters to be

determined from the experimental results and are not directly related to crystal-field parameters. The operators O_n^m are homogeneous functions of degree n of the angular momentum operators S_z , S_+ , and S_- , called the operator equivalents.⁸ They transform like the symmetry operations of the point symmetry of the site of the rare-earth ion. It is convenient to substitute

the following:

$$\begin{aligned} b_2^0 &= 3B_2^0, & b_4^0 &= 60B_4^0, & b_6^0 &= 1260B_6^0, \\ b_4^3 &= 3B_4^3, & b_6^3 &= 36B_6^3, & b_6^6 &= 1260B_6^6. \end{aligned} \quad (2)$$

When $H||z$, the transitions corresponding to $\Delta M = \pm 1$ are given to second order⁹ by

$$\begin{aligned} \pm 7/2 \leftrightarrow \pm 5/2: & \quad g\beta H = h\nu \mp (6b_2^0 + 20b_4^0 + 6b_6^0) - P \left[\frac{7}{1 \pm 4R} - \frac{4}{1 \pm 2R} \right], \\ \pm 5/2 \leftrightarrow \pm 3/2: & \quad g\beta H = h\nu \mp (4b_2^0 - 10b_4^0 - 14b_6^0) - 4P \left[\frac{1}{1 \pm 2R} \right], \\ \pm 3/2 \leftrightarrow \pm 1/2: & \quad g\beta H = h\nu \mp (2b_2^0 - 12b_4^0 + 14b_6^0) - P \left[\frac{7}{1 \pm 4R} - \frac{4}{1 \mp 2R} \right], \\ 1/2 \leftrightarrow -1/2: & \quad g\beta H = h\nu - 2P \left[-\frac{7}{1 - 16R^2} + \frac{4}{1 - 4R^2} \right], \end{aligned} \quad (3)$$

where $R = b_2^0/g\beta H$; $P = 20(b_4^3)^2/3g\beta H$. This calculation takes into account the second-order perturbation by terms of b_4^3 but neglects terms of the order of $(b_6^3)^2/g\beta H$. It turns out that these terms are only about 10^{-4} cm⁻¹ and, therefore, within the accuracy of 1–2 G can be neglected.

We have six unknowns to determine apart from the two g factors. The magnitude as well as the relative sign of the diagonal terms b_2^0 , b_4^0 , and b_6^0 , which are the dominant terms when measured at $H||z$ as seen from the inspection of Fig. 3 or Table III, can be found to a first approximation, by neglecting the off-diagonal terms proportional to P . This is justified since the transition of $+M \rightarrow +M-1$ and $-M \rightarrow -M+1$ are nearly symmetrical. The deviations are less than 5 G. The absolute sign of b_2^0 (and hence of b_4^0 and b_6^0 , since their relative signs are already known) were found in the usual way, by observing the relative intensity of the lines at low temperature (4.2°K). The observed increase in intensity of the high-field lines compared to the low-field lines indicates according to Eq. (3) that b_2^0 is positive.¹⁰ The parameter b_4^3 can be determined by measuring the spectrum in other directions ($H \neq z$). The value b_4^3 is then inserted in Eq. (3) and the value of the diagonal elements is re-evaluated and corrected. When the magnetic field lies in a plan perpendicular to the trigonal axis ($H \perp z$) the Zeeman term $g\beta \mathbf{H} \cdot \mathbf{S}$ is still the largest term. The Hamiltonian may be written in a form diagonal in the Zeeman term by a transformation to a new coordinate system, in which the new z axis is parallel to the magnetic field.

The transformation of the spin operators¹¹ gives the following form of the Hamiltonian, where only the diagonal and the appreciable off-diagonal terms have been retained.

$$\begin{aligned} H &= g\beta \mathbf{H} \mathbf{S}_z - \frac{1}{2} B_2^0 O_2^0 + \frac{3}{8} B_4^0 O_4^0 \\ &\quad + \frac{1}{16} (-5B_6^0 + B_6^6 \cos 6\alpha) O_6^0 - \frac{3}{2} B_2^0 O_2^2 \\ &\quad + \frac{5}{2} B_4^0 O_4^2 - \frac{1}{2} (7B_6^0 + B_6^6 \cos 6\alpha) O_6^2, \end{aligned}$$

where α is the angle between the new z axis and the old x axis, the off-diagonal elements in this case are appreciable, and the calculations should be carried to third order. (The transition $\Delta M = \pm 1$ to second order are given in the Appendix.)

