EPR Spectrometer for Studying Crystals under High Hydrostatic Pressure*

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(Received 9 March 1964)

A spectrometer for studying the effect of hydrostatic pressure to 10 kbar on the electron paramagnetic resonance spectra of crystals is described. A two-sample comparison method is used which greatly simplifies both the experimental procedure and the analysis. The pressure is purely hydrostatic, and the cavity coupling is readily adjustable from outside the pressure vessel.

I. INTRODUCTION

AN electron paramagnetic resonance spectrometer for studying crystals under high hydrostatic pressure has been constructed which has many distinct advantages over earlier such instruments.[1–3] Its advantages are the ease of cavity coupling adjustment under pressure, the use of a two-sample comparison, and the resulting simplicity of data analysis. Also, hydrostatic pressure is assured, and a precise pressure measurement is possible.

In Sec. II the principles of operation and the construction of the apparatus are described, in Sec. III the advantages of the two-sample system and the solution of the "cross talk" problem are discussed, and some sample data are included in Sec. IV. A traveling-wave analysis for the microwave cavity will be presented in a later paper.

II. THE EXPERIMENTAL APPARATUS

The principles of operation are as follows: The two samples are placed in the atmospheric and high pressure sections 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 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. This not only reduces the error (formerly the difference between two large numbers), but also greatly simplifies the analysis and procedure by reducing the need for considering, for example, second-order corrections, hysteresis effects, and ambient changes.

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

A. Spectrometer

The spectrometer is of the homodyne type[4] and utilizes X-band (8–12 kMc) frequencies and phase-sensitive detectors. Straight detection is used at present, however,[4] 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 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

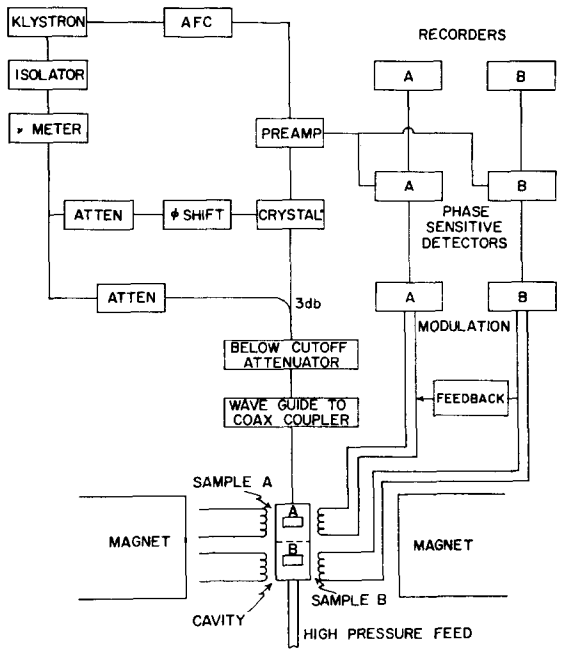

FIG. 1. High pressure EPR spectrometer schematic.

* This work was supported in part by the U. S. Atomic Energy Commission and The National Science Foundation.
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[1] W. M. Walsh, Jr., and N. Bloembergen, Phys. Rev. **107**, 904 (1957).
[2] A. W. Lawson and George E. Smith, Rev. Sci. Instr. **30**, 989 (1959).
[3] J. H. Gardner *et al.*, Rev. Sci. Instr. **34**, 1043 (1963).
[4] G. Feher, Bell System Tech. J. **36**, 449 (1957).

