Metallization and superconductivity in CsI at pressures up to 220 GPa

1998 J. Phys.: Condens. Matter 10 11519

(http://iopscience.iop.org/0953-8984/10/49/037)

J. Phys.: Condens. Matter **10** (1998) 11519–11523. Printed in the UK PII: S0953-8984(98)96519-5

Metallization and superconductivity in CsI at pressures up to 220 GPa

M I Eremets†‖, K Shimizu‡, T C Kobayashi† and K Amaya†§

† Research Centre for Materials Science at Extreme Conditions, Osaka University, Toyonaka, Osaka 560-8531, Japan
‡ Department of Physical Science, Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka 560-8531, Japan
§ Advanced Science Research Center, JAERI

Received 4 June 1998

Abstract. The pressure range for electrical transport measurements has been dramatically increased up to 220 GPa in the 0.05–300 K temperature region and at magnetic fields of up to 10 T. Metallization of caesium iodide was found at a pressure of 115 GPa. A superconducting transition with $T_c = 2$ K was observed above 180 GPa. T_c decreases with increasing pressure. The superconducting transition shifts to lower temperatures and disappears under magnetic field above 0.3 Tesla.

1. Introduction

CsI is a typical representative of simple ionic bonding. It has the lowest energy gap (about 6 eV) among alkali halides and high compressibility (twofold reductions of volume at 100 GPa). Therefore CsI is a favourable long-standing prototype for the study of the insulator-to-metal transition. CsI is isoelectronic to xenon and has similar properties. Under pressure CsI undergoes a continuous distortion starting from the B2 phase at 15 GPa through the orthorhombic symmetry intermediate phase to the hcp phase above 200 GPa [1]. First-principles calculations [2, 3] show that the metallization is caused by overlapping at the Γ-point of the filled 5p-like iodine band with the empty 5d-like caesium band around 100 GPa. Experimentally the metallization was studied only by optical methods. Extrapolation of the pressure dependence of the absorption edge gives the onset of the metallization near 100 GPa [4]. Infrared-reflectivity spectra show a relatively weak (a few per cent) increase of reflectivity at pressures above 110 GPa which was attributed to the metallization [5]. Electrical measurements are indispensable for providing metallization and studying the metallic state to search for superconductivity, but they are especially difficult to perform in a diamond anvil cell and were limited to 70 GPa [6]. Recently we succeeded in two important steps. We developed a method of clamping liquefied gases and studied metallization and superconductivity of oxygen [7]. Also, we dramatically miniaturized the electrical lead technique to study samples down to diameter of 20 μm in bevelled diamond anvils which can produce megabar pressures. We studied the metallization and superconductivity of sulphur [8]. A purpose of the present work is to study metallic CsI and to expand electrical measurements to multimegabars.

‖ To whom correspondence should be addressed.

0953-8984/98/4911519+05$19.50

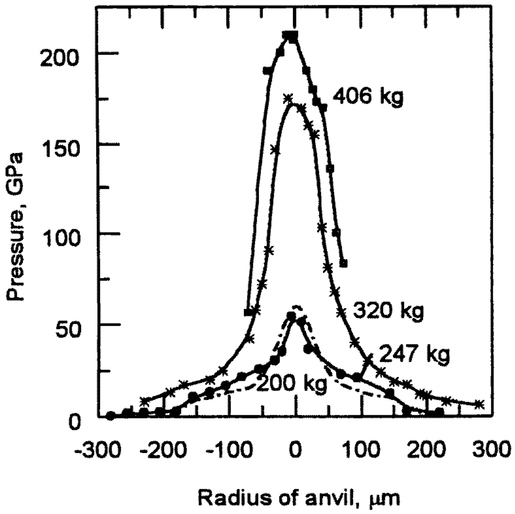

Figure 1. Pressure distribution over diameter of the diamond anvil with rhenium (dashed line) and alumina gaskets.

