8-1972

Hydrostatic Pressure Effects on the EPR Spectrum of V$^{2+}$: A1$_2$O$_3$ and Cr$^{3+}$: A1$_2$O

Charles J. Wilcox
Western Michigan University

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HYDROSTATIC PRESSURE EFFECTS
ON THE EPR SPECTRUM OF
$\text{V}^{2+}:\text{Al}_2\text{O}_3$ AND $\text{Cr}^{3+}:\text{Al}_2\text{O}_3$

by

Charles J. Wilcox

A Thesis
Submitted to the
Faculty of the Graduate College
in partial fulfillment
of the
Degree of Master of Arts

Western Michigan University
Kalamazoo, Michigan
August, 1972
ACKNOWLEDGEMENTS

I wish to thank Dr. J. E. Herman for his suggestion of a subject, and for his advice and constructive criticism over a greatly extended period of time.

Charles J. Wilcox
MASTERS THESIS M-3903

WILCOX, Charles J., 1933-1972
HYDROSTATIC PRESSURE EFFECTS ON THE EPR SPECTRUM OF V^{2+}:\text{Al}_2\text{O}_3 AND Cr^{3+}:\text{Al}_2\text{O}_3.

Western Michigan University, M.A., 1972
Physics, solid state

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CHAPTER 1
INTRODUCTION

A powerful means of studying the interaction between the crystalline field in a lattice and an impurity ion is by a variable hydrostatic pressure, which provides a means of linearly changing the crystalline field at the impurity ion site by compressing the host lattice. These changes in the crystalline field can be detected by changes in the electron paramagnetic resonance (EPR) spectra of the impurity ion in its ground state. The iron group ions Cr$^{3+}$ and V$^{2+}$ are particularly advantageous because their partially filled 3d electron shells interact strongly with the host lattice crystalline field. Because of their incomplete inner shells, these atoms will possess a net magnetic moment even when ionized.

In this experiment microwaves (ca. 3 cm. wave-length) incident upon the sample induce magnetic dipole transitions ($\Delta m=\pm 1, \Delta m=\pm 0$) among the magnetic sublevels of the ground state of the impurity ion in a strong magnetic field (ca. 3000 gauss). The crystalline field at the impurity ion site due to the surrounding ions or ligands also perturbs the impurity ion states. From the resonance absorption of microwave power for transitions between various energy levels, electronic and nuclear properties of the impurity ion in the sapphire lattice can be deduced. It is the
object of this study to determine the hydrostatic pressure dependencies of the EPR spectra of the doubly ionized vanadium ion ($V^{2+}$) and the triply ionized chromium ion ($Cr^{3+}$), which are isoelectronic in the $\alpha$-$Al_2O_3$, or sapphire lattice. Specifically, we wish to measure the change in $D$, the coefficient of the crystalline field term in the spin Hamiltonian for $Cr^{3+}$ and $V^{2+}$ ions. By also measuring the zero field splitting parameter, $D$, as a function of pressure for the first three hyperfine lines of the $V^{2+}$ ion, an additional objective was to attempt to determine any changes with pressure in the hyperfine splitting constant, $A$. Based on a point charge model Dr. J. Herman(4) predicted a pressure dependence for $A$ but his experimental quoted error was larger than the measured shift.

The $Cr^{3+}$ data is of interest in order to compare the zero field splitting of ruby as a function of pressure with work done by Nelson, Larson, and Gardner.(1) Their results disagree slightly with previous work.(2) It is felt that this may be due to errors in pressure calibration.

A high pressure EPR spectrometer has been assembled to make these measurements. The EPR spectrometer contains the same high pressure equipment as that used by A. F. Clark,(2) and by J. E. Herman.(4) A careful adjustment of the magnet has been done and the pressure system recalibrated.
The crystal symmetry of sapphire is rhombohedral with its unit cell containing two molecules of $\text{Al}_2\text{O}_3$. In this experiment some of the $\text{Al}^{3+}$ ions are substituted by $\text{Cr}^{3+}$ or $\text{V}^{2+}$ ions. The crystal structure can be generated by placing $\text{Al}_2\text{O}_3$ molecules at the corners of a cube and stretching the cube along one of its diagonals. Another $\text{Al}_2\text{O}_3$ molecule rotated 180 degrees about the molecular axis with respect to the others is inserted into the center of the distorted cube. The nearest neighbors of the $\text{Al}^{3+}$ ion (also $\text{Cr}^{3+}$ and $\text{V}^{2+}$) are six $\text{O}^{2-}$ ions, which form a distorted octahedron which has neither inversion nor reflection symmetry (figure 1).