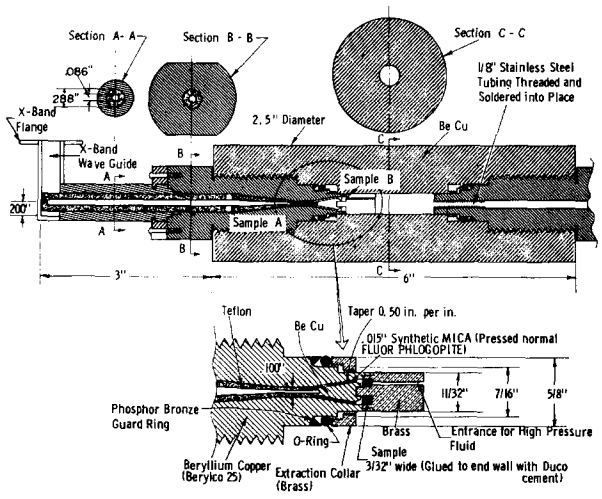

FIG. 2. Pressure bomb and microwave cavity.

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 allows the coupling to be changed readily with pressure but keeps the volume and, consequently, the stored energy and the cavity's resonant frequency change with pressure at a minimum. This portion is sealed from the atmospheric portion by a beryllium-copper cone which is seated 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-in.-diam region in which the field was constant to within 0.1 G. (A 9-in.-diam Varian rotable magnet with a 3.25-in.-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 in. The frequency dependence of the cavity with pressure is small (about 2.5 Mc/1000 atm). If one uses a thicker and shorter mica cone than indicated in Fig. 2, filling the rest of the space with Teflon, 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-T filter amplifiers adjusted to the two modulation frequencies, 228 and 800 cps. (The modulation frequencies have to be low in order for the fields to penetrate the bomb.) 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.

B. 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 atm. The accuracy is thus limited by the pressure dependence of the resistance of the Manganin wire, which is linear with pressure to within 0.5%. The measuring system was calibrated by observing the 3% volume change as mercury freezes at 7420 atm 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-in. i.d. and 0.125-in. o.d. The bomb, shown in Fig. 2, is 2.5-in. o.d. and $\frac{11}{32}$-in. 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 type[5] and the unit is designed to hold a pressure

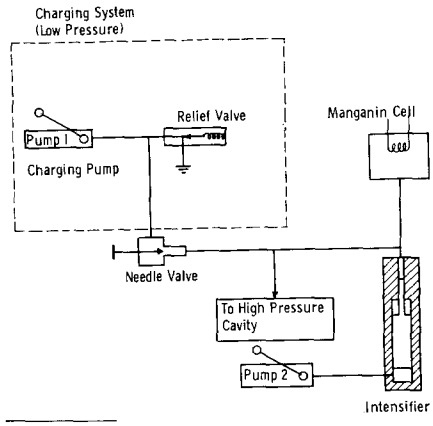

FIG. 3. High pressure system schematic.

[5] P. W. Bridgeman, *The Physics of High Pressure* (G. Bell & Sons, Ltd., London, 1931).

of 10 000 atm. Normal pentane is used as the transfer fluid and at these high pressures it becomes viscous. As much as 15 min is necessary for the pressure to be transmitted through the tubing.

The bomb is clamped into the magnet 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.

II. THE TWO-SAMPLE METHOD

Perhaps the most practical advantage of comparing the spectrum of a sample under high pressure to one at atmospheric pressure is that, during the course of the experiment, one can see at a glance that a pressure shift in the spectrum is indeed there, estimate its order of magnitude, and determine its direction without any calculations or analysis whatsoever. The fact that the two channels are identical reduces the need to consider electronic distortion of the line shape. It also eliminates any consideration of ambient changes, since the difference is always what is measured. Hysteresis effects in the magnet can also be ignored, except for homogeneity, unless a set of lines is being considered.

