Apparatus for Electron Spin Resonance Studies at Very High Pressures

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was 1.0. Below 1×10^{-9} A the slope was 1.6. Using a calibrated Bayard-Alpert gauge "upstream" the slope of 1.6 was extended down to Redhead currents of 6×10^{-13} A. A separate test with an uncalibrated gauge upstream and lower conductance capillary indicated that the slope remained the same (1.6) down to Redhead gauge currents of 3×10^{-14} A. The constant value of 1.6 suggests that the pumping speed of the system had remained constant. Assuming this to be the case, the latter current is equivalent to a nitrogen pressure of 3.4×10^{-13} Torr.

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Apparatus for Electron Spin Resonance Studies at Very High Pressures*

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Apparatus for studying electron paramagnetic resonance in solids under pressure to 60 kilobars and beyond has been developed. The high pressures are produced between dielectric Bridgman anvils, one of which serves as a microwave resonance cavity. The instrument makes possible the study, by EPR techniques, of paramagnetic atoms or ions subject to stresses which might be expected to induce changes in their electronic structure.

INTRODUCTION

MICROWAVE resonance would appear to provide an ideal diagnostic tool for the determination of the physical changes that take place in materials as pressure is applied, particularly those changes which are not accessible to x-ray analysis. Some work has been done in the intermediate pressure range to about 10 kilobars[1–3] using pressure bombs, but some of the most interesting high pressure effects are those thought to involve a change in the atom itself, and these changes generally occur at much higher pressures. Basic equipment and techniques for producing these higher hydrostatic pressures on a paramagnetic solid in a microwave bridge are described here.

DESCRIPTION OF EQUIPMENT

A block diagram of the system appears in Fig. 1. The system consists essentially of four subsystems: the pressure system; the microwave bridge; the magnetic field modulation, control, and measurement system; and the low temperature system. Each of these subsystems is described below.

Pressure System

The sample cell is a $\frac{1}{8}$-in.-diam$\times$0.030-in.-high boss in a $\frac{3}{8}\times$0.006 in. copper disk placed between a pair of Bridgman anvils, the lower of which forms the bottom face of the cell enclosure and serves as the resonant cavity of the microwave system. The sample cell is filled with Viscasil 100 000 (General Electric Company silicone fluid, viscosity at 25°C is 100 000 centistokes) or mineral oil for the pressure transmitting medium. The cell is surrounded by a multilayered band of pyrophyllite washers 0.010 in. thick $\times$0.125 in. i.d. $\times$0.375 in. o.d. separated by half-hard Berylco-25 beryllium-copper washers 0.005 in. thick with the same i.d. and o.d. (Figs. 2 and 3).

The lower anvil is essentially a right circular cylinder with height and diameter 0.700 in. made of cold-pressed alumina of an especially pure form manufactured by Electroceramics, Salt Lake City, Utah. The anvil is silver-coated by the Brashear process[4] followed by silver-plating to a thickness of about 0.001 in.

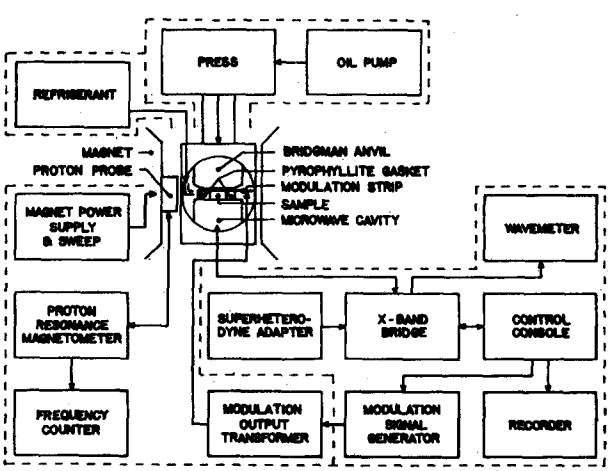

FIG. 1. Block diagram of complete high pressure magnetic resonance system.

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[1] T. Kushida, G. B. Benedek, and N. Bloembergen, Phys. Rev. **104**, 1364 (1956).

[2] G. B. Benedek and E. M. Purcell, J. Chem. Phys. **22**, 2003 (1954).

[3] W. M. Walsh, Phys. Rev. **114**, 1473 (1959); Phys. Rev. **114**, 1485 (1959); Phys. Rev. **122**, 762 (1961).

[4] *Handbook of Physics and Chemistry*, edited by Gray (Chemical Rubber Publishing Company, Cleveland, Ohio, 1958), 39th ed., p. 3050.

