

Flux Exclusion in CdS at 77 K: Superconductivity at High Temperatures?

E. Brown^(a) and C. G. Homan

*U. S. Army Armament Research and Development Command, Large Caliber Weapons Systems,
Benet Weapons Laboratory, Watervliet, New York 12189*

and

R. K. MacCrone

*Department of Materials Science, Rensselaer Polytechnic Institute, Troy, New York 12180
(Received 31 March 1980)*

The observation of flux exclusion approaching Meissner proportions ($\chi_V = -1/4\pi$ cgs units) in pressure-quenched CdS at 77 K is reported. The results can be naturally and simply interpreted on the basis of superconductivity at 77 K. If the superconductive state is not the appropriate description, then a new high-temperature collective quantum state must be invoked.

PACS numbers: 75.20.Ck, 71.30.+h, 74.90.+n

Flux exclusion, the Meissner effect, is a well-known experimental manifestation of superconductivity. In this paper we report the observation of large diamagnetism, approaching 100% flux exclusion, in pressure-quenched CdS at 77 K. The implication of a superconducting or other collective state at this temperature is the essential motivation for this communication. Although we have previously reported large diamagnetism ($\chi_V \sim -5 \times 10^{-5}$ cgs units) in pressure quenched CdS at 77 K,¹ the diamagnetism observed here is far larger, by a factor of $\sim 10^3$, than previously reported. These latest results, we believe, now unambiguously establish the collective origin of the effect.

The apparatus used in these *static* susceptibility measurements is a standard P.A.R. vibrating-sample magnetometer (VSM). The sample holder, rod, and enclosing jacket were carefully designed to ensure no frictional contact near the pickup coils. The specimen space was evacuated with use of a rotary pump and nitrogen trap.

The magnetometer itself has been subject to an exhaustive series of tests to ensure the confidence of the results and was calibrated with both a $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ sample and a nickel sphere sample for internal consistency.

The samples in this work were prepared by a technique we call "pressure quenching": the sudden release of pressure at rates of greater than 10^6 bar/sec. This technique is analogous to the well-known technique of temperature quenching by which many metastable states are realized. The electrical resistance of the CdS specimens are monitored during pressure loading to provide an accurate measure of the state immediately prior to quenching. At about 30 kbar, the elec-

trical resistance drops by about five orders of magnitude, signaling the well-known wurtzite to NaCl high-pressure phase transition.² We find that only specimens quenched from above 40 kbar show the large diamagnetism of concern here. After pressure quenching, the resistance at room temperature is more than four orders of magnitude less than the starting material and the specimens have a black sheen. Specimens which are slowly unpressurized from this pressure (P_t) almost revert to their original resistance and are a dark orange color.

Extensive chemical, scanning electron microscope, optical microscopy, x-ray diffraction, and differential scanning calorimetry tests have been performed on all starting powders, compacted pellet samples, and pressurized and pressure-quenched samples.^{1,3,4} To summarize these results, it has been determined that the samples exhibiting this anomalous magnetic behavior have transformed from the starting wurzite structure to a mixture of zincblende and NaCl structure after the pressure quench. These quenched samples had the morphology of a large fraction of powder compact matrix in which small lenticular platelets were embedded. Microhardness tests indicated that the platelets were harder than the matrix material, and chemical etching studies were in agreement with this conclusion. Optical studies with use of polarized light showed that there was less birefringence in the platelets than in the matrix. X-ray diffraction studies failed to reveal any new phase which could be identified with the lenticular platelets except possibly very broad diffuse lines from small crystallites or an amorphous phase.

It has been discovered that the source from

which the starting material is derived is important. Material of a particular lot from Alpha-Inorganic produces the strongly diamagnetic samples described here, while material from Eagle-Picher and a private source, similarly pressure quenched, does not. The starting materials were analyzed by spectrographic analysis, wet chemical analysis, and atomic absorption spectroscopy.^{1,5} An independent analysis of the Alpha-Inorganic material was performed at the National Bureau of Standards with use of x-ray fluorescence spectrometry with detection limits of the order of 10 ppm. This yields a complete high-sensitivity qualitative analysis for elements $Z \geq 11$.⁶ We do not know which impurities, if any, are directly or indirectly responsible for the diamagnetism described below.

