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Final Report - Part 3

THE HYDROSTATIC PRESSURE DEPENDENCE
OF THE
ELECTRON PARAMAGNETIC RESONANCE SPECTRA OF VARIOUS IRON GROUP IONS

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ORA Project 04385

under contract with:

NATIONAL SCIENCE FOUNDATION
GRANT NO. G-15912
WASHINGTON, D.C.

administered through:

OFFICE OF RESEARCH ADMINISTRATION ANN ARBOR

June 1963

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I. INTRODUCTION

A. INTEREST IN AND NEED FOR EPR UNDER HYDROSTATIC PRESSURE

Interest in solid-state systems has become widespread in recent years, particularly with the use of doped semiconductors as transistors and paramagnetically doped crystals for MASERS and LASERS. Electron paramagnetic resonance (EPR) utilizes a paramagnetic impurity ion in a host lattice as a means of studying both the ion itself and its interaction with the surrounding lattice. The iron group ions are particularly advantageous with their partially filled 3d electron shells and resulting net magnetic moment. Microwaves (ca. 3 cm wavelength) incident upon the crystal induce magnetic dipole transitions among the magnetic sublevels 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 its host lattice can be deduced.

The mechanism of the interaction between the crystalline field and the magnetic sublevels of the impurity ion is not well understood. Hydrostatic pressure (ca. 10,000 atmospheres) provides a means of changing the crystalline field at the impurity ion site by compressing the host lattice and thus a means of studying the interaction between the two.

It is the object of this study to determine the hydrostatic pressure dependence of the EPR spectra of various iron group ions in different crystal structures, and to interpret this behavior with respect to the most applicable

theoretical analyses.

B. REVIEW OF PREVIOUS WORK

An S state ion, such as Mn^{2+} whose $L = 0$, should have no zero field fine structure splitting. The observed splittings¹ aroused a great deal of curiosity about the effect of the crystalline field as a perturbation on the energy levels of an impurity ion.^{2,3,4} Among the resulting papers, Watanabe suggested that the non-zero contributions due to a crystalline field of cubic symmetry must be from matrix elements containing only even powers of the crystalline field.⁵ Watanabe also suggested that this could be checked by a hydrostatic pressure experiment on the EPR of such a material.⁶ Walsh performed such an experiment and found a quartic dependence for Mn^{2+} and Fe^{3+} in MgO .⁷ A paper by Powell, Gabriel, and Johnston then suggested a mechanism for ground state splitting due to odd powers of the crystalline field.⁸ In another hydrostatic pressure EPR experiment, Wait found a square dependence for Mn^{2+} in calcite. He also pointed out that according to the theory of Powell et al. Mn^{2+} and Fe^{3+} should not have the same pressure dependence in MgO , and suggested further experiments on Fe^{3+} in calcite as well as studies in other host lattices. This work is being done as part of this project.

Drickamer et al. have also done optical studies using uniaxial pressures up to 150 kbar.^{10,11,12} They have found increases in the crystalline field parameter, Dq , which are consistent with the R^{-5} law and also indications of local relaxation near the impurity ion.

C. SCOPE OF THE PRESENT PROJECT

A preliminary study of Mn^{2+} in MgO is being made to check the accuracy of the experimental instrumentation against work already done and to affirm the quartic dependence found there for the MgO cubic symmetry. Next a comparison of the effect of two different impurity ions in the same host lattice will be done by studying Fe^{3+} in calcite, which has a trigonal symmetry, and then comparing this work with the work done by Wait on Mn^{2+} in calcite.⁹ A study of V^{2+} and Cr^{3+} in sapphire, which has a trigonal symmetry, will be made to determine their relative pressure dependence since it is felt that the Cr^{3+} ion lies in a different environment than the V^{2+} ion. A further comparison of V^{2+} and Cr^{3+} will then be done in the cubic MgO. A summary of the materials and ions to be studied and their properties is shown in Table I.