Inspection of these equations shows that the Hamiltonian contains terms proportional to $\cos 6\alpha$ which means a 60° dependence, of the spectrum arising from the operator O_6^6 . This periodicity is shown in Fig. 4 and it enables one to determine the absolute value of the off-diagonal term b_6^6 . For example, measuring the difference in the magnetic field of $\alpha=0$ and $\alpha=30^\circ$ for $3/2 \rightarrow 1/2$ transitions gives $|H_0 - H_{30}| = (7/4)|b_6^6|$.

The off-diagonal terms b_4^3 and b_6^3 are more difficult to evaluate. They can be determined in principle by noticing that for every angle $\beta \neq 90^\circ$ between the trigonal axis and the direction of the magnetic field, The diagonal contributions of the operators with m even are the same for the two angles $\pm\beta$. But, the contributions of the operators with m odd, have opposite sign for these angles.

Consider the transformation of the odd operators O_4^3 and O_6^3 when the coordinate system transforms through Euler's angles $(\alpha, \beta, 0)$. The operators trans-

⁸ J. M. Baker, B. Bleaney, and W. Hayes, Proc. Roy. Soc. (London) A247, 141 (1958).

⁹ S. Geschwind and J. P. Remeika, Phys. Rev. 122, 757 (1961).

¹⁰ Appreciably the sign of b_2^0 of Gd³⁺ in LaAlO₃ is opposite to that found for Gd³⁺ in SrTiO₃ (private communication from L. Rimai).

¹¹ D. A. Jones, J. M. Baker, and D. F. D. Pope, Proc. Phys. Soc. (London) 74, 249 (1959).

form as¹²

$$\begin{aligned} O_4^3 &\rightarrow \frac{1}{8} \sin^3\beta \cos\beta \cos 3\alpha O_4^0 + \text{off-diagonal terms,} \\ O_6^3 &\rightarrow \frac{1}{16} \sin^3\beta \cos\beta (11 \cos^2\beta - 3) \cos 3\alpha O_6^0 \\ &\quad + \text{off-diagonal terms.} \end{aligned} \quad (4)$$

The largest value for O_4^3 is obtained at an angle of $\beta = 60^\circ$ and for O_6^3 at an angle of $\beta = 39^\circ$. Hence, careful measurements of all fine-structure lines at the angles of $\pm 39^\circ$ and $\pm 60^\circ$ can determine these two parameters.

However, an inspection of the angular dependence of the spectrum (see Fig. 3) shows that the slope of all lines, i.e., $dH/d\beta$ is very large. Therefore, a small misorientation of the crystal axis of the order of $\pm 1^\circ$ causes shifts of the correct magnetic fields of the line of the order of 10–30 G at $\beta = 39^\circ$ and $\beta = 60^\circ$. These shifts are larger than the contribution of these off-

