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Observation of pressure-induced superconductivity in the megabar region

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Abstract. A review of recent developments in high-pressure techniques and their application in the search for superconductivity at low temperature is presented. We have focused the discussion mainly on the experimental results obtained by our group for simple molecular systems.

1. Introduction

A diamond anvil cell (DAC) is the most powerful tool for producing ultra-high pressures in the Mbar region. We exploited the compactness of the DAC and employed it in a ^{3}He/^{4}He dilution refrigerator to achieve complex extreme conditions of ultra-high pressure and very low temperature.

We have also developed electrical and magnetic measurement techniques for use on a sample confined in a DAC. The samples studied in our experiments are simple systems such as elements like the halogens (I, Br), group VIb elements (S, O) and alkaline-earth metals (Ca), and organic or inorganic materials like $C_6I_2O_4$ and SnI_4. Magnetic materials like K_2CuF_4 and the heavy-fermion systems $CeCu_2Si_2$, UPt_3 are also studied by our group, by the use of a piston–cylinder-type pressure cell to study the heat capacity, and magnetization as well, under hydrostatic conditions.

In this paper, we review first the recently developed high-pressure techniques and then our experimental results obtained over the last ten years, on metallization and pressure-induced superconductivity of simple molecular crystals.

2. High-pressure techniques

2.1. The DAC

The DAC is now very popular with high-pressure experimentalists but remains in some respects in need of improvement. We have used natural diamonds for years and recently succeeded in producing a pressure of 2 Mbar and measuring electrical resistance. New synthetic diamonds, type IIa, of high purity and of high quality, are now available [1]. The optical properties and mechanical hardness are much improved [2]. (The crystal imperfections can be checked by, for example, x-ray topography.)

The material of which the pressure cell is normally made is pure Be–Cu that does not contain cobalt, but in some cases we employ NiCrAl alloy. This alloy is known to be

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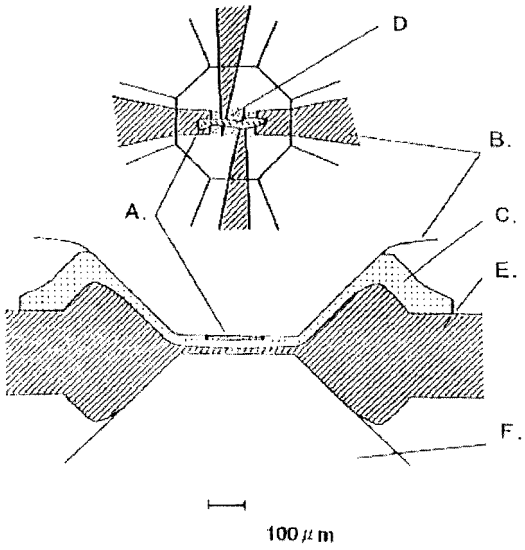

Figure 1. The DAC. A: sample; B: Pt electrodes; C: Al_2O_3 insulation; D: ruby chips; E: metal gasket; F: diamond.

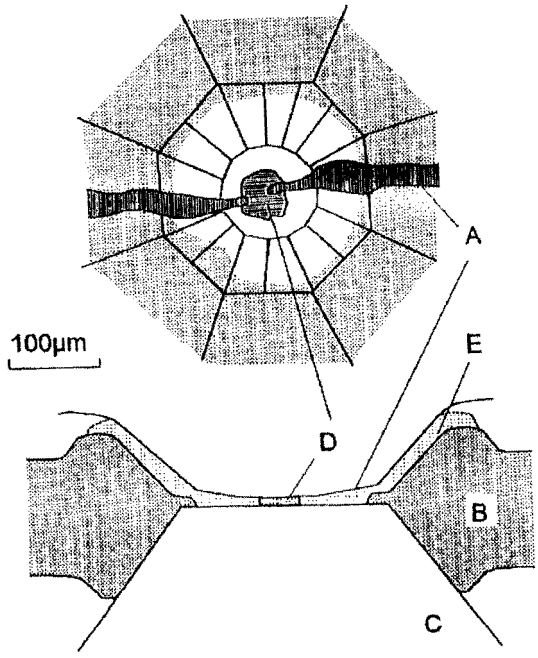

Figure 2. The configuration of the two electrodes. A: the Pt electrodes; B: the metal gasket; C: the diamond; D: the sample; E: Al_2O_3 insulation.

non-magnetic and harder than Be–Cu, but not so easy to obtain commercially. Both Be–Cu and NiCrAl are only non-magnetic at temperatures above 1 K. Below 1 K, these materials, including so-called non-magnetic stainless steel, are found to be magnetic.