TABLE I
CRYSTALS AND IMPURITY IONS

Material	Impurity Ion	Electronic Configuration	Electronic Spin	Nuclear Spin	Ground State	Symmetry at Site
Al_2O_3	V^{2+}	$3d^3$	$3/2$	$7/2$	$4F$	Trigonal
	Cr^{3+}	$3d^3$	$3/2$	0	$4F$	Trigonal
$CaCO_3$	Mn^{2+} *	$3d^5$	$5/2$	$5/2$	$6S$	Trigonal
	Fe^{3+}	$3d^5$	$5/2$	0	$6S$	Trigonal
MgO	V^{2+}	$3d^3$	$3/2$	$7/2$	$4F$	Cubic
	Cr^{3+}	$3d^3$	$3/2$	0	$4F$	Cubic
	Mn^{2+} *	$3d^5$	$5/2$	$5/2$	$6S$	Cubic
	Fe^{3+} *	$3d^5$	$5/2$	0	$6S$	Cubic

*Work performed by others to be used for comparison.

From the above studies it is hoped that information and insight will be gained into two major areas where understanding is currently lacking or is controversial. The first is that of the mechanism or mechanisms of interaction between the impurity ion and its host lattice which give zero field splittings. Such interactions as spin-orbit, spin-spin, and electrostatic should give a predictable pressure dependence if used with a valid analytical model. The importance of covalency, configuration mixing, or electron transfer should also be noticed. The second area will be that of the effect the impurity ion has upon the lattice and vice versa. Studying different ions in the same lattice and the same ion in different lattices will give a measure of the distortion caused by ions and produced in ions. Information will also be gained about such things as the ions themselves, the lattices, relaxation phenomena, and the analytical models.

II. THEORETICAL ANALYSIS

The following is a brief summary of the theoretical analysis used to determine the hydrostatic pressure effect on the "spin Hamiltonian parameters." A free ion perturbed by the crystalline and applied fields is assumed.

A. SPIN HAMILTONIAN

If the low lying states of the impurity ion arise from a common multiplet of L from the free ion, if other multiplet levels are far above, and if the perturbations due to the crystalline field are large compared with the free ion fine structure, one can write a simplified Hamiltonian for the system as follows:¹³⁻¹⁵

$$\mathcal{H}_{\text{spin}} \psi_{m_S m_I} = E_{m_S m_I} \psi_{m_S m_I} \quad (1)$$

where m_S and m_I are the electronic and nuclear magnetic quantum numbers respectively. The basis for the representation are the free ion wave functions, and

$$\mathcal{H}_{\text{spin}} = A \vec{I} \cdot \vec{S} + g \beta \vec{S} \cdot \vec{H} + \mathcal{H}_{\text{cryst.}} \quad (2)$$

where A is the hyperfine coupling constant, I and S are the nuclear and electronic spin, g is the gyromagnetic ratio, $\beta = \frac{e}{2mc}$, and H is the applied magnetic field.

The crystalline field potential $V_{\text{cryst.}} = \mathcal{H}_{\text{cryst.}}/e$ can be expanded

in a multipole expansion about the impurity ion,

$$V(r, \theta, \phi) = \sum_{l, m} a_{lm} r^l Y_{lm}(\theta, \phi) \quad (3)$$

where

$$a_{lm} = \frac{e^2}{\epsilon(2l+1)} \sum_i \frac{z_i}{R_i^{l+1}} Y_{lm}^*(\theta_i, \phi_i) \quad (4)$$

and is in terms of the coordinates of the i th neighboring ion. The symmetry of the lattice site restricts the values of l , and the wave functions, being constructed from those of 3d electrons with $l = 2$, limits the series to $l = 4$. A linear combination of spin operators that transform under rotations like each of the spherical harmonics in the expansion can then be found and used in the spin Hamiltonian. This results in the following: for an S state ion in MgO

$$\mathcal{H}_{\text{spin}} = \vec{A}\vec{I} \cdot \vec{S} + g\vec{B}\vec{H} \cdot \vec{S} + \frac{1}{6} a(S_x^4 + S_y^4 + S_z^4) ; \quad (5)$$

for an F state ion in MgO

$$\mathcal{H}_{\text{spin}} = \vec{A}\vec{I} \cdot \vec{S} + g\vec{B}\vec{H} \cdot \vec{S} ; \quad (6)$$