Without distortion each aluminum ion would be at the center of six oxygens in octahedral coordination. This results in the cubic symmetry crystalline field term $V_c$ in the spin Hamiltonian which splits the $^4\!F$ ground state of a $3d^3$ ion into three levels (figure 4). The distortion along the body diagonal creates two inequivalent sets of three adjacent oxygens (figure 2) and gives rise to the axial or trigonal symmetry crystalline field term, $V_{ax}$. Projection of the oxygens onto a plane perpendicular to the trigonal axis (c-axis) shows that the two sets of oxygen ions are not rotated exactly 180 degrees with
Figure 1. A portion of the Al₂O₃ arrangement projected upon a plane normal to the 3-fold axis C₃ and passing through the apex of a unit rhombohedron. Fractions give distances below the projection plane measured in terms of the unit rhombohedron. Atoms of Al. (or Cr.) are small, the oxygens are large circles.
Figure 2. Crystal coordination for an aluminum site in sapphire.

Figure 3. Projections of oxygens in Al₂O₃ onto a plane perpendicular to the trigonal axis.
Figure 4. Crystalline field splitting of $^4F$ ground state for a $3d^3$ ion.
respect to each other but have an additional rotation of 4°22' (figure 3). By neglecting the 4°22' offset the symmetry becomes 3m (or C\textsubscript{3v}).

The axial crystalline field term \( V_{ax} \) splits the excited states \( ^4T_2 \) and \( ^4T_1 \) as shown in figure 4. The crystalline field does not split the \(^4T_2 \) ground state. The observed zero-field splitting of the ground state arises through second order spin orbit coupling with the excited states.\(^{(4)}\) The resulting spin doublet is further split by an external magnetic field (figure 5) into four spin states specified by \( m_s \) values. For \( V^{2+} \), which has a nuclear magnetic moment \( I=7/2 \), each of these four \( m_s \) states has an eight line hyperfine structure with an approximate separation of \( m_s A \) between the hyperfine lines, where \( A \) is the hyperfine constant.

The spin Hamiltonian and the energy eigenvalues for Cr\textsuperscript{3+} in Al\textsubscript{2}O\textsubscript{3} are derived in reference 4 (appendices I and III) for a coordinate system where \( \theta \) is the angle between the \( Z \) axis along the applied magnetic field and the crystalline axis. The Hamiltonian derived is

\[
\mathcal{H} = \left( g_{II} \cos^2 \theta + g_\perp \sin^2 \theta \right) \beta H S_z \\
- D' (\cos^2 \theta - \sin^2 \theta) \left[ S_z^2 - \frac{1}{3} S (S+1) \right] \\
- D' \cos \theta \sin \theta \left[ e^{-i\theta} \left( S_z S_+ + S_+ S_z \right) + e^{i\theta} \left( S_z S_- + S_- S_z \right) \right] \\
- D' \frac{1}{4} \sin^2 \theta \left( e^{-2i\phi} S_+^2 + e^{2i\phi} S_-^2 \right),
\]

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Figure 5. Energy levels of $V^{2+}:Al_2O_3$ ground state verses applied magnetic field parallel to the C-axis.
where $g_{\|}$ is the spectroscopic splitting factor when the crystalline c-axis is parallel to the magnetic field and $g_{\perp}$ is the spectroscopic splitting factor when the crystalline c-axis is perpendicular to the magnetic field.

