Technique for high-pressure electrical conductivity measurement in diamond anvil cells at cryogenic temperatures

David Erskine and Peter Y. Yu

Department of Physics, University of California and Materials and Molecular Research Division, Lawrence Berkeley Laboratory, California 94720

Gerard Martinez

Service National des Champs Intenses, CNRS, BP 166X, 38042 Grenoble, Cedex, France

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A technique is described for making four-probe electrical conductivity measurements on bulk samples in a diamond anvil cell. The technique has been successfully applied up to 48 GPa and at temperatures below 4.2 K to measure the superconducting transition temperatures (T_c), of Pb, GaP, and Si. A method for analyzing the resistance versus temperature curve in the vicinity of the superconducting transition is also described. This method is applied to determine the pressure dependence of T_c in Si in the region where T_c varies rapidly with pressure.

INTRODUCTION

Although the diamond anvil cell (DAC) has by now played a prominent role in the field of high-pressure physics and is used in a wide spectrum of experiments ranging from x-ray diffraction, Raman scattering to infrared absorption, the DAC has seldom been used in low-temperature electrical measurements at high pressure.[1] In only one previous experiment, electrical measurements have been made in the DAC at liquid-nitrogen temperatures up to 70 GPa.[2] The technique we describe in this paper allows four-probe electrical measurements to be performed in a DAC at liquid-helium temperature at pressures up to 48 GPa. At present the highest pressure achievable with our DAC is limited by the size of our diamond anvils. From the known properties of the materials used in our cell we expect the technique to be useful even at several megabars of pressure.

Although other techniques have been developed to perform high-pressure electrical measurements at low temperatures using sintered diamond anvils,[3,4] the use of transparent anvils in the DAC affords many advantages. The diamond anvils allow: (1) use of the ruby fluorescence method for pressure determination. By the use of small ruby chips immediately adjacent to the sample, the pressure can be measured *in situ* at low temperatures. This eliminates any systematic error resulting from assuming that the sample pressure does not change during the cooling of the cell. For example, we have found that the pressure in our cell may increase by as much as up to 6 GPa upon cooling. (2) The hardness of the diamond extends the potential operating range of this technique into the megabar range. (3) Electro-optical experiments such as high-pressure photoconductivity are possible. (4) Since the pressure of the cell is always changed at room temperature, the small size of the DAC allows rapid cycling between room temperature and low temperature.

The difficulty in performing electrical measurements with a DAC lies in finding a gasket material which has high tensile strength comparable to steel, and yet is electrically insulating. Several groups have previously developed solutions to this problem. The different techniques can be organized into two camps. Some groups[5–9] abandon the steel gasket and use instead an insulating gasket made out of MgO, Mylar, mica, or a polymer film. Others[9,10] use the steel gasket, but insulate it with a hard refractory material such as a thin layer of ceramic or Al_2O_3. Reichlin[9] has shown that insulating gaskets do not have high enough tensile strength to achieve pressures above 40 GPa. Instead she found that electrical measurements in a DAC can be performed up to 40 GPa by using steel gaskets with an insulating coating of Al_2O_3 deposited by plasma spraying. Since plasma spraying facilities are not available in most laboratories we have used Al_2O_3 in powder form to insulate the steel gasket from the wires. We believe that the Al_2O_3 powder served the additional purpose of preventing the wires from being pinched off by the diamond culet edges. A detailed description of the technique and our apparatus is given in the next section. The usefulness of this technique is then illustrated by the measurement of the superconducting properties of Pb, GaP, and Si as a function of pressure.

I. TECHNIQUE FOR PREPARING CELL FOR ELECTRICAL MEASUREMENTS

Our pressure cell contains a pair of beveled diamonds (bevel angle of 4°, with a 0.4-mm-diam flat culet in the center and 4.4-mm girdle), supported by tungsten carbide rings with a 0.04-in.-diam hole in the center. At present, the cracking of these rings at the highest pressures is the most frequent cause of failure in our experiment. To help prevent cracking of the rings, they are press fitted into a steel girdle for additional support. The cell is pressurized by a small hydraulic press and has a threaded lock ring which can be used to lock in the pressure. This allows the cell to be removed from the press for insertion into an optical Dewar for electrical and optical measurements as a function of temperature. Other-

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wise the design of the cell is very similar to DAC's described in the literature.[1]

A close-up drawing of the gasket is shown in Fig. 1. The sample is placed in the center of a hole drilled in the prepressed steel gasket. The sample is typically a single crystalline fragment of dimensions about $25 \times 25 \times 100$ (μ^3). To make four-probe electrical resistance measurements, two loops of 12-μ copper wire are pressed against the sample. The wires are then bonded by silver paint to larger wires which lead outside the cell. To produce a quasihydrostatic environment, the sample is surrounded by a soft powder of either Plaster of Paris ($CaSO_4$) or steatite flakes. Fine ruby chips are placed immediately adjacent to the sample for measuring the sample pressure.