for an S state ion in calcite

$$\mathcal{H}_{\text{spin}} = \vec{A}\vec{I} \cdot \vec{S} + g\vec{B}\vec{H} \cdot \vec{S} + DS_{20} + a(S_{40} + b_3 S_{43} - b_3^* S_{4-3}) \quad (7)$$

where

$$\begin{aligned}
S_{20} &= \frac{1}{3} (3S_z^2 - S^2) , \\
S_{40} &= -\frac{1}{180} (35S_z^4 - 30S^2S_z^2 + 25S_z^2 - 6S^2 + 3S^4) , \\
S_{4\pm 3} &= \pm \frac{\sqrt{35}}{180} S_{\pm}^3 (2S_z \pm 3) ;
\end{aligned} \tag{8}$$

and for an F state ion in sapphire

$$\mathcal{H}_{\text{spin}} = A\vec{I}\cdot\vec{S} + g\beta\vec{H}\cdot\vec{S} + DS_{20} \tag{9}$$

where D and a are the axial and cubic field splitting parameters.

Experimental resonant transition energies between levels of different m_S and m_I are used to fit the spin Hamiltonian parameters g , A , and the coefficients of the expansion. It is the changes in these parameters with hydrostatic pressure that are observed and determined.

B. COMPRESSIONAL MODEL AND PRESSURE DEPENDENCE

In order to relate the observed pressure dependence to changes in the crystalline field, some model of lattice compression must be assumed. Considering the lattice and elastic constants and the lattice structure, one can choose a model such as uniform compression with only the distances between the ions uniformly changing and all the angles remaining constant. If the elastic constants are anisotropic a compression proportional to the constants can be used. (For the present it is assumed that deformation is the principle mechanism of the spin lattice interaction and that overlap or covalency will vary with pressure in a similar manner.¹⁶⁾)

The elastic constants are defined by

$$p_i = \sum_{j=1}^6 C_{ij} u_j \quad (10)$$

and the elastic moduli by their matrix reciprocal

$$u_i = \sum_{j=1}^6 S_{ij} p_j \quad (11)$$

where

$$\begin{aligned} p_1 &= p_{xx}; & p_4 &= p_{yz} = p_{zy} \\ p_2 &= p_{yy}; & p_5 &= p_{xz} = p_{zx} \\ p_3 &= p_{zz}; & p_6 &= p_{xy} = p_{yx} . \end{aligned} \quad (12)$$

p_{ij} is a stress tensor which is defined as the force in the i^{th} direction per unit area whose normal is in the j^{th} direction. Furthermore, in Eq.

(11)

$$\begin{aligned} u_1 &= u_{xx}; & u_4 &= u_{yz} + u_{zy} \\ u_2 &= u_{yy}; & u_5 &= u_{xz} + u_{zx} \\ u_3 &= u_{zz}; & u_6 &= u_{xy} + u_{yx} . \end{aligned} \quad (13)$$

u_{ij} is the strain tensor and for small deformations is, for $i = j$, the elongation in that direction per unit length. For $i \neq j$, it is the change in angle between the i^{th} and j^{th} axes.

For hydrostatic pressure $p_1 = p_2 = p_3 = -p$ and $p_4 = p_5 = p_6 = 0$; for uniaxial pressure usually $p_3 = -p$ and all the rest are zero. Due to the symmetry many of the elastic constants are zero or equal to one another and the moduli matrix simplifies also. Thus, using the elastic constants to

determine u_2 , for example, the change in position $\Delta y/y$ may be obtained.

If a point charge model is assumed the contribution to the crystalline field at the impurity ion can be calculated for each of the neighboring ions. (A distributed charge can also be used but the effect of the change in the charge distribution is small compared with its relocation.⁹) Knowing the change in position due to the change in pressure, one can calculate the change in its contribution to the crystalline field from

$$\Delta a_{\ell m} = \sum_i \left(\frac{\partial a_{\ell m}}{\partial x} \Delta x_i + \frac{\partial a_{\ell m}}{\partial y} \Delta y_i + \frac{\partial a_{\ell m}}{\partial z} \Delta z_i \right) \quad (14)$$

where the derivatives with position are obtained from Eq. (4) and the changes in position from Eq. (11). Inserting these values in the cutoff series expansion of Eq. (3), one obtains the pressure dependence to be related to the experimentally observed spin Hamiltonian parameters.