The energy eigenvalues to second order in the angle $\theta$ are

\[
U_j - \frac{3}{2} = -\frac{3}{2}X - 1 + \frac{3}{2}\sin^2 \theta - \frac{3}{2}X\left(\frac{9}{8} - 1\right)\sin^2 \theta \frac{3\cos^3 \theta \sin^2 \theta}{X + 2} - \frac{3\sin^4 \theta}{2X + 2}
\]

\[
U_j - \frac{1}{2} = -\frac{1}{2}X + 1 - \frac{3}{2}\sin^2 \theta - \frac{1}{2}X\left(\frac{9}{8} - 1\right)\sin^2 \theta + \frac{3\cos^2 \theta \sin^2 \theta}{X + 2} - \frac{3\sin^4 \theta}{2X + 2}
\]

\[
U_j + \frac{1}{2} = \frac{1}{2}X + 1 - \frac{3}{2}\sin^2 \theta + \frac{1}{2}X\left(\frac{9}{8} - 1\right)\sin^2 \theta - \frac{3\cos^2 \theta \sin^2 \theta}{X - 2} + \frac{3\sin^4 \theta}{2X + 2}
\]

\[
U_j + \frac{3}{2} = \frac{3}{2}X - 1 + \frac{3}{2}\sin^2 \theta + \frac{3}{2}X\left(\frac{9}{8} - 1\right)\sin^2 \theta + \frac{3\cos^2 \theta \sin^2 \theta}{X - 2} + \frac{3\sin^4 \theta}{2X - 2}
\]

where $X = g_{\|} \beta H_D$, $U_j = W_D$ and $W$=energy eigenvalues.

For the D shift the transition of interest is the high field transition $m=+1/2$ to $m=+3/2$. The first order terms containing D drop out for the midfield transition
The low field and midfield transitions for \( V^{2+} \) are complicated at X band frequencies due to the mixing of states via the hyperfine interaction. Both vanadium and chromium have weaker signals for the low field transition than for the high field transition.

Retaining terms to second order in \( \theta \) the \( m=+1/2 \) to \( m=+3/2 \) transition equation is

\[
\hbar \nu = g_{\text{eff}} \beta H + 2D
\]

where \( g_{\text{eff}} = g_{11} + \theta^2 \left[ g_{11} - g_{23} \frac{3g_{11}}{g_{23}} \right]. \)

The angle dependent term may be dropped because orientation of the crystal was such that \( \theta \approx 1^\circ \). Therefore, the equation used to describe the D shift of \( \text{Cr}^{3+} : \text{Al}_2\text{O}_3 \) is

\[
\hbar \nu = g_{11} \beta H + 2D
\]

The vanadium ion, \( V^{2+} \), is isoelectronic with \( \text{Cr}^{3+} (3d^3 \) configuration) but its spectrum is more complex due to the hyperfine interaction between the d electrons and the vanadium nucleus which has a nuclear spin of \( 7/2 \). This splits the spectrum into eight hyperfine lines if the applied magnetic field is parallel to the crystalline symmetry axis. For small misalignments (approximately \( 2^\circ \)) "forbidden" transitions are allowed. The disappearance of these forbidden lines is one means of aligning the crystalline symmetry axis with the magnetic field. Again, as for
chromium, the data were taken for the high field transition (m=+1/2 to m=+3/2). The transition equation for this case, as derived in reference 4, appendix I, is

\[ h\nu = g'' \beta H + 2D + mA + f \]

where \( f \) is the second order hyperfine correction. The values were overdetermined by observing the resonant conditions for the first three hyperfine lines, for which \( m \) takes the values -7/2, -5/2, -3/2.
CHAPTER III
EXPERIMENTAL SETUP

An electron paramagnetic resonance spectrometer employing a twelve inch magnet and a variable high pressure resonance microwave cavity was used for this experiment.

A. Crystal and Crystal Orientation

The crystals used in this experiment were washer-shaped single crystals. Their dimensions were:

- I.D. 0.090" ± 0.005"
- O.D. 0.240" ± 0.005"
- Thickness 0.060" ± 0.005"

The single crystals of \( \text{Al}_2\text{O}_3 + 0.1\% \text{Cr}_2\text{O}_4 \) and \( \text{Al}_2\text{O}_3 + 0.1\% \text{V}_2\text{O}_3 \) were obtained from the Linde Optical Company with the crystalline C axis in the plane of the washer within ± 2°.