Among the various materials present, the non-magnetic metal gasket in which the sample of size 10^{-7} cm^{-3} is confined is the most important for sensitive magnetic measurement. Cu–Ti, Be–Cu and stainless steel are frequently used to make such metal gaskets. Rhenium metal is very hard, but for magnetic measurements care must be taken because of the shielding effect due to its superconductivity in magnetic measurements.

2.2. Electrical resistance measurements

Figures 1 and 2 show schematically how the electrical resistance is measured. Fine alumina powder with a diameter of few microns is prepressed to form a thin insulator layer on the gasket metal surface. The sample is placed on the alumina insulator, and Pt electrodes are attached to the sample and pressed together. The insulation between the sample and the gasket can be monitored throughout the entire process of pressurizing and cooling.

The electrical resistance of the sample is normally measured by the ac four-terminal method [3] but in a case where the pressure surface is too small, we employ the incomplete four-terminal or two-terminal method, which may give extra residual resistance at low temperatures.

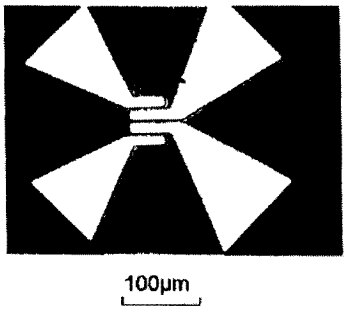

Figure 3. The pattern of the electrodes on the pressure surface of the diamond.

Instead of manually setting the electrodes on the sample, we have tried to draw electrodes directly on the pressure surfaces of the diamond. This is found to be possible by the use of a lithographic technique. We were able to make fine electrodes as shown in figure 3. However, we also noticed that these electrodes deposited on the diamond are relatively weak and easily removed by scratching or pressurizing. We are now trying to use sputtering techniques and we find that electrodes produced in this way have stronger contacts with the diamond, but the execution of the lithographic technique is not easy.

2.3. Magnetization measurements

The magnetization of the sample is measured by the use of a sensitive dc SQUID magnetometer. To perform the measurements, Nb–Ti thin wire is simply wound around the sample and connected to the SQUID probe.

In a more elaborate configuration, a pair of pick-up coils is prepared; one of them is wound around the sample and the other works to compensate the signal external to the sample, as shown in figures 4 and 5.

In this case, sometimes we use a reference sample to confirm the sample signal as regards magnitude and sign. The SQUID magnetometer is difficult to use at temperatures higher than that of liquid ^{4}He and with a relatively strong external magnetic field exceeding several hundred gauss. Using a vibrating-coil magnetometer with a SQUID probe is essentially an ac method, and so can be extended up to liquid N_2 temperature [4].

For measurements of magnetization under strong external magnetic fields, we have developed ac susceptibility techniques, modifying the conventional Hartshorn bridge method. In the modified method, we apply an ac magnetic field with the primary coil and pick up the sample magnetization via the secondary coil, which consists of an astatic pair of coils. The configurations are shown in figure 6. As all of the coils are made of thin wires of normal Cu, there are no limitations on the superconductivity. This ac susceptibility

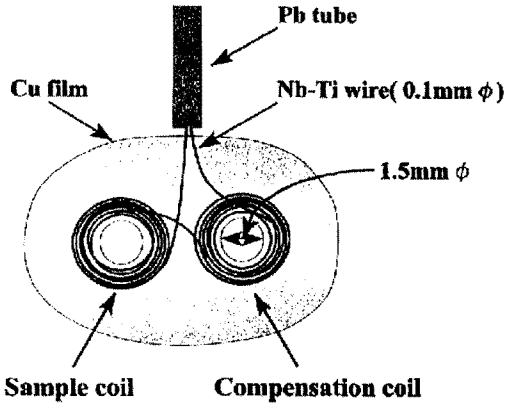

Figure 4. The configuration of the pick-up coil.