The details of our procedure for mounting the sample inside the DAC are as follows: The 440-μ-thick Inconel steel gasket is prepressed by the diamond anvils with the hydraulic press. A 200-μ hole is then drilled in the center of the resulting indentation. The gasket is then replaced on the bottom diamond and held in place by clay and RTV silicone rubber. The soft powder is placed in the hole in the gasket and tamped down with the top diamond. The excess soft powder extending beyond the 200-μ hole is removed. A thin layer of Al_2O_3 powder (1-μ size powder used for polishing) is carefully placed around the inside of the indentation in the gasket produced by the diamond, but not over the hole filled with the soft powder. This layer should be as thin as possible but continuous. It is tamped down lightly with the clean top diamond to form a "piecrustlike" layer on the gasket. With care and experience the top diamond can be removed without damaging this delicate layer. On the top diamond, two fine copper wire loops are bent to conform to the sides of the diamond up to the anvil face. The loops are bent sharply at the very center of the face with a gap of about 25 μ between the two loops. The wires should be in contact with the sides of the diamond if possible, for any gap will result in the wires moving when the two diamonds are pressed together. A very small amout of vacuum grease is smeared in the center of the top diamond face so that a sliver of the sample will adhere to it. The sample should be located perpendicular and beneath the two loops of wire. Fine ruby chips are placed on the diamond face on both sides of the sample. They should be close to, but not touching, the sample. The two cell halves should be compressed in the hydraulic press very slowly initially to allow the powder grains and any vacuum grease to ooze around the sample and fill any voids. The electrical resistance of the two wire loops, the resistance across the sample, and the resistance between the loops and the gasket should be monitored continuously as the cell is compressed. This initial compression is the crucial step of the experiment. If the wires do not break at this point nor short to the gasket, and the sample does not shift from underneath the wires, then it is likely that they will not do so at higher pressure. So far in our limited experience with this technique, we have not been forced to abandon an experiment because of breakage of wires or shorting of the wires to the gasket at high pressure.

During this initial compression the size and shape of the hole in the gasket should not change significantly. If too much Al_2O_3 powder or soft powder has been used, there may not be sufficient friction between the gasket and the diamond to contain the pressure in the central region of the anvil. In this case the powder may ooze outward and break the wires, or the hole may grow and distort. If too little soft powder has been used, the Al_2O_3 powder may move into the 200-μ hole and surround the sample resulting in large pressure inhomogeneity.

II. EXPERIMENTAL PROCEDURE

For cryogenic experiments, the DAC is mounted in a copper block with a calibrated silicon diode thermometer

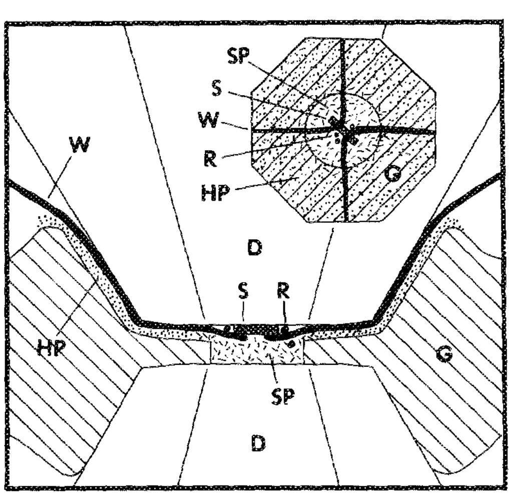

FIG. 1. Schematic side view of the gasket area while the inset shows top view. Sample (S) is surrounded by soft powder (SP) and pressed against copper wires (W), which are insulated from the steel gasket (G) by Al_2O_3 powder (HP). Fine ruby chips (R) near the sample are for pressure measurement. (D) are diamond anvils.