Naturally occurring chromium has a 9.5% abundance of the \( \text{Cr}^{53} \) isotope with a nuclear spin of 3/2. All other isotopes of chromium have a nuclear spin zero. The chromium substitutes for aluminum in a plus three valence state and the \( \text{Cr}^{3+}\):\( \text{Al}_2\text{O}_3 \) crystals give strong signals.

Naturally occurring vanadium is primarily the \( \text{V}^{51} \) isotope having a nuclear of 7/2. When vanadium sapphire is grown from a mixture of \( \text{Al}_2\text{O}_3 \) and \( \text{V}_2\text{O}_3 \) powder, vanadium is predominately trivalent with a small concentration of
$V^{4+}$. A fairly high concentration of $V^{2+}$ is produced (about 0.01%) by exposing the crystals to X-rays. The plus three state is not observed at room temperature \(^{(3)}\) and the plus four state does not interfere with the plus two spectrum.

The signal strength for $V^{2+}$ was considerably weaker than for $Cr^{3+}$ because the conversion efficiency to $V^{2+}$ is small and the signal is spread over eight hyperfine lines. The signal-to-noise ratio for $Cr^{3+}$ averaged about 300 with some ratios as high as 1700, whereas for $V^{2+}$ the average was about 60 with a maximum ratio of signal-to-noise of only 90.

The crystals were placed in the magnetic field with their cylindrical axis coincident with the axis of rotation of the magnet. Individual adjustment of the lab jacks supporting the waveguide and the sample cavity allowed a small adjustment in the alignment of the two axes. The vanadium sapphire crystal was oriented by observing the disappearance of the "forbidden" transitions which occur between the high field hyperfine lines when the axis is not aligned with the applied magnetic field. Also, the high field transition ($m=+1/2$ to $m=+3/2$) occurs at the highest field when the c-axis and the field are aligned.

The chromium sapphire (ruby) crystal was oriented by using the fact that its high field transition also occurs at the highest field when the applied field is along the crystalline c-axis. Maximum signal strength is also
Figure 6. EPR resonance for a $3d^3$ ion Al$_2$O$_3$ for X band as a function of applied magnetic field and the field's angle to the crystalline axis.
received when the c-axis and the applied magnetic field are aligned. Orientations to within $\pm 1^\circ$ were obtained by these methods.

B: Experimental Apparatus

The sample was placed in the high pressure microwave resonant cavity which was located in a D.C. magnetic field. The magnetic field about the sample was produced by a twelve inch magnet with a three inch gap. The magnetic field was measured in terms of "proton kiloHz." by using a NMR probe placed next to but outside of the high pressure sample holder. A marginal oscillator of the Q multiplier type with CuCl-doped water was used. Assuming the difference between the sample and the NMR probe remained constant over the magnetic region scanned, then a measurement of the change in the applied field at the NMR probe would give a measurement of the change in the applied field at the sample. The procedure was to sweep slowly through the resonant frequency twice. The second time through the sweep is stopped exactly where the recorder shows the derivative to be half way between the maximum and the minimum. The NMR probe frequency and the resonant microwave cavity frequency at this point are recorded.

The X band frequency from the klystron is coupled through the rf magnetic field to the sample cavity which is built into one of the end plugs of the high pressure
bomb. The sample cavity is of the shorted co-axial type. The microwave magnetic field is maximal and the electric field is minimal at the sample position to reduce the non-magnetic losses (figure 7). The microwave frequency is stabilized at the cavity resonant frequency by an automatic frequency control circuit which uses 10 KHz. frequency modulation and a feedback network. The sample is surrounded by normal pentane, the high pressure transfer fluid. The maximum sensitivity of the apparatus will be achieved with the smallest sample cavity and the largest Q factor of the unloaded cavity resonator. Therefore, the cavity is made as small as practical (about 8 wave lengths long). The change of cavity resonant frequency with pressure due to change of dielectric constants of insulators in the cavity is small (ca. 5MHz. per 1000 atm.).