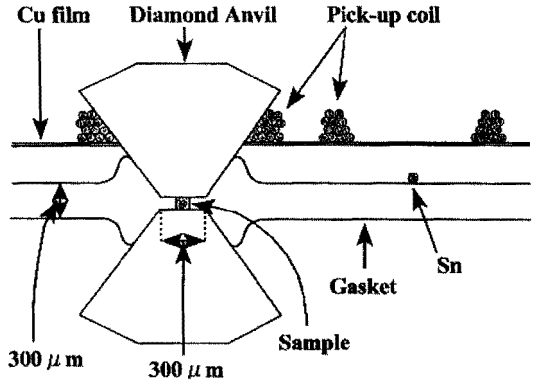

Figure 5. A pair of pick-up coils and the sampling.

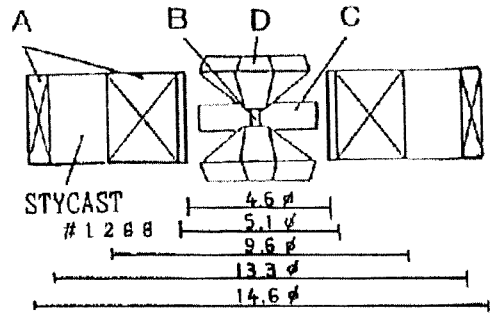

Figure 6. A schematic view of the coil set for an ac susceptibility measurement. A: primary (outer) and secondary (inner) coils; B: the sample; C: the metal gasket; D: the diamond.

measurement, even if the sensitivity is lower by one order of magnitude than that of the standard SQUID system, is still useful when the SQUID system is not available.

2.4. Pressure measurement

Measurement of the applied pressure is performed by introducing small ruby tips around the sample and by measuring the shift of the wavelength of the luminescence from the ruby under pressure [5]. This method was found to be useful for the determination of pressures above 2 Mbar in the case of CsI [6].

2.5. The cooling system

The combination of the DAC and a refrigerator enables us to work under complex extreme conditions of ultra-high pressure of 2 Mbar and very low temperatures down to 30 mK in our case. The combination is quite simple. Connecting the DAC to the bottom of the mixer of the refrigerator, the measurement of the sample temperature is made with the thermometer attached on the pressure cell. In the case of electrical resistance measurements, the sample is cooled directly by the Pt electrode as well as by the diamonds, but for samples surrounded by insulating pressure media and no electrodes, special care is necessary for determination of the sample temperature. If necessary, external magnetic fields up to 18 T can be achieved.

As for pressure determination at low temperature, it is desirable to introduce an optical fibre system attached to the refrigerator and to perform *in situ* measurements. Instead, however, we measure the pressure at low temperature using either a nitrogen cryostat or an optical cryostat designed for our purpose. The pressure determined at room temperature is checked at low temperature and confirms the difference and reproducibility, and then the cell is attached to the refrigerator. For low-temperature study, it is also desirable to employ an automatic pressure control system.

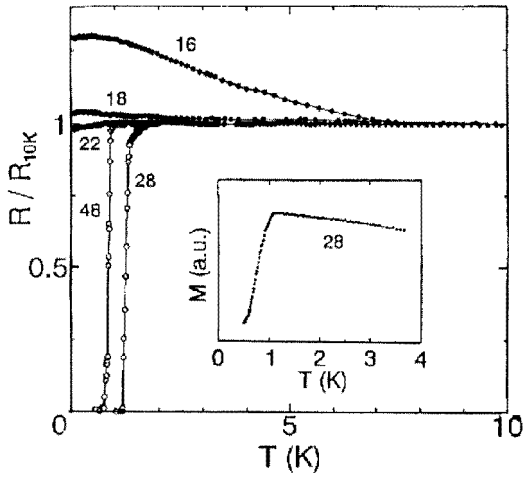

Figure 7. The temperature dependence of the reduced electrical resistance of iodine, showing the transition to the superconducting state. The inset shows the Meissner effect.

3. Pressure-induced superconductivity

3.1. Iodine and bromine

In the process of developing high-pressure tools, we searched for the metallization and pressure-induced superconductivity of simple systems.

The first successful searches were carried out on elements in the halogen group: iodine [7] and bromine [8]. Molecular crystals of iodine form an insulator at ambient pressure. Application of pressure, however, changes iodine to a metal, and that change occurs before its molecular dissociation. Monatomic iodine is metallic, as reported elsewhere [9]. We are very interested in the onset of the superconductivity of solid iodine in various crystal phases under pressure. The search for superconductivity was performed successfully, and we were able to observe the superconductivity as shown in figure 7 on the basis of both the electrical resistance and the Meissner effect.