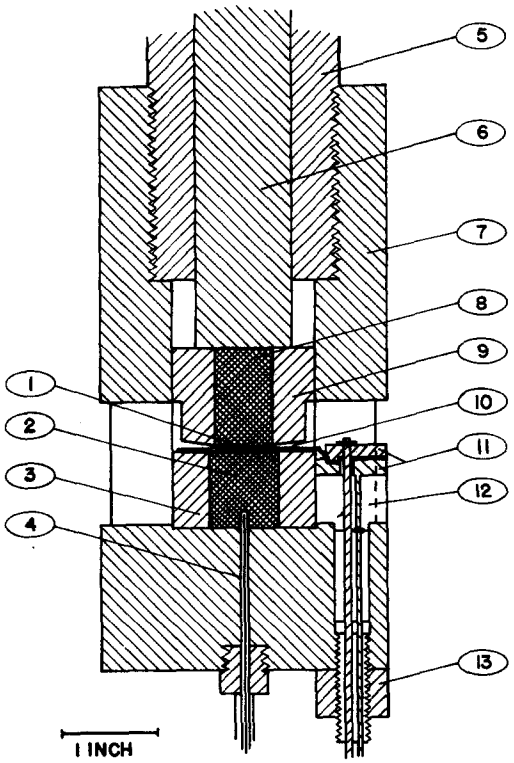

FIG. 2. Schematic diagram of high pressure head. (1) Sample cell (see Fig. 3 for detail), (2) combined pressure anvil and microwave cavity, (3) beryllium-copper binding ring for pressure anvil, (4) coaxial line for coupling microwaves, (5) beryllium-copper sleeve for coupling to hydraulic press, (6) beryllium-copper pressure ram, (7) beryllium-copper pressure head, (8) Bridgman-type tapered pressure anvil, (9) beryllium-copper binding ring for pressure anvil, (10) silver modulation strip (see Fig. 3), (11) modulation clamp (see Fig. 3), (12) plastic insulating support for modulation clamp, (13) locking nut for modulation clamp.

The upper anvil is of Bridgman's design.[5] A flat circular face of $\frac{3}{8}$-in. diameter is massively supported by tapering the anvil material at an angle of 6 to 12° out to a diameter of $\frac{1}{2}$ in. The length of the cylinder is 1 in. The material is hot-pressed alumina manufactured by Norton Company of Worcester, Massachusetts. This material, though stronger than the cold-pressed alumina, did not prove to be sufficiently pure for the microwave cavity and was therefore not used for the lower anvil.

Both anvils are supported by beryllium-copper (Berylco-25, The Beryllium Corporation of America, Reading, Pennsylvania) binding rings which have been hardened by heat treating. The wall thicknesses of the binding rings are $\frac{1}{2}$ in. for the upper anvil and $\frac{3}{8}$ in. for the lower anvil. The alumina is pressed into the binding ring against a tapered $\frac{3}{4}$° interference of 0.002 in., Molycote being used as a lubricant.

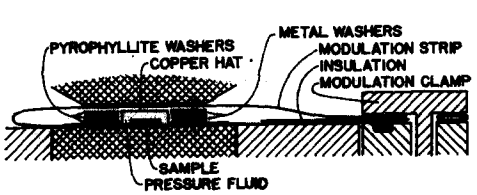

FIG. 3. Schematic detail of sample cell showing modulation system.

[5] P. W. Bridgman, Proc. Am Acad. Arts. and Science 81, 165 (1952).

The anvils are placed in a pressure head as indicated in Fig. 2. Each of the three components of the pressure head assembly is fabricated from half-hard heat-treatable Berylco-25, beryllium-copper. The head is 3 in. in diameter. Clearance of 0.020 in. is allowed between the sleeve and the ram of the pressure head.

The pressure head assembly is coupled to a Rodgers 150-ton hydraulic cylinder press by means of a hard steel coupler screwed into a hard steel disk which is in turn bolted to the cylinder. The press and pressure head assembly are supported above the magnet by a heavy table.

Two pressure pumps are employed. A Sprague S-216c-150 with a pressure amplification of 160 to 1 is operated from compressed air for rapid pumping. A Pine Hydraulic hand pump, No. 1000, provides a vernier.

Microwave Bridge

The system employs a Varian V-4500-41A low-high power microwave bridge with a Varian V-K352s superheterodyne accessory. The latter was designed and built by Varian Associates to meet our requirements. The bridge supplies 200 to 400 mW of power at X band. Microwave coupling to the cylindrical alumina-filled cavity has been achieved both with a loop and with a straight probe. In the former case a $\frac{1}{16}$-in.-wide by $\frac{1}{4}$-in.-diam semicircular slot is cut into the bottom of the alumina to accommodate the loop which is the terminus of a conductor coaxial with a 0.118-in.-diam hole drilled through the bottom of the pressure head. An N-type coaxial connector at the bottom of the head facilitates coaxial coupling to the wave guide. Matching is achieved by means of a double stub tuner. When the TM_{112} mode is used, coupling is best achieved by means of a straight probe projecting about $\frac{1}{8}$ in. into a $\frac{1}{16}$-in.-diam vertical hole drilled midway between the axis and the wall of the cylindrical alumina cavity. In this case matching is accomplished by varying the distance the probe projects into the hole.