The high pressure portion of the cavity is sealed from the atmospheric portion (figure 7) by a BeCu cone seated on insulating conic sections of synthetic mica (pressed normal flour phlogopite) and Teflon. This sealing cone is part of the center conductor of the coaxial cavity. The cavity entrance is at the waveguide-to-coax converter and the coupling is adjusted with a below cutoff attenuator preceeding the converter (figure 8).

The EPR absorption of microwave power will cause a change in the Q of the cavity with a resultant change of the microwave power reflected to the detector crystal.
Figure 7. Sample cavity

Section A-A
- X-Band Flange

Section B-B
- 25" Diameter
- .086" BeCu

Section C-C
- 1/8" Stainless Steel Tubing Threaded & Soldered into Place
- .288" BeCu

- Teflon
- 0.50 in. per in.
- .015" Synthetic MICA (Pressed Normal FLUOR PHLOGOPITE)
- Entrance for High Pressure Fluid

- BeCu
- Beryllium Copper (Berylco 25)
- Bearing Bronze Guard Ring

- O-Ring
- Brass

- Extraction Collar (Brass)

- Sample 3/32" Wide (Glued to end wall with Duco cement)
The signal from the detector crystal diode is then fed through a preamp to a phase-sensitive detector and is plotted on a 5" strip chart recorder. A modulation frequency is superimposed onto the D.C. magnetic field which is swept linearly in time. Generally the highest feasible modulation frequency is used in order to operate above the region of flicker noise. In microwave spectroscopy the flicker noise (1/f noise) of the backward diode used dominates for a modulation frequency below 10 KHz. However, to insure adequate penetration of the bomb by the magnetic modulation field a frequency of 40 Hz. was used for Cr$^{3+}$: Al$_2$O$_3$ and 400 Hz. for V$^{2+}$:Al$_2$O$_3$.

C. The High Pressure System

The components of the high pressure system are shown schematically in figure 9. The system has a low pressure charging section and a 20:1.5 piston intensifier to obtain the high pressures. The plugs in the sample cavity and the calibration bomb are sealed with rubber, Teflon, and bearing bronze ring seals of the unsupported type. These seals set a practical limit to the pressure of about 9000 atmospheres. The pressure is determined with a manganin cell and a Wheatstone bridge circuit using a precision four decade resistance box and galvanometer. The sensitivity of the measuring circuit was one atmosphere. The accuracy was therefore limited by the linearity of the
Figure 8. Spectrometer block diagram
Figure 9. High pressure system schematic.
resistance of the manganin wire with pressure, which was within 0.5%.

The pressure system was calibrated by observing the 3% volume change when mercury freezes at 7420 atmospheres at 0°C. This was done by pumping the pressure transfer fluid, normal pentane, through the thick walled, cold worked, stainless steel tubing (0.0075"I.D., 0.125"O.D.) into a hardened steel bomb containing mercury enclosed in a balloon to prevent its contact with the metal. If mercury is in direct contact with the pressurized steel bomb it will attack the high stress points and cause the bomb to fracture. To make the transition point more readily apparent the calibration bomb was constructed with a much larger volume than the high pressure sample cavity.

D. The Magnetic Field

The magnetic field was provided by a Varian electromagnet which was converted from a 1" gap high resolution NMR magnet by changing to 12" cylindrical pole faces with a 3" gap and adding a rotatable base for EPR work. Before any EPR data was taken a profile of the magnetic field was made by placing a CuCl-doped NMR probe at various coordinate points in the magnetic field. The high pressure sample cavity was held in place by two bronze supports in the magnetic field but it could be adjusted vertically. Therefore, the vertical direction was the first coordinate
of the magnetic field plotted (figure 10).

The magnetic field is not measured at the sample but outside the sample cavity. In a homogeneous field any change at the sample site can be measured by a change in the field at the NMR probe. If there is a large inhomogeneity in the magnetic field, then a change in the field at the NMR probe no longer represents the change in the field at the sample site. Therefore the magnetic field should be as homogeneous as possible.
Figure 10. Original magnetic field in the vertical direction.