C. AREAS OF DEVELOPMENT

The above analysis has worked reasonably well and should be adequate. There was some indication that the spin Hamiltonian parameters were not a perfect fit, however;⁹ if it becomes experimentally feasible, a Koster-Statz analysis¹⁷ might give a better fit. The effect might be due to covalency in some of the bonds as indicated earlier, and an analysis utilizing molecular orbital theory^{18,19} should be informative. Since the effects due to configuration mixing²⁰ have not been considered at all thus far, they will be examined. It would also be of interest to correlate high pressure optical work such as that done by Drickamer et al.¹⁰⁻¹² with EPR pressure studies on the same sample.

III. INSTRUMENTATION

A. GENERAL DESCRIPTION

At each electron paramagnetic resonance condition the microwave frequency, the magnetic field, and the pressure must be determined. Since the pressure shifts are very small (ca. 1 g in 3000 g), this has to be done with a degree of precision which is small compared with the shift. This is accomplished with a crystal frequency standard, a proton probe, and a manganin cell respectively.

But, since it is difficult to relate the magnetic field at the sample which is inside the pressure bomb to the probe measurement outside the bomb and since the precise locating of the absorption proved to be difficult, an alternative method was desirable. It was decided to use two samples, one inside the high pressure portion of the cavity and one inside the atmospheric portion, and simply relate the change in the first to the change in the second. This not only reduced the error (formerly the difference between two large numbers) but greatly simplifies the analysis and procedure by reducing the need for considering such things as second order corrections, hysteresis effects, and ambient changes.

The principles of operation are as follows: The samples are placed in the two portions of the microwave resonant cavity, which is located in a DC magnetic field. The magnetic field about each sample is modulated at a different frequency. The microwave power absorbed by the cavity is then fed as signal to two phase sensitive detection systems, each of which is sensitive

to one of the two modulation frequencies. The signals from both samples are thus separated and plotted out on a pair of identical recorders. Thus the percentage change can be directly determined, and with a calibrated field sweep the relative shift can be directly measured in gauss.

The high pressure is generated by a hand pump, magnified with a piston intensifier, and fed to the beryllium-copper bomb through thick walled stainless steel tubing.

B. SPECTROMETER

The spectrometer is of the homodyne type²¹ and utilizes X band (8-12 kMc) frequencies and phase sensitive detectors. Straight detection is used at present, however,²¹ and the bypass arm in the microwave system has been built in for future use. Referring to Fig. 1, the microwaves are generated by the klystron and coupled through the electric field into the coaxial cavity with the coupling adjusted by a below cutoff attenuator. The reflected power is then detected by a crystal detector. The microwave frequency is locked on to the cavity by an automatic frequency control which uses a 10 kc frequency modulation and signal feedback.

The cavity is coaxial and built into one of the plugs of the high pressure bomb as shown in Fig. 2. The cavity entrance is at the waveguide to coaxial converter and about 8 wavelengths from the high pressure sample. Just the last portion of the cavity, shown in detail in Fig. 2, is at high pressure; this not only allows the coupling to be changed readily with pressure but keeps the volume and consequently the stored energy at a minimum. This portion is sealed from the atmospheric portion by a beryllium-copper cone which is seated