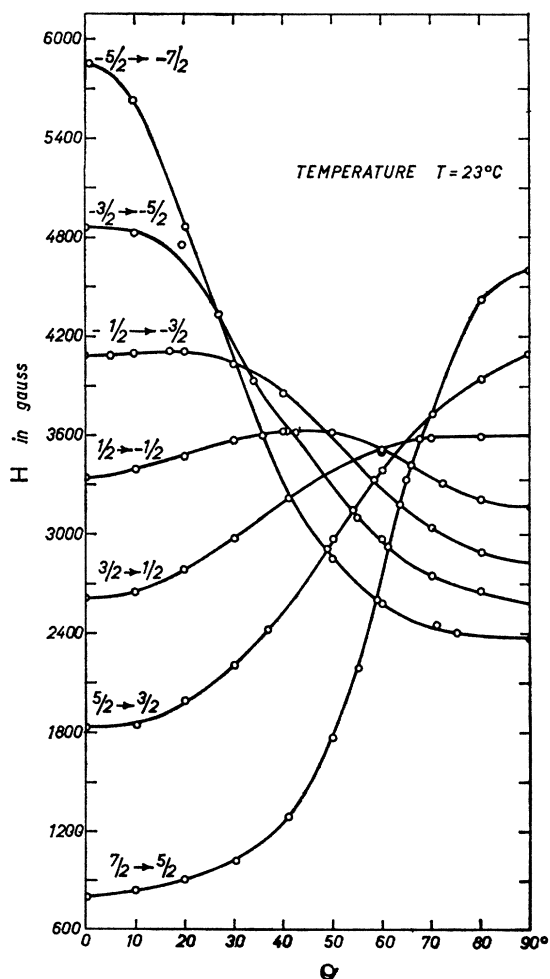


FIG. 3. Angular variation of the ESR of Gd³⁺ in LaAlO₃. (The data are taken at room temperature).

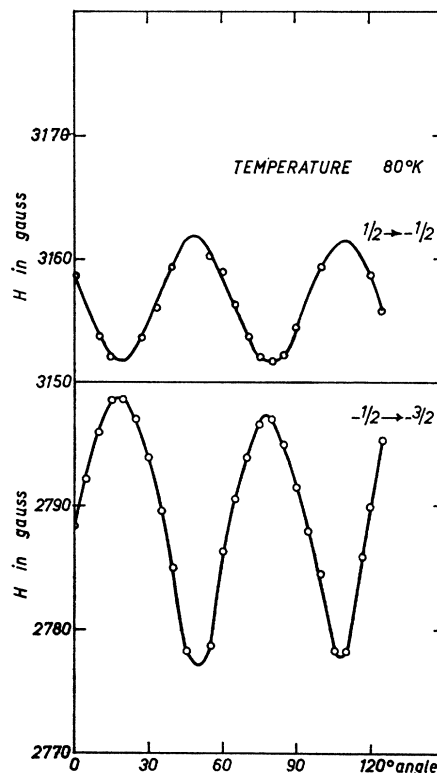


FIG. 4. Angular variation of the ESR spectrum in a plane perpendicular to the trigonal axis of Gd³⁺ in LaAlO₃. The data are taken at 80°K.

diagonal components and this method was, therefore, abandoned.

For this reason, we have used a different approximation. The temperature dependence of the diagonal elements show that b_2^0 is strongly temperature dependent whereas b_4^0 and b_6^0 change only slightly. To a good approximation the value of b_4^0 and b_6^0 can be accounted for from the cubic-field contribution. Only a small correction arises from the higher order trigonal components. This point of view is reinforced by noticing that the value b_4^0 in LaAlO₃ is about the same as that found by Sierro¹³ in SrTiO₃ in the cubic phase.

With this assumption, we can approximate the Hamiltonian to

$$H = g\beta HS_z + B_2^0 O_2^0 + H_{\text{cub}}^d, \quad (5)$$

where the H_{cub}^d are the cubic operators transformed from the [100] to the [111] direction,⁸ i.e.,

$$\begin{aligned} H_{\text{cub}}^d &= B_4^0 (O_4^0 + 20\sqrt{2} \cdot O_4^3) \\ &\quad + B_6^0 (O_6^0 - (35/\sqrt{8})O_6^3 + (77/8)O_6^6). \end{aligned}$$

Comparing the two expressions of Eqs. (1) and (2) we find the relations

$$b_4^3 = \sqrt{2}b_4^0, \quad b_6^6 = (77/8)b_6^0, \quad b_6^3 = -(\sqrt{2}/4)b_6^0. \quad (6)$$

¹² J. M. Baker and F. G. B. Williams, Proc. Phys. Soc. (London) 78, 1340 (1961).

¹³ J. Sierro, Helv. Phys. Acta 39, 904 (1961).