Proton cycles/sec., deviation from maximum (27 MHz)

-100
-200
-300
-400

.05 GAUSS
DEVIAION

center of magnetic field

inches deviation from the center
CHAPTER IV

EXPERIMENTAL RESULTS

A. Field Profile

Normally the magnetic field between the pole pieces decreases from the axis to the edge of the pole pieces. By conditioning the magnet for a period of time at a higher strength than that at which the sample will be run, then gradually reducing the magnetic field to the desired strength (dishing the field), the magnetic field can be made to remain constant or even to increase over a limited region from the pole axis to the edges. Figure 11 shows the magnetic field profile at 1.02 amperes before dishing and after dishing at 1.25 amperes for 20 minutes and then reducing to 1.02 amperes. Dishing not only flattened the magnetic field profile but it appears skewed also. The distance between the pole caps was measured and .0025" shims were placed behind each pole cap at the top to make them parallel. When a magnetic profile was made the magnet appeared to be overshimmed (figure 12). It also appears to be slightly overdished when conditioned at 1.40 amperes. One shim was removed and the dishing current reduced to 1.35 amperes for the final magnetic profile (figure 13). The magnetic profiles for the X-direction (horizontal) and the Z-direction are shown in figures 14
and 15 respectively. The magnetic variations over a one inch dimension are

Y (vertical) \(0.025\) gauss,

X (horizontal) \(0.03\) gauss,

Z \(0.07\) gauss,

when dishing at 1.35 amperes for 20 minutes.
Proton cycles/sec.
deviation from maximum

○ Before dishing (current 1.02 amps.)
○ After dishing (current at 1.25 amps for 20 minutes and then returned to 1.02 amps.)

Figure 11, Effect of dishing the magnetic field.
Figure 12. The effect of overshimming the magnetic field.

Inches from the center
Figure 13. Magnetic profile, vertical direction.
Figure 14. Magnetic profile, horizontal direction.
Proton cycles/sec., deviation from maximum.

Figure 15. Magnetic profile, Z direction.
Proton cycles/sec., deviation from maximum.

Inches from the center of the magnet.
Inches from the center of the magnet.
B: Pressure Calibration

The high pressure calibration bomb was cooled in an ice-water mixture at a pressure within 10% of the transition point for 48 hours prior to a calibration run. Since normal pentane becomes viscous at high pressures, the system was allowed to equilibrate for an additional four hours close to the transition pressure. The pressure was then further increased a partial pump stroke at a time (a wooden block was used to limit the pump handle travel to less than one half). Because the pressure charging unit containing the pump and the manganin wire cell were connected to the high pressure bomb by approximately fifteen feet of small diameter tubing it was found necessary to allow 30-40 minutes after each stroke to allow the pressure to equilibrate before recording the change in resistance. When the transition pressure was reached an additional stroke of the pump handle solidified the mercury and produced no increase in pressure. Actually the pressure increased beyond the transition point before the mercury began to solidify. This is similar to super-cooling in a liquid where the temperature will drop below the fusion point before nucleation takes place. Once solidification started it continued until the pressure was equalized at 7420 atmospheres. Thus a decrease in resistance was noted at the transition condition (as per following table).
After one or two additional strokes all of the mercury was solidified and the pressure again increased with each stroke of the pump handle. In this way the pressure at which the volume change occurred was determined to within ±0.1%.

If a similar procedure was followed except that the bomb was cooled and equilibrated only eight hours the transition pressure appeared to be about 1% high. When the time between pressure increases was of the order of six minutes the transition pressure was observed to be as much as 10% higher than the final results.

The following is a sample of the data used for pressure calibration.

<table>
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<th>TIME</th>
<th>RESISTANCE</th>
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</tr>
<tr>
<td>12:03</td>
<td>77.61</td>
<td>1.55</td>
</tr>
</tbody>
</table>

Using these results, resistance readings were converted to atmospheres of pressure by the equation

\[ P = 0.9826R - 49.1 \]

where \( R \) is the resistance measured in ohms.