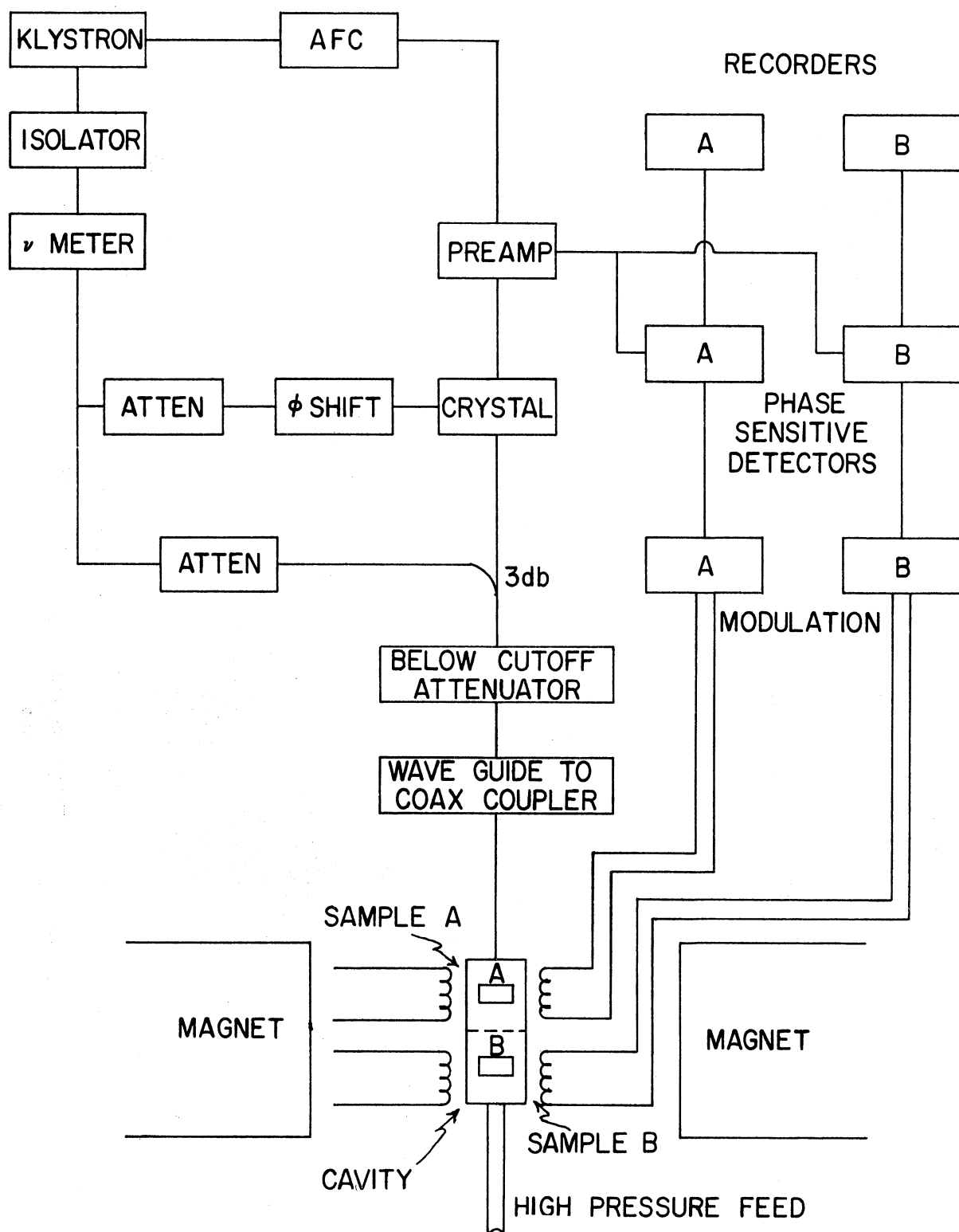


Fig. 1. Spectrometer schematic.