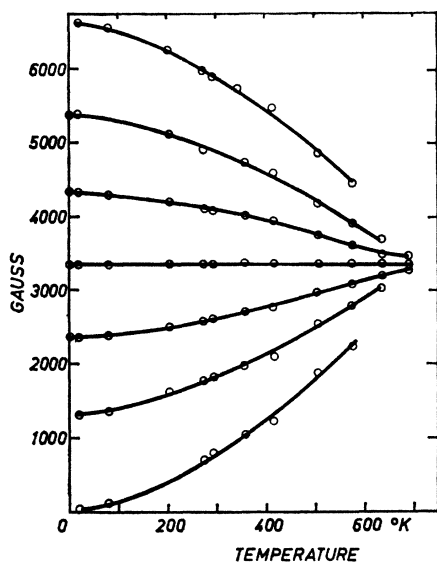


FIG. 5. The positions of the $\Delta M = \pm 1$ transitions as a function of the temperature.

With these cubic relations we can estimate b_6^3 and b_4^3 and this found to be $b_4^3 = 8.5 \times 10^{-4} \text{ cm}^{-1}$ and $b_6^3 = -0.35 \times 10^{-4} \text{ cm}^{-1}$ at room temperature. Additional support for this approximation is obtained from the following. It is found experimentally that $b_6^6 \approx (77/8)b_6^0$ and, therefore, one of these relations is verified. Secondly, if the other two relations are included one can calculate the experimental values of the magnetic field to an accuracy of 1 G. The sign of b_6^6 is determined by the sign of b_6^0 and is given in parenthesis in Table III.

TEMPERATURE DEPENDENCE OF THE ESR SPECTRUM

The spectrum was measured at 4.2°, 20°, 80°, 203°, 273°, at the fixed points of liquid helium, hydrogen, nitrogen, carbon dioxide, and ice. In this region of temperature, the linewidth was not very temperature dependent. Table II gives the measured linewidth between half-power points as a function of the temperature.

Table III gives the parameters of the spin Hamiltonian at various temperatures. The positions of the

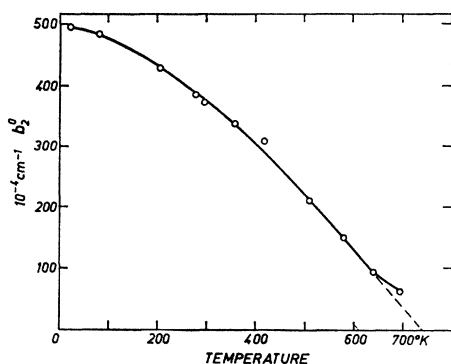


FIG. 6. Temperature dependence of b_2^0 .

$\Delta M = \pm 1$ transitions as a function of the temperature are shown in Fig. 5.

The dependence of b_2^0 as a function of temperature is plotted in Fig. 6. Inspection of this figure shows that this curve has 3 interesting parts. In the low-temperature region 4–20°K the axial field parameter b_2^0 is nearly independent of temperature. Extrapolation to absolute zero results in $b_2^0 = 492 \times 10^{-4} \text{ cm}^{-1}$. Between 20 to 300°K there is some curvature and the relationship can be approximated by $b_2^0 = D^0(1 + bT + cT^2)$. At temperatures higher than 300°K there is an approximate linear relationship between b_2^0 and T . Extrapolation of this curve to the points when $b_2^0 = 0$ finds the phase-transition temperature at $720 \pm 15^\circ\text{K}$. This result agrees well with the value of $T = 708 \pm 25^\circ\text{K}$ found by Geller and Bala, who used hot-stage microscopy technique to determine the phase transition.

Figure 7 gives the temperature variations of b_4^0 . It is seen that there is only a relatively small change in the value of b_4^0 over a large temperature range. Extrapolation to 700°K gives a value of $(5.1 \pm 0.2) \times 10^{-4} \text{ cm}^{-1}$.

DISCUSSION

The main result of this study is the confirmation of the continuous change of the crystal-field splitting as a function of temperature. This change in the trigonal phase is very large. In the linear higher temperature range the slope of this curve is about 1 G/°C. This strong gradient can, therefore, be used as a secondary thermometer and possibly a source for temperature stabilization. Assuming that one can follow the extreme $\pm 7/2 \leftrightarrow \pm 5/2$ lines which are proportional to a first approximation to $6b_2^0$, one can probably stabilize to about one hundredth of the linewidth or to within 0.15 G which is equivalent to about 0.03°K. It is possible to improve on this by using more homogeneous crystals. This method has certain advantages. The temperature range is from about 20 to 600°K. In addition, the sample can be fairly small if a sensitive spectrometer is used. However, we have not tested to what extent these results are reproducible in different samples under different conditions of preparation. This crystal may also be used as a maser oscillator in which the operating frequency may be changed by heating the sample by rf means.