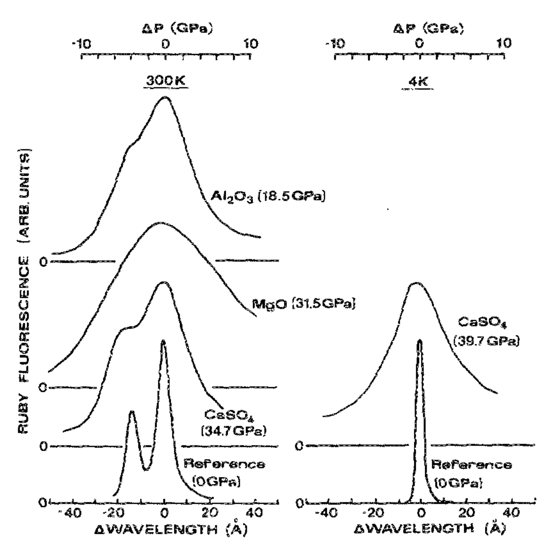

FIG. 2. Ruby fluorescence spectra measured in powders of different degrees of hardness, showing broadening due to varying amounts of pressure inhomogeneity. The emission wavelengths (horizontal axis) are plotted relative to the R_1 peak. The difference in pressure between the two $CaSO_4$ spectra is due entirely to contraction of the cell during cooling. The reference spectra are from a ruby chip outside the cell.

placed in thermal contact with one of the anvils. The resistance (R) of the sample is measured by passing an ac current of 100 Hz and 0.5 mA through the sample and measuring the ac voltage drop across the sample with a lock-in amplifier. Sample resistances of 0.01 Ω can be measured with excellent signal-to-noise ratio. To determine the sample pressure, the fluorescence spectra of the ruby chips adjacent and surrounding the sample are measured at the same cryogenic temperatures as the resistance experiment. A ruby chip mounted on the cell outside the pressurized region provides the reference wavelength for the ruby fluorescence at ambient pressure. We assume that pressure coefficient (0.365 nm/GPa) of the ruby fluorescence at low temperatures is identical to the room-temperature value.[11]

To measure the superconducting transition temperature of the sample, the cell is cooled and warmed over a temperature (T) range spanning the transition at a slow enough rate that the R vs T curves on cooling and warming show no hysteresis. The cell is always warmed to room temperature before the pressure is changed.

III. RESULTS

A. Pressure homogeneity

The use of a soft powder to transmit the pressure to the sample raised the question as to how hydrostatic and homogeneous is the pressure. One would expect that the softer the powder, the more homogeneous (and presumably more hydrostatic also) is the pressure. This correlation is demonstrated in Fig. 2 where several measured ruby fluorescence spectra (RFS) are shown for ruby chips embedded in powders of different degrees of hardness. Room-temperature spectra are taken with Al_2O_3, MgO, and $CaSO_4$ powders as the pressure medium, respectively. We take the linewidth of the R_1 and R_2 lines as measure of the pressure inhomogeneity. Note how the broadening of the RFS for the $CaSO_4$ powder at 35 GPa is less than the broadening for the other two powders at lower pressure. A spectrum for $CaSO_4$ is also taken at 4.2 K, when the intrinsic linewidth of the R_1 line would be completely negligible compared to the pressure-inhomogeneity-induced broadening.

By measuring the fluorescence of various ruby chips surrounding the sample, we can also estimate the pressure variation inside the cell over a volume of a typical sample. For $CaSO_4$ powder this variation is about 1.7 GPa. We have also found that this pressure variation remains more or less constant even when the pressure was increased. We will show later that this result is consistent with our superconductivity measurements in Si at high pressure.

B. Superconductivity in the high-pressure phases of Pb, GaP, and Si

As illustrations of the usefulness of the DAC in making electrical measurements at high pressure and at low temperatures, we have used our cell to study the pressure dependence of the superconducting transition temperatures in Pb, GaP, and Si at pressures up to 48 GPa. In case of Si and GaP, these materials are semiconductors at atmospheric pressure but become metallic at pressures above 10 and 22 GPa, respectively.

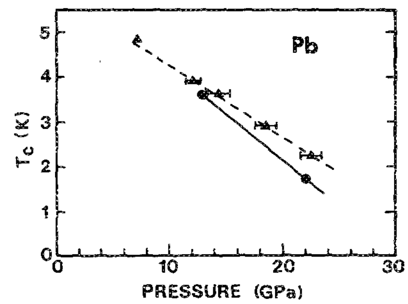

FIG. 3. Comparison of T_c vs P in Pb measured by our DAC (solid triangles) and by a Bridgeman-type of opposed anvil device (solid circles) from Ref. 13.