2. Experiment

Pressure was generated by diamonds with 300 μm diameter tips and a 10° bevelled angle cone and a 50 μm diameter flat surface at the top and measured with the aid of ruby grains of diameter $\sim$1 μm placed on top of the CsI sample. The spectra are resolved up to the highest pressures with shape and width very close to that taken for hydrogen [9] manifesting small shear stresses in CsI. Therefore, we used quasihydrostatic pressure calibration [10]. At pressures above 150 GPa ruby spectra were obscured by enhanced luminescence of diamond. To reject it, we effectively used a modulation technique similar to [11] but ultimately simpler [12]. Preparation of the insulating gasket and electrodes is described in [8]. For measurements of resistance, pressure and Raman spectra in the 2–300 K range we used an optical cryostat with a loading system and a DAC [12]. At temperatures down to 50 mK we used ^{3}He/^{4}He dilution refrigerators supplied with a magnet of up to 14 T. Pressure was generated at room temperature, after which the cell was clamped and slowly cooled. Measurements in the optical cryostat showed that pressure is kept nearly constant during cooling, increasing only by 8 GPa at 180 GPa. We assumed that this increase is the same upon cooling to millikelvins.

We compare pressure distribution and stresses in diamonds with the insulating gasket and the metallic one (figure 1). The pressure gradient over the anvil is smaller and the lateral supporting pressure is higher than that for the rhenium gasket. We observed no cracks during loading and even after releasing of pressure from 130 GPa. We also measured Raman spectra from diamond anvils at the surface and inside the diamond anvils, similar to [13], by probing a small volume of the focused laser beam: $\approx$10 μm^3. The maximum shift at the centre of the culet was at 1710 cm^{-1} at 206 GPa. Stresses along the axis of the anvil are dramatically reduced within 20 μm depth (figure 2). Thus the region of the highest stresses is located very nearly to the top of the anvils similar to a conical indenter. This shape is known from the theory of elasticity as favourable for achieving the highest pressures [12]. The next obvious step for increasing pressure is reduction of the anvil tip and probably further increase of the bevelled angle.

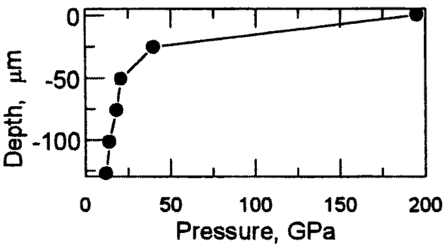

Figure 2. Pressure distribution inside the diamond anvil along its axis.

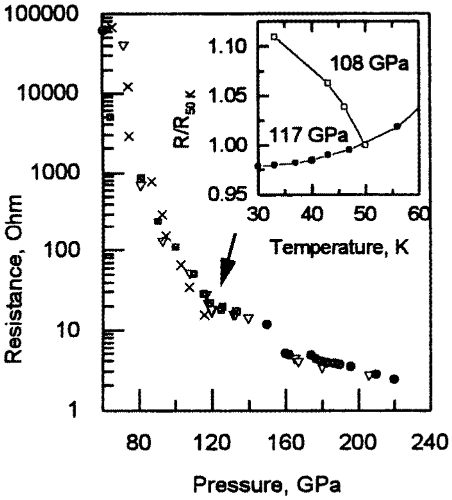

Figure 3. Pressure dependence of resistance of CsI at temperatures around 10 K (circles) and 300 K for different runs.

3. Results and discussion

Under compression above 45 GPa the resistance of CsI becomes measurable and strongly decreases with pressure (figure 3). A pronounced kink is observed at about 115 GPa. To confirm the metallization at this point, we also measured the temperature dependence of resistance. We conclude that CsI metallizes at 115±3 GPa. This result well supports optical experiments [4, 5]. The phenomenological Herzfeld's theory [14] predicts metallization of CsI at the density of 24.7 $cm^3 mol^{-1}$, that is well consistent with the measured molar volume ≈24 $cm^3 mol^{-1}$ at 115 GPa. First-principles calculations [2, 3] give pressure of metallization around 100 GPa.

In the metallic state, at the pressures around 120–140 GPa CsI is a poor metal; it is grey and has low reflectivity. Above 200 GPa its reflectivity is comparable to that of platinum electrodes. At 150–160 GPa there is a decrease of resistance which might be associated with a transition to the hcp phase.