Placing both samples in the same cavity so that the transitions in each occur at the same microwave frequency provides many advantages. Second-order frequency corrections in unshifted parameters are completely eliminated. Also, if the pressure perturbations are small, and they usually are, most second-order perturbations can be neglected since these would be second-order corrections to a pressure shift which is second order to begin with. The fact that both samples are at the same frequency allows some very helpful simplifications in the analysis. For example, consider the spin $-\frac{1}{2}$ to $\frac{1}{2}$ transition for Cr^{3+} in Al_2O_3 with the magnetic field along the c axis of the crystal,[6]

$$h\nu = g_z\beta H = g_z'\beta H', \tag{1}$$

where the primes indicate under pressure. Solving for $\Delta g_z = g_z' - g_z$ is simplified by the equality above to

$$\Delta g_z = g_z(H-H')/H' = -g_z\Delta H/H'. \tag{2}$$

Thus, a precise measurement of a g shift involves only an ordinary field measurement and no frequency measurement. In a similar manner the $\frac{1}{2}$ to $\frac{3}{2}$ transition

$$h\nu = g_z\beta H + 2D = g_z'\beta(H+\Delta H) + 2(D+\Delta D) \tag{3}$$

[6] E. O. Schulz-Du Bois, Bell System Tech. J. 38, 271 (1959).

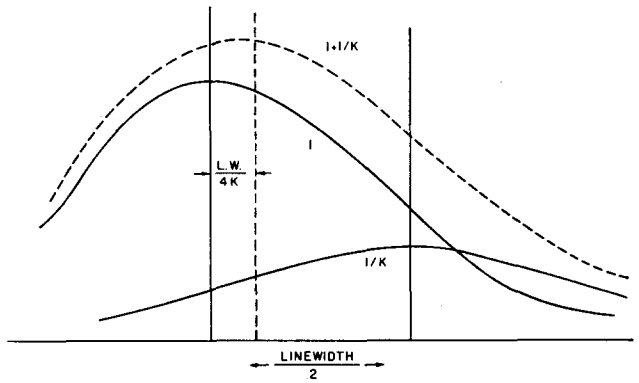

FIG. 4. Maximum shift in line center for two overlapping lines (cross talk determination).

simplifies to (since g shifts are very small),

$$2\Delta D = -g_z\beta\Delta H. \tag{4}$$

Also, if there is a close set of lines that falls within the sweep range so that the unshifted spectrum can be used to calibrate the shifted spectrum (see Sec. IV), no measurements whatsoever are needed. In this case, however, linearity of the field sweep to first order is necessary.

The only disadvantage of the two-sample method, and the major problem of any two-signal system, is the channel separation or "cross talk." In our case, the separation is electronically quite simple and narrow-band amplifiers and phase-sensitive detectors assure that signals carried on each of the two modulation frequencies are definitely separated. To be certain that the signal carried on one of the modulation frequencies is due entirely to one sample is not as simple.

If one defines a measure of cross talk K_A as the ratio of the signal from sample A that is carried through on channel A to the signal from sample B that is carried through on channel A, then K_A and K_B can be measured experimentally by using two different samples. A lower limit must then be set for K. The center of the absorption line, which is what is measured in this experiment, will be shifted most by a second signal when the second signal is $\frac{1}{2}$ linewidth away as shown in Fig. 4, so that its maximum slope occurs at the true center. The observed center of the sum (or difference, depending on polarity) of the two signals will then be shifted by $\frac{1}{4}K$ times the linewidth. The choice of minimum permissible K is thus determined by the linewidth and the expected pressure shifts, and in our case, was about 10.

The primary criterion in determining the location of the second sample was that it be at a maximum in the microwave fields in the coaxial cavity, yet be as close as possible to the high pressure sample so that they both remain in the homogeneous portion of the dc magnetic field. This separation then determined the size of the modulation coils so that a pair of coils centered on one sample

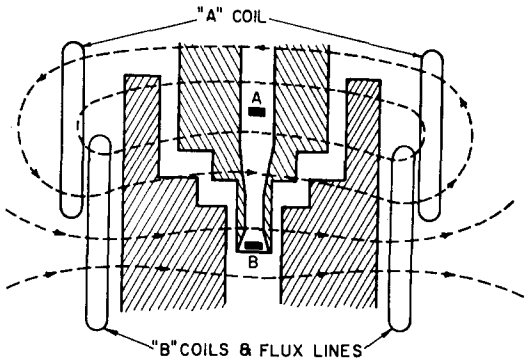

FIG. 5. Schematic of bomb, modulation coils, and flux lines.