The theory of the axial splitting for S -state ions

TABLE II. Linewidth in G as a function of temperature.*

Transitions	Temperature in °K				
	203	273	293	415	505 575
7/2 → 5/2	14	16	17	20	
5/2 → 3/2	11	12	14	16	
3/2 → 1/2	8.5	9.5	12	13	16
-1/2 → -1/2	7	7.5	8	12	13 20
-1/2 → -3/2	9.5	10	13	14	15
-3/2 → -5/2	12	12.5	15	16	
-5/2 → -7/2	14	15	17	20	

* The accuracy of the measurement is ± 2 G.

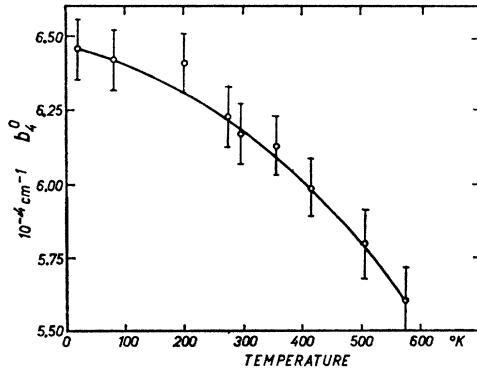
TABLE III. Temperature dependence of the parameters in the spin Hamiltonian in units of 10⁻⁴ cm⁻¹.^a

Frequency of measurement in Mc/sec	Temperature (°K)	g_{11}	g_{\perp}	b_2^0	b_4^0	b_6^0	b_6^6
10 909.7	20	1.9909	1.979	+490.7	+6.46	+0.9	(+)8.0
10 855.0	80	1.9911	1.978	479.2	6.42	0.9	10.2
9347.3	203	1.9904	1.978	426.7	6.42	0.9	7.2
9339.4	273	1.9911	1.984	383.8	6.23	0.9	9.4
9420.5	293	1.9908	1.986	371.2	6.17	1.0	7.6
9309.7	358	1.9915		337.9	6.13	1.0	9.9
9310.5	415	1.9910		307.0	5.99	1.0	
9280.0	505	1.9910		208.3	5.80	1.0	
9330.0	575	1.991		150.6	5.60	0.9	
9235.0	635	1.991		93.0			
	689	1.991		67.0			

^a The error in the parameters below room temperature is the following: $g_{11} = \pm 0.0005$, $g_{\perp} = \pm 0.010$, $b_2^0 = \pm 1$, $b_4^0 = \pm 0.3$, $b_6^0 = \pm 0.2$, $b_6^6 = \pm 1.2$, all in units of 10⁻⁴ cm⁻¹. The accuracy at higher temperature is progressively worse.

and in particular for the gadolinium ion is not on a firm basis. In general, there are two sets of processes, those which are linear in the axial crystal field strength, V_{ax} , and those which are quadratic, V_{ax}^2 . To a good approximation one may write $b_2^0 = AV_{ax}(1 + BV_{ax})$, where A and B are complicated constants, depending on a number of mechanisms and in particular on the spin-orbit coupling, on the spin-spin interaction, and on the energy separation of the excited states from the ground state. These constants are probably not very temperature dependent. Hence, the temperature dependence is mainly connected with the changes in the crystal field. From our data it seems likely that the linear processes dominate over most of the temperature range, except at relatively low temperatures.

We should like to comment briefly on the comparison of the phase transitions in the three perovskite systems BaTiO₃, SrTiO₃, and LaAlO₃. The temperature dependence of the ESR spectrum in BaTiO₃ shows that there is sudden collapse of tetragonal fine structure near the transition temperature into the cubic spectrum.¹⁴⁻¹⁶ The spectrum in SrTiO₃ as measured by R. Rubins show that there is a smooth transition from the tetragonal to the cubic-field spectrum, except that near


 FIG. 7. Temperature dependence of b_4^0 .