1. Pb

Our motivation for studying the pressure dependence of the superconducting transition temperature (T_c) of Pb is that Pb has been introduced by Wittig[12] as a manometer at high pressure and low temperatures in cells with opaque anvils. Wittig used the room temperature Pb and GaP phase transitions at 14 and 22 GPa, respectively, as fixed points to calibrate his Pb manometer. He assumed that the pressure in his cell remained unchanged when it was cooled down to low temperatures to determine the T_c of Pb. Thus the lead superconducting manometer has never been directly calibrated against the ruby scale.

Our data for T_c of lead versus pressure, where the pressure was determined by measuring the RFS at low temperatures is shown in Fig. 3, together with Wittig's result. For a given T_c, we obtain consistently a higher pressure than Wittigs's. We believe that this difference is due to Wittig's assumption that the cell pressure does not change upon cooling from room temperature to liquid-He temperatures.

2. GaP

The insulator to metal transition in GaP has been determined optically by Piermarini and Block[13] to occur at 22 GPa. This is generally believed to be a first-order phase transition accompanied by a large change in volume. By monitoring the resistance of an undoped, single crystalline sample of GaP we have found that the sample resistance began to drop sharply at 18.5 GPa. The transition was sluggish with a time constant of several minutes. After the sharp onset the resistance continued to decrease with pressure over a range of 2–3 GPa. In the conducting phase, the T_c of GaP was found to be almost pressure independent, increasing only slightly from 3.5 to 4 K as the pressure is increased to 48 GPa. Yakovlev *et al.*[14] has reported a higher T_c of around 6 K in GaP. However, the pressure at which this T_c was measured was not reported. Upon decompression at room temperature, instead of returning to its original transparent semiconducting state with an orange color, the sample remained opaque and conductive, indicating it had transformed into a metastable phase. The structure of this metastable phase is unknown.

3. Si

The pressure dependence of T_c in the high-pressure metallic phases of Si has been reported recently by two groups using two different designs of the pressure cell.[15,16] Whereas one group found that T_c in Si decreased from about 8 to 3.5 K when P increased from 15 to 25 GPa, the second group found a considerably smaller change of from about 5 to 4 K for a pressure increase of from 15 to 43 GPa. It was not clear as to why the two results differ so much. By using our DAC to repeat the experiment, it is hoped that this discrepancy may be understood.

We have performed the T_c vs P measurement on single crystals of Si from two different sources. One sample is n-type lightly doped with $2\times10^{14}\ \mathrm{cm}^{-3}$ of phosphorous, while the other is p-type heavily doped with $6\times10^{19}\ \mathrm{cm}^{-3}$ of boron. We found no difference in the pressure dependence of their T_c so only the result from the lightly doped sample will be presented.

In Si we found that R did not always decrease smoothly to zero as the sample is cooled below T_c. For pressure below 30 GPa the transition to the superconducting state was typically quite sharp (width of transition is about 0.1 K) so T_c can be determined rather precisely. However, at P between 35 and 42 GPa, the R vs T curves typically showed steps and these structures changed with pressure. Figure 4(a) shows examples of this. These results can be explained either by the fact that the pressure gradient over the sample was changing or that T_c is not changing with pressure monotonically anymore. From the RFS we conclude that the pressure gradient was not changing so we have interpreted the structures in $R(T)$ as due to strong variations in T_c with P.

To determine the pressure dependence of T_c from the experimental $R(T)$ curves for $P>35$ GPa we have developed the following model. In this model we assume that the sample is at a uniform temperature, but has a pressure (P) that varies only along its length given by some function $P(x)=P_{\text{ave}}+\Delta P(x)$, where P is the mean pressure, ΔP is the pressure deviation from the mean, and x is some normalized position along the sample length (i.e., the sample is assumed to lie between $x=0$ and 1). Since T_c is a function of pressure, T_c also varies along the length of the sample as $T_c(x)=T_c[P(x)]$. We assume that the sample is of uniform cross section and that only the portions of the sample where $T>T_c(x)$ have a nonzero resistivity. The measured sample resistance is then assumed to be proportional to the total length of the sample where $T>T_c(x)$:

$$R=R_0\int_0^1\theta(T-T_c)dx, \tag{1}$$

where $\theta(x)$ is the step function defined by $\theta(x>0)=1$ and $\theta(x<0)=0$. R_0 is the low-temperature resistance of the sample when the entire sample is normal. Thus for a given function of P vs x and of T_c vs P, we can obtain the T_c vs x curve. From the T_c vs x curve the resistance R of the sample at a given temperature T is equal to the sum of those lengths of the sample whose T_c is below T. The above procedure for obtaining the $R(T)$ curve from the T_c vs P and P vs x curves is shown schematically in Figs. 5(a)–5(d).