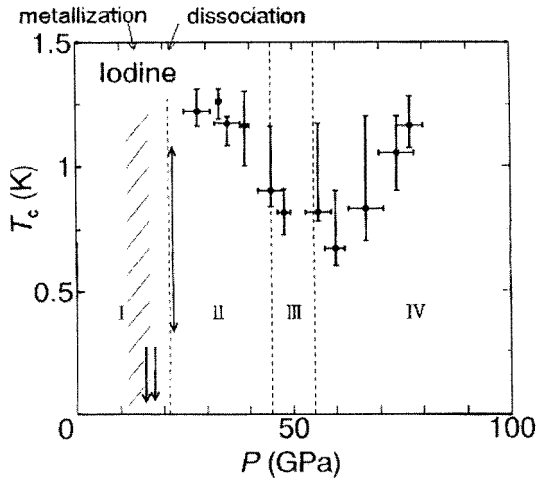

Figure 8. The pressure dependence of T_c for iodine.

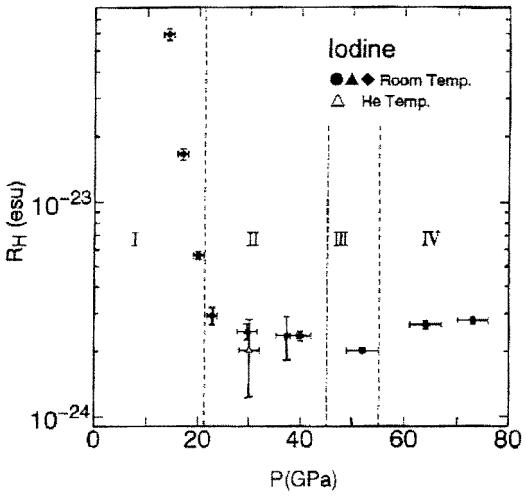

Figure 9. The pressure dependence of the Hall coefficient of iodine.

The pressure dependence of the transition temperature T_c is shown in figure 8. The interesting point is that the superconductivity appears in the monatomic phases and not in the molecular metallic phase. The next point concerns the pressure dependence of T_c in the highest-pressure cubic phase. Experimentally, the sign is positive, but it is negative according to the first-principles band calculation of Suzuki and co-workers [10]. We have also performed a Hall effect study [11] in which we showed that the carrier is definitely a hole. Among the various elements studied, iodine is the first example of a hole metal superconductor. The carrier density changes at the boundary of the molecular dissociation as shown in figure 9; the absence of superconductivity may be attributed to the low carrier density before the molecular dissociation. The pressure dependence of the Hall coefficient is also in contradiction with the theoretical prediction.

The discrepancy stated above may be partly ascribed to the lack of information on lattice vibrations or electron–phonon coupling in theoretical work, or the quality of the applied pressure, non-hydrostatic and uniaxial, in the experimental work. The absence of superconductivity for the molecular metallic state may be of interest when compared with

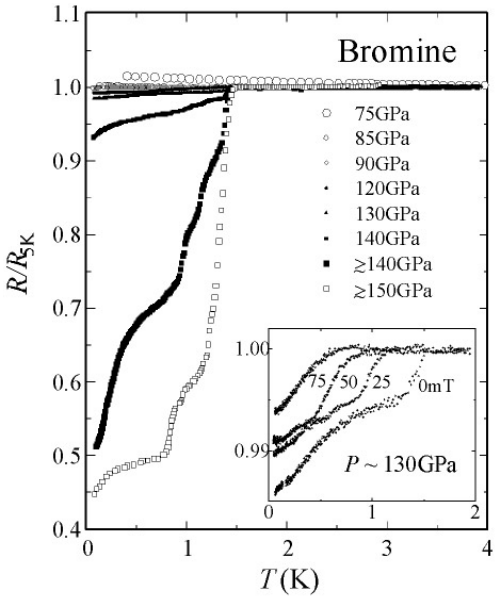

Figure 10. The temperature dependence of the reduced resistance of bromine at several pressures. The inset shows the magnetic field dependence.

the situation for similar systems like oxygen and hydrogen.