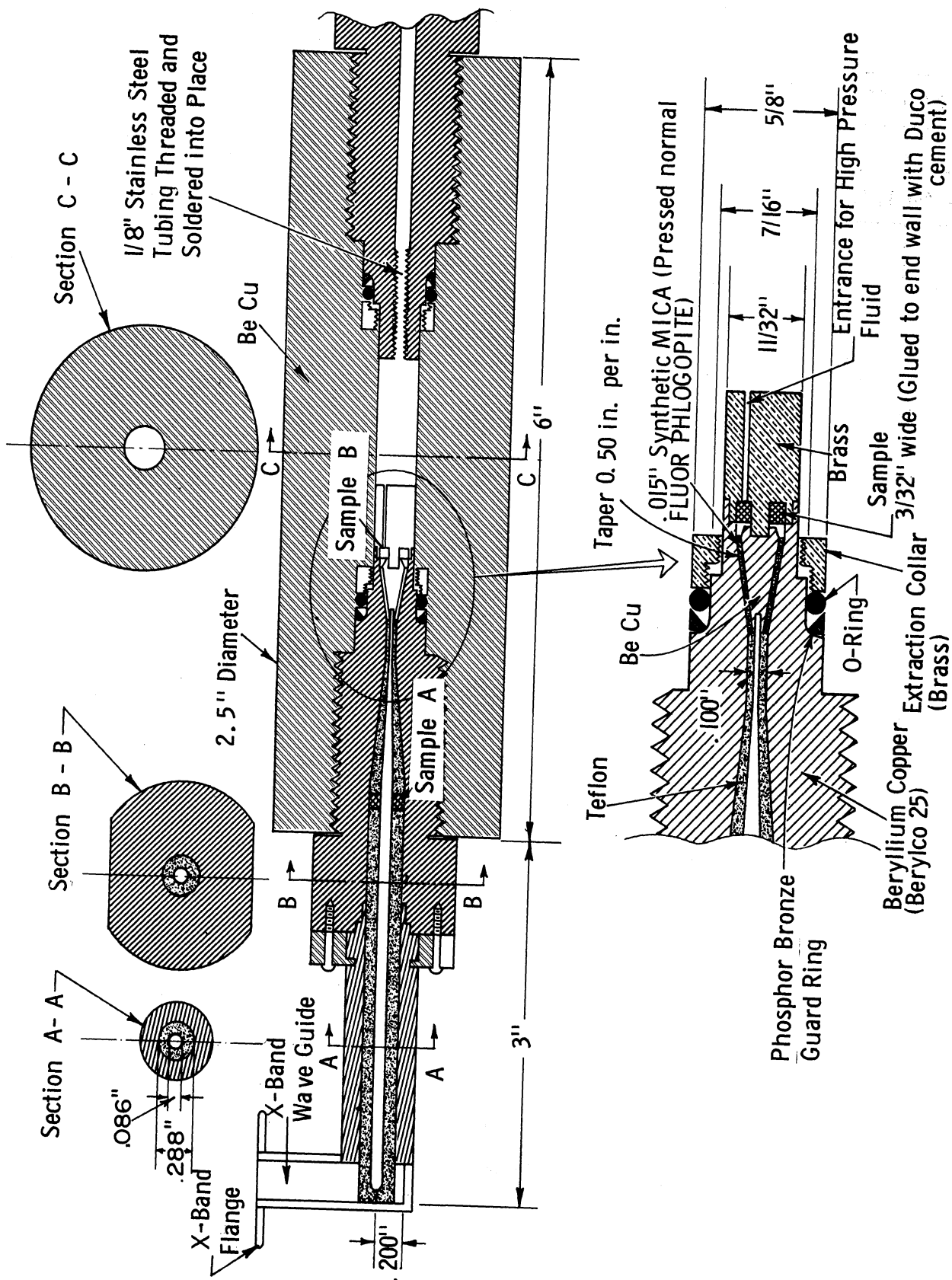


Fig. 2. Pressure bomb and microwave cavity.

on an insulating cone of synthetic mica (pressed normal fluor phlogopite).

The sealing cone is part of the center conductor of the coaxial cavity.

The high pressure sample is located at the end of the cavity. It is usually in the shape of an annulus about the center conductor and surrounded by pentane, the high pressure fluid. The identically oriented low pressure sample is placed part way up the cavity, and the rest of the cavity is filled with teflon.

The location of the second sample was determined by three requirements. First, it had to be beyond the cone and yet in a comparable magnetic field. The fields do not have to be exactly identical since it is the change in one absorption line with respect to the other that is measured. The magnetic field homogeneity was increased tenfold with the addition of simple ring shims which yielded a 3" diameter region in which the field was constant to within 0.1 gauss. (A 9" D Varian rotatable magnet with a 3.25" gap is used.) Second, the modulation of the magnetic field at one sample due to the modulation of the other had to be at a minimum. This was accomplished by placing each sample in the null of the modulating field of the other modulation coil. Third, the sample had to lie near a maximum of the microwave field. These requirements fixed the separation at 1.87". The frequency dependence of the cavity with pressure is small (ca. 2.5 Mc per 1000 atm). The cavity "Q" is about 500.