Some of the actual experimental data establishing the magnitude and sign of the susceptibility are shown in Fig. 1. The response of the magnetometer with a relatively inactive sample attached to the rod and run under identical conditions is also shown in Fig. 1. It is quite clear that the instrument is operating properly, that the magnitude of the observed signals are well above instrument noise, and that the results accurately represent the diamagnetism of the CdS samples. The Dewar was topped with liquid nitrogen every time the input to the magnetometer

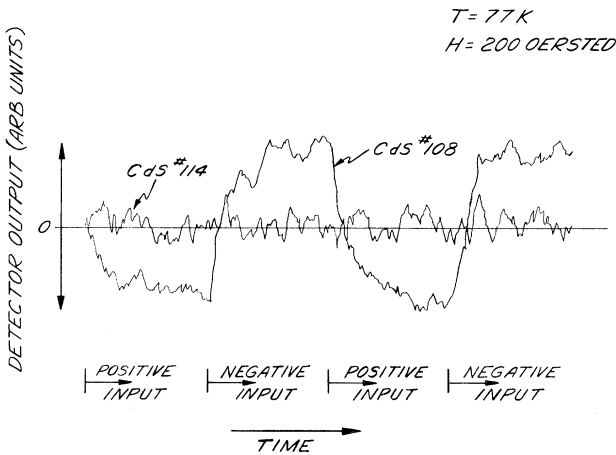


FIG. 1. Experimental recorder tracings of magnetometer output. Input from pickup coils periodically reversed as indicated. The polarity was such that the response is positive (upward) for a diamagnetic sample with input negative. The noise and stability of the instrument is indicated by the trace labeled CdS No. 114. CdS No. 114 has returned to a magnetic behavior similar to as-received material from the response shown in Fig. 2(b) after annealing. (See text.) The large diamagnetic response of CdS No. 108 is evident.

was reversed. This operation introduces transient noise into the system, so we take as the reading the mean value of the signal in the 200 sec prior to reversing the input. At this field, 200 Oe, the specimen signal is clearly above background noise and corresponds to a diamagnetic moment of $7.6 \times 10^{-3} \text{ G cm}^3$. Complete flux exclusion at this field would correspond to a diamagnetic moment of $4.8 \times 10^{-2} \text{ G cm}^3$. We would like to emphasize that over the last year, every experimental precaution we could conceive has been taken and every test made to ensure the validity of this result.

From a series of measurements such as those shown in Fig. 1, the results shown in Fig. 2(a) were obtained. Curve A was obtained on a sample which had been mounted in the magnetometer

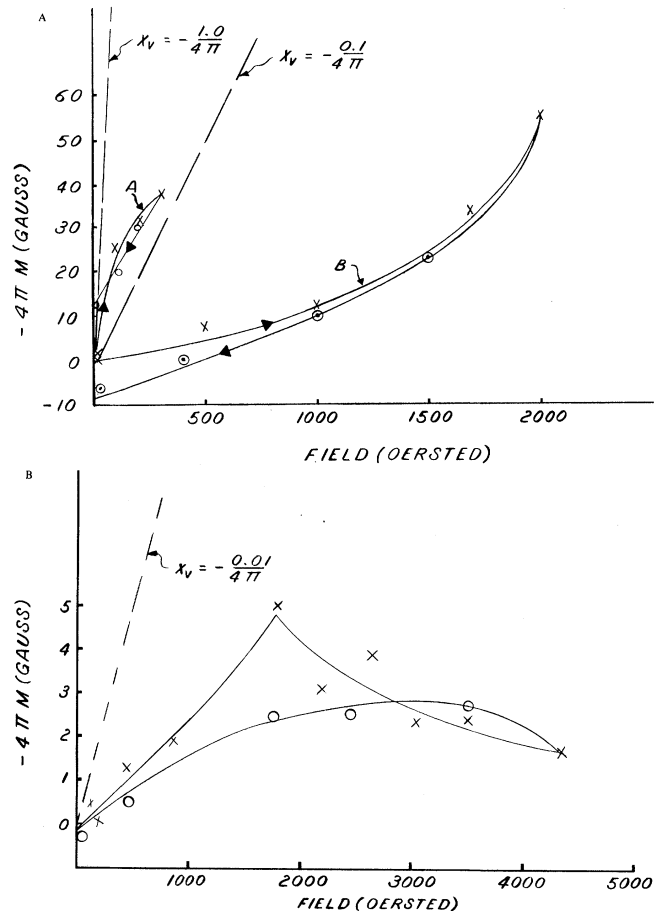


FIG. 2. (a) The diamagnetic moment of pressure quenched CdS No. 108 at 77 K as a function of magnetic field. Curve A, first run; curve B, second run; see text. Crosses, increasing field; circles, decreasing field. (b) The diamagnetic moment of pressure quenched CdS No. 114 at 77 K as a function of magnetic field. Crosses, increasing field; circles, decreasing field.

at zero field at room temperature and then cooled to liquid-nitrogen temperatures at a rate of 100 K/min. This entire process was accomplished within two hours after the room-temperature pressure quench. In this run, we note the initial Meissner-like susceptibility at low field and the diamagnetic remanence when the field was reduced to zero after reaching 300 Oe.