We have also observed pressure-induced superconductivity for bromine at pressures above 80 GPa as shown in figure 10, where solid bromine is monatomic, like iodine. It is expected that there is universality among the solid halogens as regards metallization.

3.2. Sulphur and oxygen

In group VIb, superconductivity is found under pressure for Te and Se with T_c-values of 4.5 K and 6.9 K, respectively. Quite recently, we observed metallization and superconductivity of sulphur under pressure [12]. The metallization is shown in figure 11, in

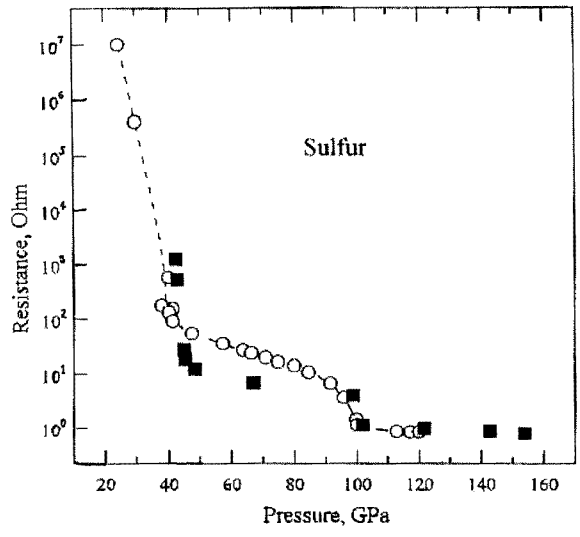

Figure 11. The pressure dependence of the electrical resistance of sulphur at room temperature.

which we notice that there exist steps around the pressures of 40 GPa and 90 GPa. It is known that just above the pressure boundary between the unknown S-II phase and the orthorhombic S-III phase, the optical reflectivity increases [13] and the observed resistance decrease terminates.

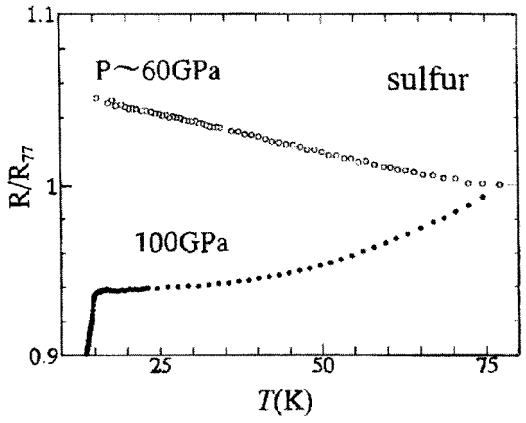

Figure 12. The temperature dependence of the reduced resistance of sulphur. The transition to the superconducting state occurs at 15 K at 100 GPa.

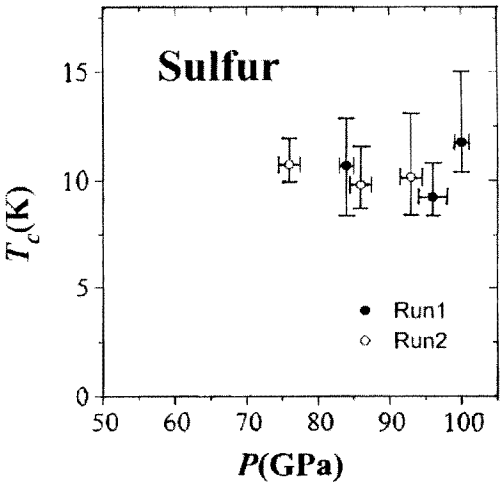

Figure 13. The pressure dependence of T_c for sulphur. T_c disappears at pressures below 78 GPa.

We have observed an abrupt resistance drop at 15 K under 100 GPa for the first time, as shown in figure 12. Subsequently, we studied the pressure dependence of T_c at around 80 GPa. The T_c versus pressure diagram given in figure 13 shows the disappearance of T_c below 80 GPa.