The absorption signal is fed into a preamplifier and then to two phase sensitive detectors whose first stages are twin-tee filter amplifiers adjusted to the two modulation frequencies, 228 cps and 800 cps. These are

followed by the lock-in amplifiers. The outputs are then plotted by two identical recorders with synchronized charts driven by the same chart drive shaft.

C. HIGH PRESSURE SYSTEM

The components of the high pressure system are shown schematically in Fig. 3. Most of the components were manufactured by Harwood Engineering. The system has a low pressure charging section and high pressure generating equipment. Hand pumps are used with a 20:1.5 piston intensifier used to obtain the high pressure. The pressure is determined with a manganin cell and bridge circuit using a precision four decade resistance box and galvanometer. The sensitivity of the measurement circuit has been determined to be less than 1 atmosphere. The accuracy is thus limited by the pressure dependence of the resistance of the manganin wire or about 1%. The measuring system was calibrated by observing the 3% volume change as mercury freezes at 7420 atmospheres and 0°C. This was done using a specially constructed Invaro oil hardening steel bomb with a much larger volume than the experimental bomb.

The high pressure is transferred to the bomb through thick walled, cold worked stainless steel tubing with a 0.0075" inside diameter. The bomb, shown in Fig. 2, is 2.5" O.D. and 11/32" I.D. and open on both ends. The bomb, the two end plugs, and the sealing cone are made of Berylco 25, a nonmagnetic, high strength beryllium copper alloy which is machined in the annealed state and heat treated afterwards. The plugs are sealed with rubber, teflon, and phosphor bronze ring seals of the unsupported type²² and the unit is designed to hold a pressure of 10,000 atmospheres. Normal pentane is used as the transfer fluid and at these high pressure it becomes viscous. As much as