This sample was then slowly warmed *in situ* to ambient temperatures overnight in the remanent field of our magnet (42 Oe). On the next day, after reducing the field to 0 Oe at room temperature, the sample was cooled to liquid-nitrogen temperatures as before. Curve B in Fig. 2(a) was then obtained by subjecting the sample to a maximum field of 2000 Oe and finally returning to zero field. We note the marked decrease in the susceptibility from the previous day and the now paramagnetic remanence of the sample.

Figure 2(b) shows data taken from another sample prepared in an identical manner but which had been "annealed" at ambient temperatures for about six hours before this first run was taken. We note the much reduced (compared to the previous sample) but nonetheless large diamagnetic susceptibility ($\chi_V = -2 \times 10^{-4}$ cgs units) of this sample. The shape of this diamagnetic response is very similar to that obtained from type-II superconductors (for example, TaNb alloy⁷ measured at 4.2 K). After slowly warming this sample *in situ* to room temperature and recooling as previously described, it was found that the magnitude of the susceptibility had decreased below the sensitivity of our magnetometer ($|\chi_V| < 10^{-5}$ cgs units). This response is illustrated in the control curve in Fig. 1. All susceptibility values are calculated using the entire sample volume of 3×10^{-3} cm³.

The magnetic properties of the pressure quenched CdS at 77 K are very similar to the magnetic properties of well-known type-II superconductors observed at much lower temperatures.⁷⁻⁹ It is tempting to postulate superconductivity at 77 K as being responsible for these observations, while recognizing that significant and presently not understood effects may also contribute to this data.

A variety of mechanisms have been suggested for superconductivity at high temperatures. These include excitonic mechanisms,¹⁰⁻¹³ proximity effects,¹⁴ dislocations,¹⁵ etc.

We note that many of the ingredients for superconductivity as proposed are present in our specimens: dislocations from the pressure treatment,

two or more phases in intimate contact, and of course excitons. Of further interest, the metastability of the resultant crystallographic phases suggests that soft-mode instabilities may also be present.

We recognize that the measurement of the electrical conductivity as a function of magnetic field would confirm the presence of superconductivity in our samples. We are currently developing contactless techniques, required by the complex morphology of our samples, to make this critical determination.

The experimental observations which are in most accord with a superconducting explanation are the following two: (a) The initial slope at increasing small field. As shown in Fig. 2(a), the initial slope yields a volume diamagnetic susceptibility, $\chi_V > 0.25/4\pi$ cgs units, corresponding to a greater than 25% flux exclusion in this sample. The granular structure and/or lenticular platelets of our samples provide a ready explanation for the difference between this experimental value and complete Meissner exclusion expected for the low-field behavior of an ideal type-II superconductor. (b) The shape of the *M-H* curve of Fig. 2(b). This behavior is very similar to that of the well-known type-II superconductors.^{7,8} The considerably reduced exclusion may again be readily explained by either the complex structure or the metastability described previously.^{1,5}

Experimental observations which are not readily explained by conventional superconductivity are the next two: (c) The metastability of the magnetic effects. However, this metastability, as shown in Fig. 2(a), may have nothing to do with the physical cause of the magnetic behavior. (d) The diamagnetic remanence shown in Fig. 2(a). This behavior may be due to a complex magnetic structure of a mixture of type-II superconducting and paramagnetic phases. We note that this remanent behavior may represent a non-equilibrium state in the thermodynamic sense, reached by an irreversible process.

Superconductivity at these temperatures presently provides the most natural and simple explanation of these results. However, the state described here may not be accompanied by zero resistance. In the event of finite conductivity, it is clear that a new "high temperature" collective quantum state must be involved.

The physical role of pressure quenching in producing specimens of CdS with this unusual magnetic response is not clear at the present time. Whether such pressure treatment provides the

appropriate morphology of a platelet structure, provides the metastable crystallographic phases, introduces unique damage such as dislocation networks, changes the microchemistry by varying the stoichiometry, or a subtle mixture of several of these components, to produce the appropriate microscopic physical conditions is not known at this time. Our experience indicates that pressure quenching is a necessary condition for such effects. However, it is not a sufficient condition, since other grades of starting powders, differing only slightly in the impurity spectrum in the ppm range, do not show these magnetic effects even though receiving identical treatments.