¹⁴ W. Low and D. Shaltiel, Phys. Rev. Letters **1**, 51 (1958).

¹⁵ D. W. Horning, P. C. Rempel, and H. E. Weaver, J. Phys. Chem. Solids **10**, 1 (1959).

¹⁶ D. Shaltiel, thesis, Technion, Haifa, 1959 (unpublished).

the transition temperature the lines broaden. This broadening mechanism may be connected with a tunneling frequency between the three equivalent tetragonal positions. The ESR of rare-earth elements indicate also a strong temperature dependence of b_2^0 below the phase transition. In the case of LaAlO₃ the situation is similar to that of SrTiO₃. The transition temperature is at much higher temperature, the temperature variation of b_2^0 is larger than in SrTiO₃. The trigonal spectrum merges gradually into the cubic-field spectrum. It seems that the domain formation in these two systems LaAlO₃ and SrTiO₃ may be very similar in nature, except that in SrTiO₃ the distortion is along the tetragonal and in LaAlO₃ along the trigonal axis. It would be of interest to study the spectra of parametric impurities near the transition temperature in considerable detail.

APPENDIX

Energy levels of gadolinium in a trigonal field with H perpendicular to the trigonal axis ($H \perp z$), ($\alpha = 0$).

$$\pm 7/2 \leftrightarrow \pm 5/2:$$

$$g\beta H = h\nu \pm 3b_2^0 \mp (15/2)b_4^0 \mp (3/8)(b_6^6 - 5b_6^0) \\ + \frac{(45/4)[b_2^0 - b_4^0/6 - (1/8)(b_6^6 + 7b_6^0)]^2}{2g\beta H \mp 3b_2^0 \mp (33/4)b_4^0} \\ + \frac{(21/4)[b_2^0 - (5/2)b_4^0 + (5/56)(b_6^6 + 7b_6^0)]^2}{2g\beta H \mp 5b_2^0 \pm (15/4)b_4^0 \mp (1/2)(b_6^6 - 5b_6^0)},$$

$$\pm 5/2 \leftrightarrow \pm 3/2:$$

$$g\beta H = h\nu \pm 2b_2^0 \pm (15/4)b_4^0 \pm (7/8)(b_6^6 - 5b_6^0) \\ + \frac{(45/4)[b_2^0 - b_4^0/6 - (1/8)(b_6^6 + 7b_6^0)]^2}{2g\beta H \mp 3b_2^0 \mp (33/4)b_4^0} \\ + \frac{15[b_2^0 + b_4^0 + (1/16)(b_6^6 + 7b_6^0)]^2}{2g\beta H \mp b_2^0 \mp (9/2)b_4^0 \pm (7/8)(b_6^6 - 5b_6^0)} \\ + \frac{(21/4)[b_2^0 - (5/2)b_4^0 + (5/56)(b_6^6 + 7b_6^0)]^2}{2g\beta H \mp 5b_2^0 \pm (15/4)b_4^0 \mp (1/2)(b_6^6 - 5b_6^0)},$$

$\pm 3/2 \leftrightarrow 1/2$:

$$g\beta H = h\nu \pm b_2^0 \pm (18/4)b_4^0 \mp (7/8)(b_6^6 - 5b_6^0)$$

$$+ \frac{15[b_2^0 + b_4^0 + (1/16)(b_6^6 + 7b_6^0)]^2}{2g\beta H \pm b_2^0 \pm (9/2)b_4^0 \mp (7/8)(b_6^6 - 5b_6^0)}$$

$$- \frac{15[b_2^0 + b_4^0 + (1/16)(b_6^6 + 7b_6^0)]^2}{2g\beta H \mp b_2^0 \mp (9/2)b_4^0 \pm (7/8)(b_6^6 - 5b_6^0)}$$

$$- \frac{(45/4)[b_2^0 - b_4^0/6 - (1/8)(b_6^6 + 7b_6^0)]^2}{2g\beta H \mp 3b_2^0 \mp (33/4)b_4^0}$$

$$+ \frac{(21/4)[b_2^0 - (5/2)b_4^0 + (5/56)(b_6^6 + 7b_6^0)]^2}{2g\beta H \mp 5b_2^0 \pm (15/4)b_4^0 \mp (1/2)(b_6^6 - 5b_6^0)}$$