C: \( \text{Cr}^{3+} \) in Sapphire

Data for the EPR absorption as a function of pressure were taken for the single field resonance line of the I=0 \( \text{Cr}^{3+} \) ion when the applied field and the crystalline symmetry axis were aligned. For the principle chromium isotope no hyperfine interaction exists (figure 16) and the data were analysed using the following relationship derived in reference 4 appendix II,

\[ h\nu = g\beta H + 2D \]

Pressure shifts were determined relative to the parameters obtained by Schultz-Dubois\(^{6}\) and Laurence and Lamb\(^{7}\).
$g_{\parallel} = 1.9840 \pm 0.0006$

$2D = 11.493 \pm 6$ MHz.

Using a least squares fit to the experimental data, the pressure dependence observed for the zero-field splitting parameter, $D$, was

$$\frac{A_{2D}}{2D} = (1.75 \pm 0.05) \times 10^{-3}/\text{katm}.$$ 

$D$: $V^{2+}$ in Sapphire

The $V^{2+}$ ion is isoelectronic with Cr$^{3+}$ (3d$^3$ configuration) but its spectrum is more complex. Due to the hyperfine interaction with the vanadium nucleus ($I=7/2$) the spectrum is split into eight hyperfine lines for the case of the applied magnetic field parallel to the crystalline axis (figure 18).

Data were taken for the high field transition ($m=+1/2$ to $m=+3/2$) for reasons discussed above.

A computer program was used to calculate the pressure shifts of $2D$ and $A$ in the transition equation ((4) Appendix I).

$$\hbar \nu = g_{\parallel} \beta H + m_{I} A + f$$

A least squares fit to the experimental data gives the values,

$$\frac{A_{2D}}{2D}_{-7/2} = (1.52 \pm 0.05) \times 10^{-3}/\text{katm}.$$ 

$$\frac{A_{2D}}{2D}_{-5/2} = (1.49 \pm 0.05) \times 10^{-3}/\text{katm}.$$ 

$$\frac{A_{2D}}{2D}_{-3/2} = (1.52 \pm 0.05) \times 10^{-3}/\text{katm}.$$
Figure 16. A typical EPR spectrum for Cr$^{3+}$. 

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D-shift in Cr$^{3+}$:Al$_2$O$_3$
for $M=1/2$ to $M=3/2$
transition at $\theta=0$
Figure 18. A typical eight line spectrum for $V^+$. $M_I = 7/2$, $M_I = -7/2$. 
Figure 19.

D-shift in $\gamma^+, Al_2O_3$
for $M=1/2$ to $M=3/3$
transition at $\Phi=0$.

$M_I=\gamma-\frac{1}{2}$
Although some refinement should be added to the MFK spectrometer for greater sensitivity it does give reasonably satisfactory results in its present state. Hydrostatic compression of the sapphire lattice containing iso-electronic $V^{2+}$ and $Cr^{3+}$ impurities has shown that the crystalline field parameter, $B$, in the spin Hamiltonian varies linearly with pressure within the accuracy of the measurement to $8,000$ atmospheres. The pressure dependence observed for the $D$ shift of the $Cr^{3+}$ ion,

$$\frac{\Delta D}{D} = (1.75 \pm .05) \times 10^{-3}/\text{Kbar},$$

is nearly the same, within limits of error, as that reported by Nelson, Larson, and Gardner$^1$.  

$$\frac{\Delta \delta}{\Delta P} = (6.0 \pm 0.4) \times 10^{-4} \text{cm}^{-1}/\text{Kbar}$$

or $$\frac{\Delta D}{D} = (1.59 \pm 0.1) \times 10^{-3}/\text{Kbar}.$$  

An error in pressure calibrated by Clark$^2$ would explain the difference in his results and those reported by Nelson, Larson, and Gardner$^1$. The average pressure dependence observed for the $D$ shift of $V^{2+}$ ions was

$$\frac{\Delta D}{D} = (1.51 \pm .05) \times 10^{-3}/\text{Kbar}.$$  

The error in the determination of the $D$ shift for vanadium was too great to determine any pressure dependence for $A$, the hyperfine interaction constant. Subsequently, by
making refinements in the equipment, J. L. Albain \(^{(8)}\) was able to measure the pressure dependence of \(A\).