had a null at the other as shown in Fig. 5. Without the pressure bomb and with proper orientation of the coils, $K_A=10$ and $K_B=10^3$ were obtained. However, with the bomb, $K_A=10^4$ and $K_B=1$. Consideration of these values and the bomb shape (schematically shown in Fig. 5) and the fact that the skin depth at these frequencies is considerably smaller than the bomb thickness, leads to the conclusion that the modulation was being caused by induced currents. Therefore, another method had to be used to eliminate the cross talk in channel B. Since this was due to the field modulation about sample B being carried up to and around sample A, but not vice versa, a portion of the B modulation signal can be inverted and fed into the A modulation to exactly cancel the cross talk. Thus K_B can be set by a phase and amplitude adjustment of this feedback to be as large as desired or even infinity. Thus cross talk was reduced to less than one part in 10^4.

IV. SAMPLE DATA

When there is more than one line falling within the sweep range of the dc magnetic field, the data taking is extremely simple. The known line separations on the atmospheric pressure chart provide a calibration for the high pressure chart. Using identical chart paper on identical recorders driven by the same shaft assures equality of recordings. (It was found, however, that the chart paper grid spacings and drive hole spacings are not always reliable.) Figure 6 shows a sketched pair of recordings for the first three fine structure lines for Mn^{++} in MgO. In actual practice the signals are driven a long way off scale in order to more accurately determine where the center of the absorption line falls (derivatives are plotted and constant line shape is assumed).

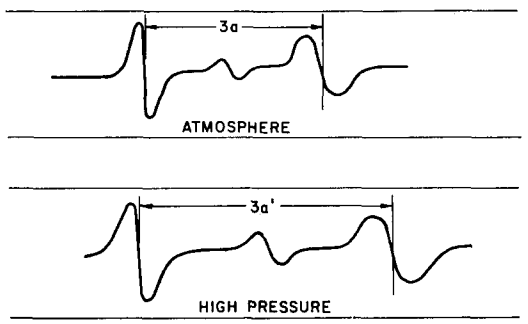

FIG. 6. First three fine structure lines for Mn^{2+} in MgO at $\theta=0°$.

If no close set of lines is available, the procedure is to stop the sweep exactly when the recorder shows the derivative to be zero and measure the field with a nuclear magnetic resonance probe. Similarly, the field is measured for the shifted line. The relationship of the field at the probe to that at the sample is of no concern as long as it is constant, since the difference is what is measured. Figure 7 shows a sample collection of data for a fine structure line of Cr^{+++} in Al_2O_3.[7]

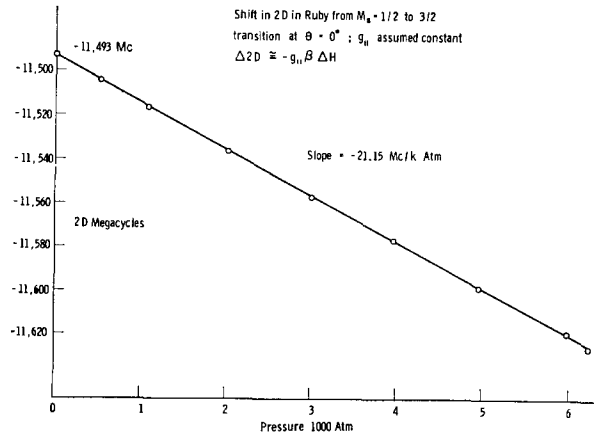

FIG. 7. Pressure shift of the zero field splitting in ruby.

ACKNOWLEDGMENTS

The authors wish to thank Professor Richard H. Sands and Professor Chihiro Kikuchi for stimulation and support, and Herman Roemer for assistance in the fabrication of the high pressure cavity.

[7] A. F. Clark, R. H. Sands, and C. Kikuchi, Bull. Am. Phys. Soc. 9, 36 (1964).