The reverse procedure of determining T_c vs P from the experimental R vs T curves is unfortunately not unique. However, in the case of Si we found that the reverse process could yield a unique T_c vs P curve provided the pressure distribution function $\Delta P(x)$ did not change with pressure. To obtain this distribution function $\Delta P(x)$ we make use of

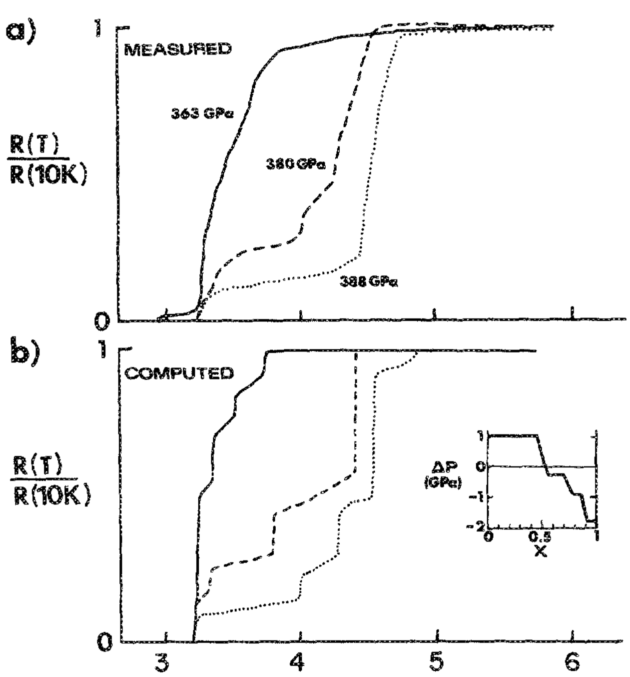

FIG. 4. (a) Measured resistance versus temperature curves for Si for several pressures showing the evolution in the structure in the transition region. (b) Computed $R(T)$ curves for Si for the same pressures as in (a). The computed curves are based on the pressure distribution shown in the inset, using the model described in the text.

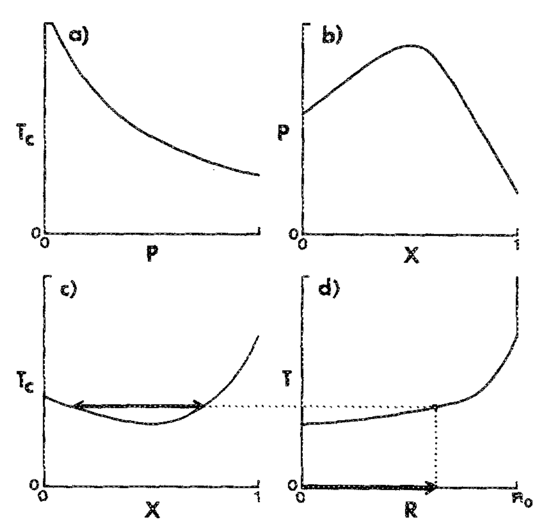

FIG. 5. Schematic representation of the procedure for calculating the superconducting transition line shape $R(T)$ from the pressure dependence of T_c and sample pressure distribution $P(x)$. (a) and (b) show hypothetical functions of T_c (P) and $P(x)$ which are assumed to be known. These two functions are combined to form the $T_c(x)$ curve in (c). For a given T, the length of the sample with T_c below T [as given by the bold arrow in (c)] gives R at T. The values of R obtained in this way are plotted vs T in (d). Arbitrary units are used for T and P.