Magnetic Field System

The gross magnetic field is produced by a Spectromagnetic Industries model L12-A, 12-in. low-current magnet energized by a Varian V 2100B power supply. The air gap is 4 in. with homogeneity of approximately $\pm\frac{1}{2}$ G over a volume of 1 cu in. at the center. The EPR control system provides a linear sweep of several speeds. A proton resonance magnetometer is used to measure the magnetic field strength.

The modulation system was particularly troublesome for two reasons: (1) the large amount of metal between external modulation coils and the sample restricted the modulation frequency to low values, and (2) impurities in the alumina microwave cavity gave rise to resonances which tended to obscure sample resonances.

The first condition led to the development of the superheterodyne system as mentioned above. Since crystal noise in the first detector drops off approximately inversely as the square of the frequency and since the large amount of metal prevents the use of external high frequency modulation of the sample, a local oscillator is used to form an appropriate difference frequency in the low noise range which carries the resonance information.

The second difficulty required the development of a modulation scheme which gives a large modulating field only in the immediate neighborhood of the sample. A single strip of silver $\frac{1}{8}$ in. wide by 0.001 in. thick placed perpendicular to the gross magnetic field carries the modulation current directly over the sample. This thin silver strip seems not to disturb significantly the symmetry of the pressure system: symmetry is essential for achieving high pressures. The return path for the current is through one of the beryllium-copper support washers (see under Pressure System, above). Several other schemes for the return current have also been successful. The development of this internal modulation scheme makes possible the use of high frequency modulation also. The sensitivities of 100-kc modulation and the superheterodyne system are comparable.

Low Temperature System

A low temperature apparatus has been incorporated into the system to provide another thermodynamic variable for the magnetic resonance studies. This feature permits studies to be made of many paramagnetic materials which have relaxation times too short at room temperature to give sufficiently narrow lines to be observed. It also provides valuable temperature dependent resonance information.

The sample is cooled by flowing liquid nitrogen onto the lower anvil at the desired rate. Cooling of the sample itself is considerably aided by the large thermal conductivity at low temperatures of alumina with which the sample is in contact. The temperature is monitored using a thermocouple near the sample. The flow system consists of a $\frac{1}{4}$-in. thin-walled brass tube, which is insulated with Styrofoam, leading from the top of a Dewar containing liquid nitrogen under pressure. A valve at the top of the Dewar controls the rate of flow. With this system, temperatures between the boiling point of nitrogen and room temperature can be reached.

OPERATION

Brief descriptions of the cavity mode identification and selection, the pressure calibration, and a sample of the results for ruby are given here.

Identification and Selection of Cavity Modes

Due to the large dielectric constant of alumina ($\sim$9.37) and the large size of the cavity anvil many cavity modes can be excited in the tuning range of the klystron (8.5 to 10.0 kMc). These modes were somewhat displaced from their calculated frequencies presumably because of the slight taper in the cylinder and the deformation of the top of the cavity for the sample cell. The picture was further complicated by the presence of numerous modes in the system extraneous to the cavity, but these could generally be distinguished by their lower Q.

Identification of the cavity modes required a number of experiments including a study of the mode shifts produced by the taper and sample cell in a scaled air cavity, varying the method of mode excitation, and varying cavity geometry to verify expected mode shifts. The various modes were also studied for the signal-to-noise ratio and, as expected, the optimum modes were determined to be the TE_{113} and the TM_{112}, the latter being favored because of the ease with which it is excited.

Calibration

Pressure calibration of the small sample cell posed a special problem. To permit the use of resistance transitions in various metals as pressure calibration points, a lower anvil with an axial platinum wire 0.020-in. diameter was fabricated. The anvil material was AL-300 Wesgo resin-bonded, machinable alumina which, after machining, was fired to hard ceramic. During firing the alumina shrinks down tightly on the wire. This anvil is supported by a hardened beryllium-copper binding ring in the same way as the anvils described above. The sample of metal under test is crimped, soldered, or otherwise fastened to the platinum wire and the circuit is completed by grounding the other end of the sample to the wall of the copper sample cell.

Wire samples used were cerium (transition at $P_t \cong 7$ kilobars[5]), bismuth ($P_t = 25.4$ kilobars[6]), thallium ($P_t = 36.7$ kilobars,[6] but difficulty in handling this metal in the minute sample cell has allowed only one successful pressure calibration run), ytterbium ($P_t \approx 39.5$ kilobars,[7] this metal was used even though its resistance transition is not very sharp in order to provide a calibration point in the region of the thallium point), and barium ($P_t = 58.6$ kilobars[8]).