From both the structural sequence and the increase of T_c for group VIb, we expect the transition temperature T_c of oxygen, if there is one, to be higher than that of sulphur. The metallization of solid oxygen has been demonstrated already in optical reflectivity experiments [14]. We tried to confine liquid oxygen in a sample hole of a rhenium gasket covered with an alumina insulating layer. After the confinement, the electrical resistance was monitored with increasing pressure [15]. The resistance becomes measurable above the pressure of 60 GPa and shows a steep decrease up to 100 GPa, as shown in figure 14. The temperature dependence of the resistance changes from semiconducting to metallic at

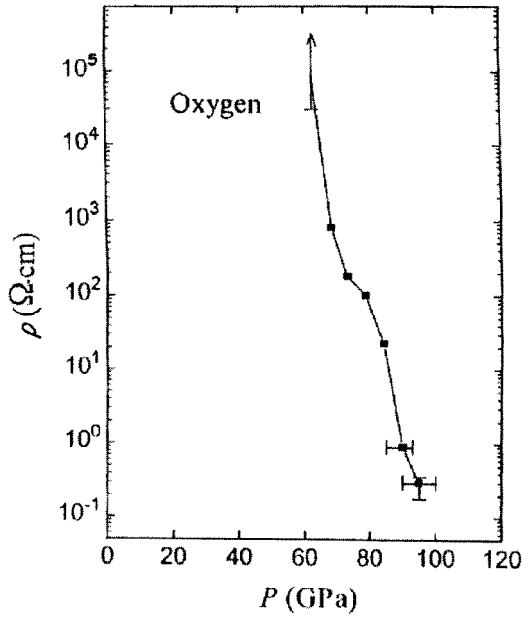

Figure 14. The pressure dependence of the electrical resistivity of oxygen at room temperature.

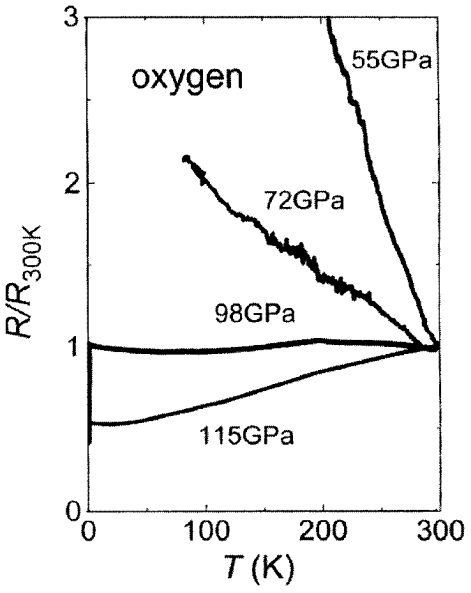

Figure 15. The temperature dependence of the reduced resistance of oxygen at several pressures. Above 98 GPa, a transition to the superconducting state occurs.

pressures between 72 GPa and 98 GPa, as seen in figure 15. An abrupt resistance drop suggesting the onset of superconductivity appears at around 0.6 K for pressures exceeding 100 GPa; a typical example is shown for the pressure 120 GPa in figure 16. We also studied the magnetic field dependence of the resistance drop to confirm the superconductivity. The inset of figure 16 shows a magnetic field dependence like that of a usual superconductor, giving a critical field of 2000 G [16].

Thus, the observed superconductivity of oxygen may be expected to be present even in the molecular metallic state, in contrast to the case for iodine. The high-pressure phase

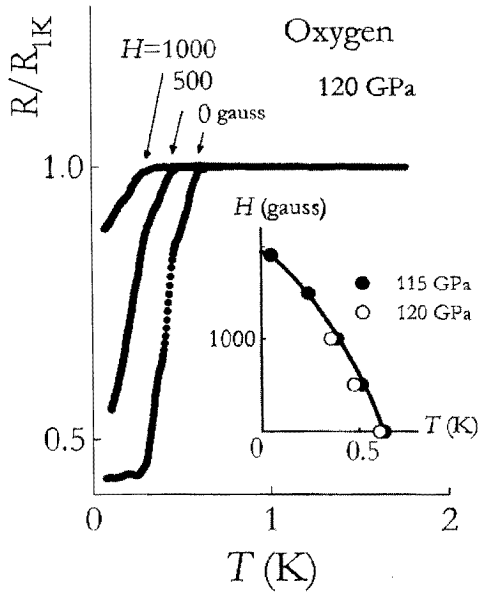

Figure 16. The magnetic field dependence of T_c for oxygen near 120 GPa. The inset shows the T_c–H_c dependence for pressures of 115 GPa and 120 GPa.

above 96 GPa is interpreted by supposing that the solid oxygen remains in the molecular state [17].