 $1/2 \rightarrow -1/2$:

$$g\beta H = h\nu - \frac{15[b_2^0 + b_4^0 + (1/16)(b_6^6 + 7b_6^0)]^2}{2g\beta H + b_2^0 + (9/2)b_4^0 - (7/8)(b_6^6 - 5b_6^0)}$$

$$- \frac{15[b_2^0 + b_4^0 + (1/16)(b_6^6 + 7b_6^0)]^2}{2g\beta H - [b_2^0 + (9/2)b_4^0 - (7/8)(b_6^6 - 5b_6^0)]}$$

$$+ \frac{(45/4)[b_2^0 - b_4^0/6 - (1/8)(b_6^6 + 7b_6^0)]^2}{2g\beta H - 3b_2^0 - (33/4)b_4^0}$$

$$+ \frac{(45/4)[b_2^0 - b_4^0/6 - (1/8)(b_6^6 + 7b_6^0)]^2}{2g\beta H + 3b_2^0 + (33/4)b_4^0}$$

For $\alpha=30$ one has to change the sign of b_6^6 , i.e., $b_6^6 \rightarrow -b_6^6$.

Paraelectric Response of KD_2PO_4

R. M. HILL AND S. K. ICHIKI

General Telephone and Electronics Laboratories, Inc., Palo Alto, California

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The dielectric behavior of KD_2PO_4 in the paraelectric region, i.e., above the Curie temperature, has been measured up to 3.5×10^{10} cps. For frequencies above the crystal resonances, the complex dielectric coefficient exhibits a relaxation behavior very similar to that observed in triglycine sulfate. A model, which assumes a Gaussian distribution of Debye dipoles, fits the data quite well and appears to establish this representation as a valid one for "soft" ferroelectrics.

IT was shown recently¹ that the dielectric behavior of triglycine sulfate (TGS), in the paraelectric region above the Curie temperature could be adequately described by assuming a Gaussian distribution of Debye relaxation times among the dipoles of the crystal. To determine whether this type of behavior is a general characteristic of these "soft" ferroelectrics or represented only the behavior of monoclinic TGS, the measurements of clamped, complex dielectric coefficient were extended to deuterated potassium dihydrogen phosphate, KD_2PO_4 , which is a tetragonal crystal with a Curie temperature nearly 100°C below that of TGS.

The results reported in this paper show that the model proposed for dipolar relaxation in TGS also gives a good representation of the KD_2PO_4 response.

The complex dielectric coefficient for KD_2PO_4 single crystals were measured from 1 kc/sec through 35 kMc/sec, using measurement techniques essentially identical to those reported previously.¹ Temperature control between -70 and 0°C was provided by circulating an organic fluid, heptane, through the measurement cell. Heptane, which remains liquid to below -70°C , has both a low loss and a low dielectric con-

stant, 1.97, over the frequency range studied. A steady flow rate of 100 cc/min was maintained through the waveguide section and the fluid temperature was controlled by raising or lowering the heptane reservoir in an acetone-dry ice bath. Thin Teflon gaskets sealed heptane off from the rest of the waveguide circuit. This technique provided excellent thermal contact between the crystal and waveguide portions of the measurement cell.

A Curie plot of typical low-frequency data is shown in Fig. 1. The 1000-cps data represent the "free" crystal response, i.e., the contribution of the piezoelectrically coupled, mechanical resonances is present. The 15-Mc/sec data represent the "clamped" crystal response above all significant mechanical resonances. The Curie constants, 4280°C at 15 Mc/sec and 4050°C at 1000 cps, are almost the same but are about 25% higher than the most recently reported value.² The transition temperature was about -52.5°C for both cases but the intercept temperature changed from -61.5 to -54.8°C for the clamped and free case, respectively.

¹R. M. Hill and S. K. Ichiki, Phys. Rev. 128, 1140 (1962).

²R. J. Mayer and J. L. Bjorkstam, J. Phys. Chem. Solids 23, 619 (1962).