[6] G. C. Kennedy and P. N. LaMori, Publication No. 195, Institute of Geophysics, University of California.
[7] H. Tracy Hall, Inorg. Chem. (to be published).
[8] J. D. Litster and G. B. Benedek, J. Appl. Phys. 34, 688 (1963), quoting G. C. Kennedy.

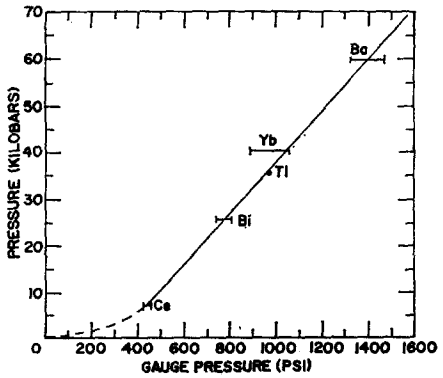

FIG. 4. Pressure calibration curve. The horizontal lines indicate the maximum spread of several calibration runs of Ce, Bi, Yb, and Ba. Only one pressure calibration point for thallium appears. The dashed portion of the curve indicates an extrapolation to zero pressure.

The calibration curve obtained appears in Fig. 4. Evidently considerable deformation of the pyrophyllite washers surrounding the cell takes place before the cell itself is significantly compressed, thus making the pressure curve uncertain near the origin.

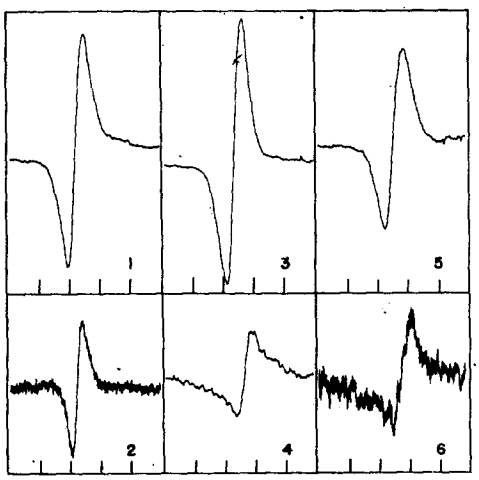

FIG. 5. Sample resonances in ruby under pressure: (1) $m_s=\frac{1}{2}\rightarrow m_s=-\frac{1}{2}$ transition at 10 kilobars, (2) $m_s=\frac{3}{2}\rightarrow m_s=\frac{1}{2}$ transition at 10 kilobars, (3) $m_s=\frac{1}{2}\rightarrow m_s=-\frac{1}{2}$ transition at 30 kilobars, (4) $m_s=\frac{3}{2}\rightarrow m_s=\frac{1}{2}$ transition at 30 kilobars, (5) $m_s=\frac{1}{2}\rightarrow m_s=-\frac{1}{2}$ transition at 50 kilobars, (6) $m_s=\frac{3}{2}\rightarrow m_s=\frac{1}{2}$ transition at 50 kilobars. In upper graphs, each division represents 96 G. In lower graphs, each division represents 169 G.

Sample Resonances in Ruby Under Pressure

Figure 5 shows resonance patterns of ruby taken at 10, 30, and 50 kilobars. The two patterns shown at each pressure are those due to the transition in which the spin quantum number changes from $\frac{1}{2}$ to $-\frac{1}{2}$ and from $\frac{3}{2}$ to $\frac{1}{2}$ with the gross magnetic field oriented parallel to the c axis of the single ruby crystal.[9] The pressure transmitting medium was Viscasil in each case. The ruby sample was a roughly circular disk 0.007 in. thick by approximately 0.050 in. in diameter.

The apparatus described herein provides a new tool for the study of very high pressure effects in materials which exhibit paramagnetic resonance. This tool is very sensitive to minute changes in the crystalline field of a sample and therefore reveals the need for a truly hydrostatic pressure medium at the elevated pressures under consideration. Some lack of consistency in the zero field splitting of ruby (calculated from the spin Hamiltonian: $\mathcal{H}=\frac{1}{2}\delta S_z^2+\beta H g_{\|} S_z$)[9] from run to run which correlates with increasing linewidths at pressures above 15 kilobars suggests that Viscasil does not produce a strictly hydrostatic pressure in this region. Litster and Benedek[10] conclude that silver chloride becomes a hydrostatic pressure medium above 15 kilobars, but our experience has been that the thin ruby sample is broken by the silver chloride before the hydrostatic condition is reached.

The high pressure limit has not been established for this apparatus. Resonances have been observed in ruby well above the barium transition. The limiting element appears to be the strength of the lower alumina anvil cavity.

ACKNOWLEDGMENTS

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[9] J. E. Geusic, Phys. Rev. **102**, 1252 (1956).
[10] J. D. Litster and G. B. Benedek, J. Appl. Phys. **34**, 688 (1963).