Theoretical study of the magnetism of oxygen under pressure predicts the disappearance of the moment as the metallic state is approached [18]. On the other hand, the direct exchange interaction among the oxygen molecules should increase exponentially with the decreasing of the inter-molecular distance. Therefore, the Néel temperature for antiferromagnetic ordering must have its maximum value at a certain pressure before the magnetic moment disappears. This expectation, however, seems to be very difficult to confirm experimentally, as the antiferromagnetic susceptibility is too small to detect. A nuclear magnetic resonance experiment on oxygen is desirable.

3.3. $C_6I_4O_2$

Onodera and co-workers studied the electrical resistance of various organic molecular crystals under pressure and, among them, iodanil $C_6I_4O_2$ was found to show a considerable resistance drop under pressure and was thought to be an organic molecular metal. We tried to measure the temperature dependence of the electrical resistance to confirm a metallic behaviour under pressure [19].

Figure 17 shows the temperature dependence of the electrical resistance of iodanil under several fixed pressures. Experimental results show that iodanil becomes metallic under pressures above 35 GPa. Furthermore, the temperature dependence of the resistance studied at low temperatures showed an abrupt drop in the resistance at 2.5 K and for pressures above 52 GPa, as shown in figure 18. The drop is attributed to the onset of superconductivity. The critical temperature T_c seems to decrease with increasing pressure up to the measured value of 78 GPa. Further confirmation of the superconductivity by the Meissner effect is currently being sought.

The infrared spectroscopy experiments carried out by Nakayama [20] reveal that the iodanil molecule is not yet destroyed, at least up to 52 GPa, while most of the organic

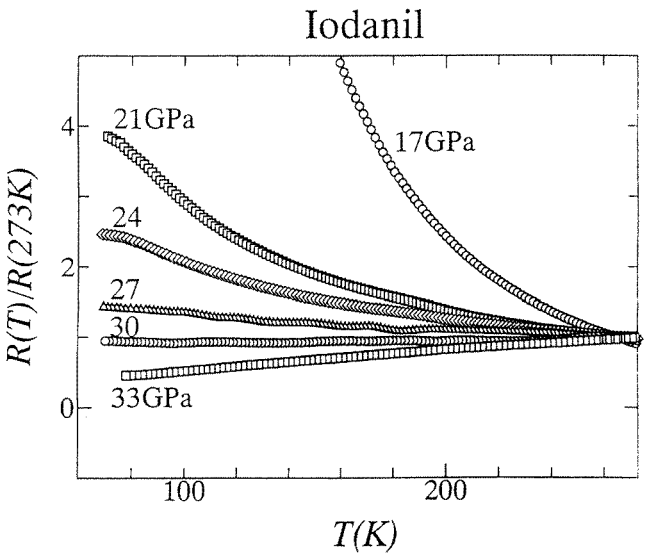

Figure 17. The temperature dependence of the reduced resistance of iodanil at several pressures. At pressures above 30 GPa, iodanil shows metallic behaviour.

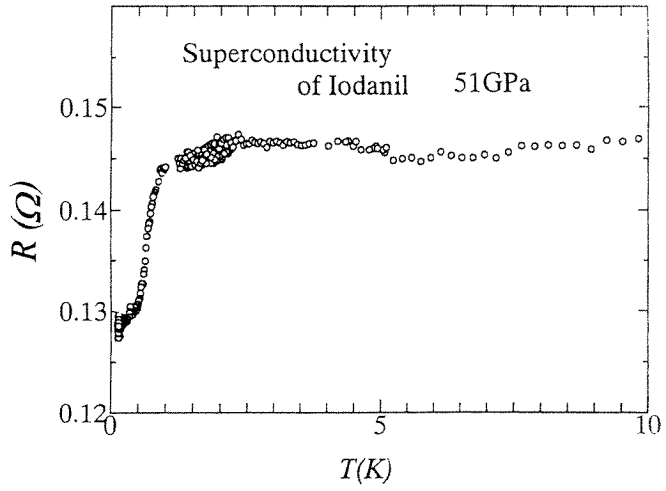

Figure 18. The temperature dependence of the electrical resistance of iodanil at 51 GPa. The resistance drop at 2 K is attributed to the transition to the superconducting state.

molecules are dissociated or otherwise polymerized under pressure, and exhibit large hysteresis in the electrical resistance and x-ray diffraction peaks. Therefore, iodanil may be the first example of an organic superconductor of a single-molecular (non-polymeric) system.