The similarity of our results with the recent reports of large diamagnetism in CuCl, measured by an ac technique at high pressure, is noted.¹⁶ One suggested possibility is the disproportionation reaction



To explain the observed susceptibilities required the assumption of an electrical conductivity for Cu far greater than known values. Only one valence state of Cd is known to exist, so that a similar explanation of our observations, such as suggested in Eq. (1), is precluded. Our measurement involves static magnetic fields so that eddy currents cannot be involved.

Finally, we do not mean to imply that the temperature reported in this paper is an upper limit for this diamagnetic response in pressure-quenched CdS. We chose this temperature for experimental convenience to establish the phenomena. In fact, we have preliminary data at higher temperatures approaching ambient conditions which indicate similar diamagnetic behavior.

We would like to acknowledge helpful discussions with D. P. Kendall and P. J. Cote. The fluorescent analysis was carried out at National Bureau of Standards under the auspices of G. J. Piermarini. We are indebted to W. Yaiser for his continued technical assistance. This work was supported in part by the U. S. Army armament Research and Development Command under Contract No. DAAA22-80M 3126 and by the U. S. Air Force under Contract No. AFOSR-79-0126.

^(a)On sabbatical leave from the Physics Department, Rensselaer Polytechnic Institute, Troy, N. Y. 12180. Present address: Department of Physics, Linköping, Sweden.

¹C. G. Homan, D. P. Kendall, and R. K. MacCrone, *Solid State Commun.* **32**, 521 (1979).

²G. A. Samara and H. G. Drickamer, *J. Phys. Chem. Solids* **23**, 457 (1962).

³C. G. Homan and D. P. Kendall, *Bull. Am. Phys. Soc.* **24**, 316 (1979). Details will be presented in Benet Weapons Laboratory Report No. ARLCB-TR-79-004 (unpublished), available on request.

⁴P. J. Cote, G. P. Capsimalis, and C. G. Homan, private communication, and to be published.

⁵Optronic-grade CdS powder from Alpha Inorganics, stock No. 20130: Fe, 12 ppm; Mg, 3.6 ppm; Cu, 4.2 ppm; Ag, 3.5 ppm; Bi, <1 ppm; Al, <1.4 ppm; Ge, <1 ppm. Not detected: Ni, <1 ppm; Mn, <0.46 ppm; Pb, <0.07 ppm; Cr, <2.8 ppm; and Co, <1 ppm. Eagle Picher ultrahigh-purity-grade powder: The nominal analysis provided by the manufacturer was qualitatively examined by the spark emission technique. This analysis suggested less total impurities than the Alpha Inorganic material and showed traces of Fe, Mg, Cu, Ag, Bi, Al, and Ge. Not detected were Ni, Mn, Pb, Cr, and Co.

⁶Optronic-grade CdS powder from Alpha Inorganics, stock No. 20130 analyzed by use of x-ray fluorescence spectroscopy [U. S. National Bureau of Standards Report No. 553-33-Y-80, 1980 (unpublished)] showed trace elements detected: Cl, K, Fe, Cu, Zn, and Ge.

⁷J. W. Heaton and A. C. Rose-Innes, *Cryogenics* **4**, 85 (1964).

⁸J. Evetts, A. Campbell, and D. Dew-Hughes, *Philos. Mag.* **10**, 339 (1964).

⁹J. D. Livingston, *Phys. Rev.* **129**, 1943 (1963).

¹⁰B. I. Halperin and T. M. Rice, *Rev. Mod. Phys.* **40**, 755 (1968).

¹¹A. A. Abrikosov, *Pis'ma Zh. Eksp. Teor. Fiz.* **27**, 235 (1978) [*JETP Lett.* **27**, 219 (1978)].

¹²V. L. Ginzburg, *Pis'ma Zh. Eksp. Teor. Fiz.* **14**, 572 (1971) [*JETP Lett.* **14**, 396 (1971)].

¹³T. H. Collins, A. B. Kunz, and R. S. Weidman, in *Recent Advances in Quantum Theory of Polymers*, edited by J. Ehlers *et al.*, Lecture Notes in Physics, Vol. 113 (Springer-Verlag, New York, 1979), p. 240.

¹⁴D. Allender, J. Bray, and J. Bardeen, *Phys. Rev. B* **7**, 1020 (1973).

¹⁵C. Elbaum, *Phys. Rev. Lett.* **32**, 376 (1974).

¹⁶A. review of the pertinent CuCl literature is given by T. E. Geballe and C. W. Chu, *Comments Solid State Phys.* **9**, 115 (1979).