At pressures above 180 GPa, we found a drop in the temperature dependence of resistance, figure 4. The onset of this step is about 2 K at 180 GPa and shifts to 1.3 K at 216 GPa. The most valuable argument for superconductivity of CsI is the characteristic behaviour of this resistance drop with increasing magnetic field: the step shifts to lower

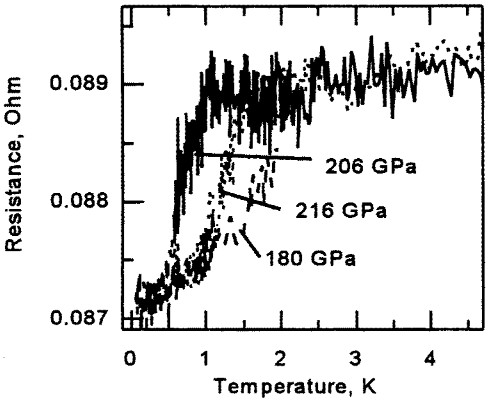

Figure 4. A superconducting transition in CsI at different pressures.

temperatures and disappears. Extrapolation of the magnetic dependence to zero temperature gives the value of the critical magnetic field as 0.3 T. A detailed discussion of the observed superconductivity is presented in [15].

4. Conclusions

We observed metallization of alkali halide—CsI—at 115 GPa for the first time by direct measurements of electrical conductivity. In the metallic state of CsI we found a superconducting transition with the critical temperature $T_c \approx 2$ K at 180 GPa shifting to 1.3 K at 216 GPa. We doubled the previous pressure limit up to 220 GPa for electrical measurements at static pressures. Now it overlaps well with the domain of the shock-wave technique where electrical measurements are common. We performed electrical and optical experiments at the high pressures in combination with other extremes: millikelvin temperatures and high magnetic fields up to 10 Tesla.

Acknowledgments

We appreciate the help of Dr K Syassen for his critical reading of the manuscript. This work was supported by CREST, JST and COE grant 10CE20004 Japan.

References

[1] Mao H K, Wu Y, Hemley R J, Chen L C, Shu J F and Finger L W 1989 *Science* **246** 649
Mao H K, Wu Y, Hemley R J, Chen L C, Shu J F, Finger L W and Fox D E 1990 *Phys. Rev. Lett.* **64** 1749
[2] Aidun J, Bukowinski M S and Ross M 1984 *Phys. Rev.* B **29** 2611
Satpathy S, Chritensen N E and Jepsen O 1985 *Phys. Rev.* **32** 6793
[3] Asokamani R, Subramoniam G and Amirthakuman M 1992 *Recent Trends in High Pressure Research, Proc. 13th AIRAPT Int. Conf. (Bangalore, 1991)* ed A K Singh (Oxford University Press–IBH) p 434
[4] Williams Q and Jeanloz R 1986 *Phys. Rev. Lett.* **56** 163
Makarenko I N, Goncharov A F and Stishov S M 1984 *Phys. Rev.* B **29** 6018
[5] Reichlin R, Ross M, Martin S and Goettel K A 1986 *Phys. Rev. Lett.* **56** 2858
[6] van Straaten J and Silvera I F 1987 *Rev. Sci. Instrum.* **58** 994
[7] Shimizu K, Suhara K, Ikumo M, Eremets M I and Amaya K 1998 *Nature* at press
[8] Eremets M I, Amaya K, Shimizu K and Kobayashi T C 1998 *Rev. High Pressure Sci. Technol.* **7** 469

Eremets M I 1997 *Proc. Adriatico Res. Conf. Simple Systems at High Pressures and Temperatures: Theory and Experiment (Trieste, 1997)* (ICTP) http://www.ictp.trieste.it/∼pub_off/sci-abs/smr999

Kometani S, Eremets M, Shimizu K, Kobayashi M and Amaya K 1977 *J. Phys. Soc. Japan* **66** 818

[9] Eggert J H, Moshary F, Evans W J, Goettel K A, and Silvera I F 1991 *Phys. Rev.* B **44** 7202

[10] Mao H K, Xu J and Bell P M 1986 *J. Geophys. Res.* **91** 4673

Hemley R J, Zha C S, Jephcoat A P, Mao H K and Finger L W 1989 *Phys. Rev.* B **39** 11 820

[11] Chen N H and Silvera I F 1996 *Rev. Sci. Instrum.* **67** 4275

[12] Eremets M I 1996 *High Pressures Experimental Methods* (Oxford: Oxford University Press) pp 59, 210

[13] Hanfland M and Syassen K 1985 *J. Appl. Phys.* **57** 2752

[14] Herzfeld K F 1927 *Phys. Rev.* **29** 701

[15] Eremets M I, Shimizu K, Kobayashi T C and Amaya K 1998 *Science* **281** 1333