3.4. SnI_4

Among various simple inorganic molecules, SnI_4 is of special interest as it is a so-called re-entrant-type crystal. SnI_4 crystallizes at ambient pressure but becomes amorphous under pressure. A pressures above 60 GPa, it recrystallizes and the process is known to be reversible. Such a re-entrant crystallization is also seen in the case of sulphur and H_2O [21]. The search for and study of superconductivity are closely concerned with the metallization in the amorphous state under pressure. The high-pressure phase of SnI_4 is also of interest,

having fcc structure like that of solid iodine. The lattice constants under fixed pressure are found to be very close to each other.

At first, we expected the transition to the superconducting state to occur at lower temperature for pure solid iodine, regarding Sn atoms in SnI_4 as impurities.

In fact, superconductivity was found in our experiment even for the amorphous state, and the observed transition temperature for the fcc phase was unexpectedly higher than that for pure iodine [22].

Acknowledgments

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References

[1] Sumitomo Electric Company, synthetic type IIa diamond.
[2] Goncharov A F, Hemley R J, Mao H K and Shu J 1998 *Phys. Rev. Lett.* **80** 101
[3] Shimizu K, Yamauchi T, Tamitani N, Takeshita N, Ishizuka M, Amaya K and Endo S 1994 *J. Supercond.* **7** 921
[4] Ishizuka M and Amaya K 1994 *IEEE Trans. Magn.* **30** 1048
[5] Mao H K 1989 *Simple Molecular Systems at Very High Density* ed A Polian, P Loubeyre and N Boccara (New York: Plemum) pp 221–36
[6] Eremets M I, Shimizu K, Kobayashi T and Amaya K 1998 *Science* **281** 1333
[7] Shimizu K, Tamitani N, Takeshita N, Ishizuka M, Amaya K and Endo S 1992 *J. Phys. Soc. Japan* **61** 3853
[8] Shimizu K, Amaya K and Endo S 1995 *Rev. High Pressure Sci. Technol.* **6** 498
[9] Sakai N, Takemura K and Tsuji K 1982 *J. Phys. Soc. Japan* **51** 1811
[10] Sakamoto H, Shirai M and Suzuki N 1995 *J. Phys. Soc. Japan* **64** 3860
Sakamoto H, Oda T, Shirai M and Suzuki N 1996 *J. Phys. Soc. Japan* **65** 489
[11] Yamauchi T, Shimizu K, Takeshita N, Ishizuka M, Amaya K and Endo S 1994 *J. Phys. Soc. Japan* **63** 3207
[12] Kometani S, Eremets M I, Shimizu K, Kobayashi M and Amaya K 1997 *J. Phys. Soc. Japan* **66** 2564
and see also
Struzhkin V V, Hemley R J, Mao H K and Timofeev Y A 1997 *Nature* **390** 382
[13] Luo H, Desgreniers S, Vohra Y K and Ruoff A L 1991 *Phys. Rev. Lett.* **67** 2998
[14] Desgreniers S, Vohra Y K and Ruoff A L 1990 *J. Phys. Chem.* **94** 1117
[15] Shimizu K, Suhara K, Amaya K and Endo S 1996 *J. Phys. Soc. Japan* **65** 1527
[16] Amaya K, Shimizu K, Takeshita N, Kometani S, Eremets M I, Onodera A, Endo S, Takai M, Hamaya N and Shirotani I 1998 *Rev. High Pressure Sci. Technol.* **7** 688
[17] Shimizu K, Suhara K, Ikumo M, Eremets M I and Amaya K 1998 *Nature* **393** 767
[18] Otani M, Yamaguchi K, Miyagi H and Suzuki N 1998 *Rev. High Pressure Sci. Technol.* **7** 178
[19] Yokota T, Takeshita N, Shimizu K, Amaya K, Onodera A, Shirotani I and Endo S 1996 *Czech. J. Phys. Suppl.* S2 **46** 817
[20] Nakayama A 1998 private communication
[21] Hemley R J, Chen L C and Mao H K 1989 *Nature* **338** 638
[22] Takeshita N, Kometani S, Shimizu K, Amaya K, Hamaya N and Endo S 1996 *J. Phys. Soc. Japan* **65** 3400