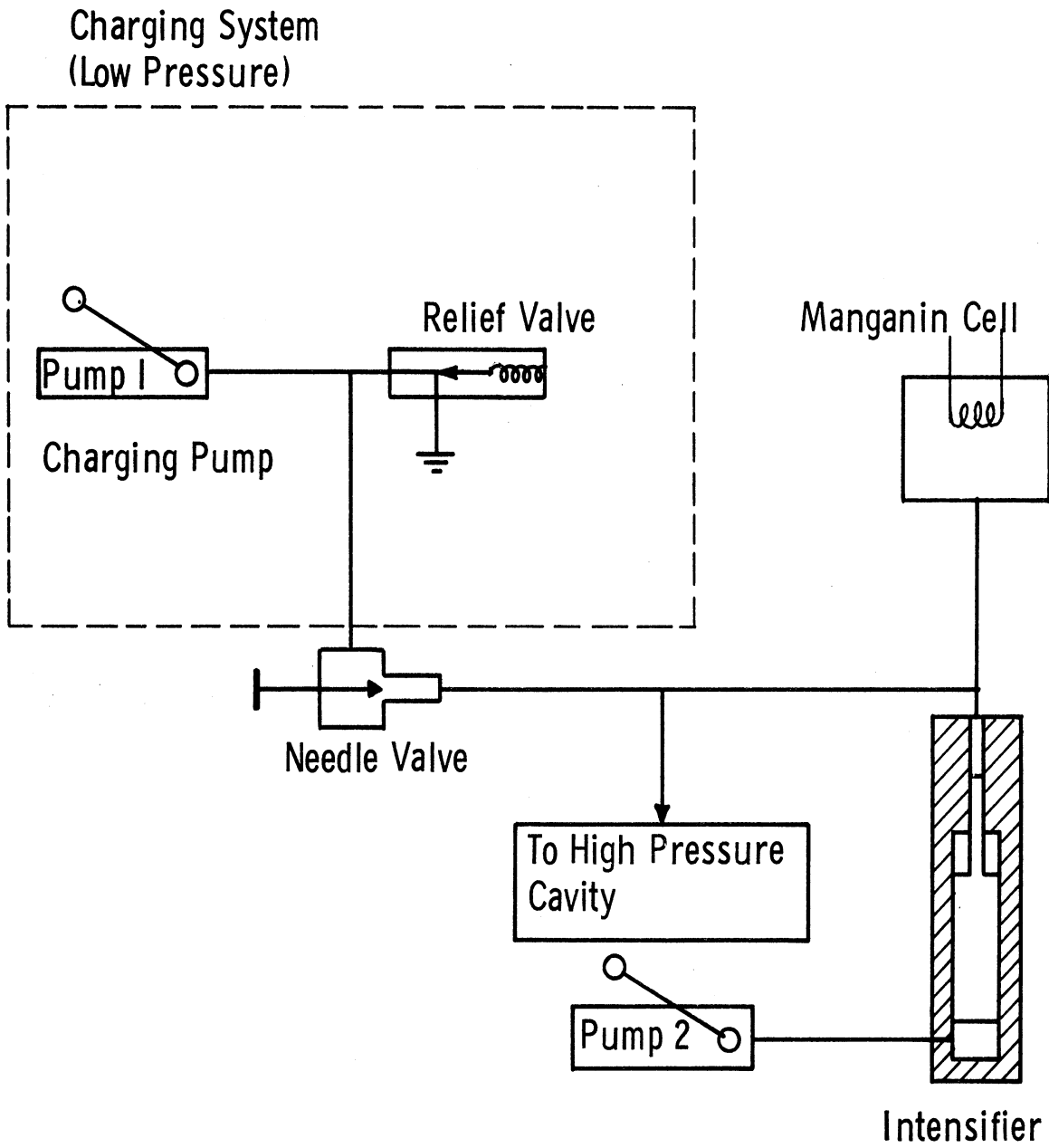


Fig. 3. High pressure system schematic.

15 minutes is necessary for the pressure to be transmitted through the tubing.

The bomb is clamped into the manget by means of brass clamps attached to circular brass caps which are clamped over the magnet's pole pieces. These brass caps also hold the ring shims and the modulation coils. The clamps permit motion only in the vertical direction along the two-sample axis, which is also the axis of magnet rotation. This allows precise centering and accurate repositioning.

D. FURTHER MODIFICATIONS

Since the complete system is operating well at present, no immediate changes are contemplated. However, some changes which may become necessary are being investigated.

The most desirable change would be that of going to lower temperatures. The biggest problem is involved with using a transfer fluid that is sure to remain fluid. This limits temperatures to about 300°K, and the possible fluids either to a 50-50 mixture of 2 methyl butane and n pentane²³ or to petroleum benzene.²⁴ Other desirable changes would be to improve the cavity "Q" value, shorten the cavity, and reduce klystron noise.

The sensitivity of the spectrometer will also be determined by using a known EPR sample as well as by neutron activation analysis of the present MgO sample. The sapphire and calcite samples have already been obtained but the V²⁺ in MgO will have to be made by coating an MgO crystal with vanadium pentoxide, heating the sample, and then X-raying it.²⁵

IV. SUMMARY OF PROGRESS TO DATE

The complete experimental apparatus is operating well and the following have been successfully completed: adaptation of the whole system to the new magnet, conversion of the microwave spectrometer to homodyne, addition of the second channel in the detection system, making provisions for the second sample in the cavity, fourfold improvement of the "Q" of the cavity, construction of a new bomb, calibration of the pressure system, shimming the magnet, and determination of noise sources and of "cross talk" between samples. The largest noise source at present is the klystron and cooling it should reduce the noise to that of the crystal. By placing a DPPH sample at one of the sample positions, the cross talk was determined to be less than one part in 10^4 .

Initial tests with Mn^{2+} in MgO have been tried and give reasonable results. They indicate one major problem, however—that of zero drift of the signal with magnetic field. This is felt to be due to one of two things: oscillation of the long center conductor of the coaxial cavity due to the modulation, or some contaminant which causes a broad resonance about $g = 2$. Since precise determination of the zero condition is necessary, this drift will be eliminated before any new crystals are studied. Samples have been obtained for all the projected studies except the V^{2+} in MgO, which will have to be made.

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