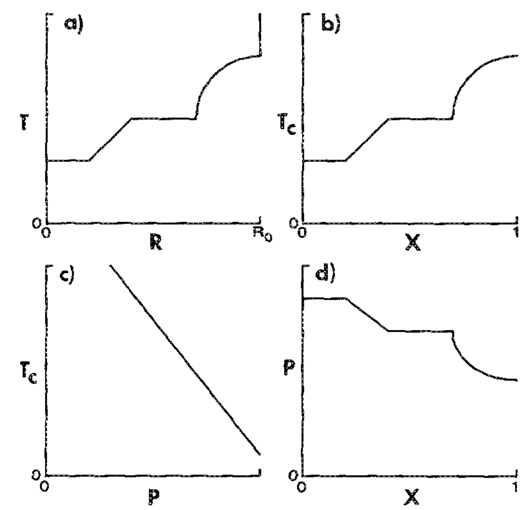

FIG. 6. Procedure for obtaining a pressure distribution function $P(x)$ from the shape of a superconducting transition. A hypothetical superconducting transition is plotted as T vs R in (a). $T(R/R_0)$ is then taken to represent $T_c(x)$ as shown in (b). Suppose the dependence of T_c on P is known and is shown in (c). This information is combined with $T_c(x)$ to yield the $P(x)$ curve in (d).

the fact that for $P < 30$ GPa T_c is linear with P. This allows us to construct a $\Delta P(x)$ curve, shown in the inset of Fig. 4, which reproduces the experimental $R(T)$ curve for $P < 30$ GPa. The process of constructing the P vs x curve is shown schematically in Figs. 6(a)–6(d). It should be noted that the function $\Delta P(x)$ so deduced is related to the actual pressure distribution across the sample in a very complicated manner, which has to take into account the three-dimensional nature of the sample and of the conduction paths.

Using the $\Delta P(x)$ vs x curve in the inset of Fig. 4(b) and Eq. (1) we constructed the T_c vs P curve shown in Fig. 7 from the experimental $R(T)$ curves. As $R(T)$ started to change its shape above 30 GPa, the T_c for the higher pressure points are adjusted so that the new structures are reproduced. Figure 4 compares the reconstructed R vs T curves

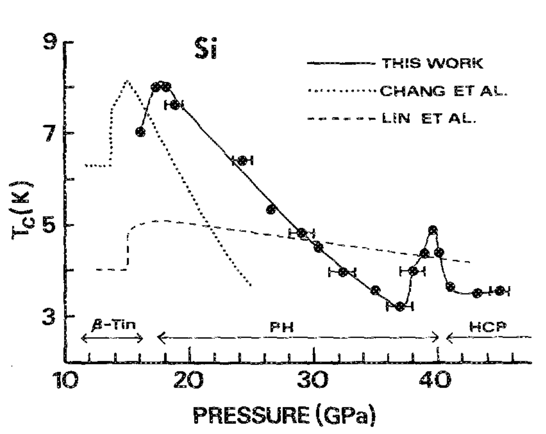

FIG. 7. Pressure dependence of T_c in Si determined by three different groups using three different types of pressure cells. The horizontal bars around our data points indicate the spread in pressure over our sample as estimated from ruby chips around the sample. Arrows show crystal structure transition pressures measured by x-ray diffraction (Ref. 18).

with the experimental curves for several pressures in the 35–43 GPa range. The evolution of the structures in the experimental curves as the pressure is changed is reproduced reasonably well by the theoretical curves. This supports the validity of our assumption that the distribution $\Delta P(x)$ is essentially constant as the pressure is increased.

The T_c of Si as measured by Chang *et al.*[15] on single crystals of Si using a sintered diamond anvil cell are shown for comparison in Fig. 7 as a dotted curve. The shift between our data and theirs can be attributed to their use of a superconducting lead manometer for their pressure measurement. If they had used instead our results on Pb to calibrate their Pb manometer their results would be in better agreement with ours. Also shown as the dashed curve in Fig. 7 are the data of Lin *et al.*[16] on powdered Si. Since our results on Si agree qualitatively much better with those of Chang *et al.* than with those of Lin *et al.*, we have to conclude that the difference between the results of those two groups has to do with their starting samples being crystalline or in powder form. A discussion of the physics of the Si results will be published elsewhere.[17]

IV. DISCUSSION

With the technique described in this paper, four-probe electrical measurements can be made on initially single-crystalline samples at liquid-He temperatures up to at least 48 GPa with reasonably small pressure inhomogeneity. With smaller diamond anvils electrical measurements in the megabar pressure range should be possible. The technique has been applied to measure the superconducting properties of Pb, GaP, and Si. A model has also been proposed to explain the evolution in structure seen in the superconducting transition of Si due to the finite pressure gradient across the sample.

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