INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **14** (2002) 11249–11253 PII: S0953-8984(02)39348-2

High-pressure studies on a new superconducting clathrate: Ba_6Ge_{25}

H Q Yuan[1], F M Grosche, W Carrillo-Cabrera, S Paschen, G Sparn, M Baenitz, Yu Grin and F Steglich

Max Planck Institute for the Chemical Physics of Solids, Nöthnitzer Str. 40, 01187 Dresden, Germany

E-mail: yuan@cpfs.mpg.de

Received 1 June 2002
Published 25 October 2002
Online at stacks.iop.org/JPhysCM/14/11249

Abstract

The effect of pressure on the low-temperature states of the newly discovered clathrate Ba_6Ge_{25} is investigated by means of measurements of the electrical resistivity. At ambient pressure, Ba_6Ge_{25} undergoes a two-step structural phase transition between 230 and 180 K from metallic behaviour to a high-resistivity state characterized by a mean free path of about 3 Å. Interestingly, a Bardeen–Cooper–Schrieffer-like (BCS-like) superconducting transition occurs at $T_C \approx 0.24$ K from the resulting 'bad metal'. With increasing pressure, the structural phase transition is depressed but T_C increases drastically. T_C reaches a maximum value of 3.85 K at the critical pressure $p_C \approx 2.8$ GPa, where the structural distortion is completely suppressed and the system exhibits metallic behaviour. Higher pressures lead to a slight decrease of T_C.

1. Introduction

Clathrates, a relatively unexplored class of compounds in which molecules or atoms of one substance are enclosed within the crystal structure of another, have been attracting growing attention recently (for example, see [1]). The renewed interest mainly stems from the following aspects:

(i) the discovery of superconductivity in the Ba–Na–Si_{46} series [2],
(ii) its potential for thermoelectric applications [3] based on the concept of combining a 'phonon glass' and an 'electron crystal' [4],
(iii) probably useful optical materials because of their wide band gaps [5],
(iv) potential superhard materials due to the low compressibility [6].

[1] Author to whom any correspondence should be addressed.

Recently, Carrillo-Cabrera *et al* discovered a new type of clathrate, Ba_6Ge_{25} (clathrate-IV), when exploring the Ba–Ge phase diagram [7], which was then independently reported by another two groups [8]. Ba_6Ge_{25}, crystallizing with the structure type of $Ba_6In_4Ge_{21}$ [9], is characterized by a 3D chiral framework of condensed Ge_{20} pentagondodecahedra (pdods) embedded in a 3D channel labyrinth. Each pdod is centred by a Ba atom (Ba1 site) and the remaining Ba atoms (Ba2 and Ba3) occupy the cavities in the zeolite-like labyrinth created by the dense piling of pdods. In each formula unit, there are two Ba1 sites, three Ba2 sites and one Ba3 site, together with 8 threefold-bond Ge atoms and 17 fourfold-bond Ge atoms. According to the Zintl concept, each formula unit of Ba_6Ge_{25} gives four conduction electrons, corresponding to a relatively small charge-carrier concentration of approximately 5×10^{21} cm^{-3}. Four formula units form a cubic unit cell with a lattice parameter $a = 14.5564(2)$ Å in Ba_6Ge_{25}.

Detailed studies of Ba_6Ge_{25} have been performed at ambient pressure [10–12]. X-ray and ^{137}Ba NMR studies indicate a large lattice expansion with a typical thermal hysteresis effect upon cooling down and warming up around 200 K. This first-order structural transition was further confirmed by measurements of specific heat, resistivity, Hall effect, susceptibility, thermopower and thermal conductivity. Of particular interest here is the investigation of the structural instability and its relation to the superconductivity of Ba_6Ge_{25}, first observed in our electrical resistivity measurement, by applying hydrostatic pressure.

2. Experimental details

Polycrystalline Ba_6Ge_{25} has been prepared by a radio-frequency melting technique in an argon protective atmosphere [7]. Powder x-ray diffraction and microphotography identify a single phase. The electrical resistivity measurement at pressures up to 3.4 GPa has been performed by a low-power AC four-terminal method using a BeCu/maraging steel hydrostatic clamp cell filled with a pressure-transmitting medium of 1:1 iso- and n-pentane. The large volume of this cell allows simultaneous measurements on seven or more samples, which offers an opportunity to study different samples under the same conditions. The pressure was obtained to within ± 0.05 GPa from the resistively determined superconducting transition temperature of Sn. In order to reach higher pressures, a Bridgman cell is employed, with which we can reach a pressure of about 10 GPa.

3. Results and discussion

The temperature dependence of the electrical resistivity of Ba_6Ge_{25} at different pressures is presented in figure 1, where (a) shows the high-temperature phase transition, (b) and (c) show the superconductivity in detail. Absolute resistivity was obtained by scaling the sample resistance to the published values measured at ambient conditions [10, 11]. The dashed and solid curves in figure 1(a) exhibit the cooling-down and warming-up processes respectively, from which a typical thermal hysteresis is observed, indicating a first-order phase transition. At ambient pressure, the resistivity of Ba_6Ge_{25} shows an evident two-step structural transition at $T_{S1} \approx 230$ K and $T_{S2} \approx 196$ K. Above T_{S1}, the system exhibits metallic behaviour, whereas the resistivity undergoes a drastic increase through the transition at T_{S2} to about 1 mΩ cm. Below this jump, the resistivity continues to rise and saturates below 10 K at about $\rho_0 \approx 1.5$ mΩ cm, corresponding to a mean free path of about 3 Å only. Strikingly, a superconducting transition occurs at $T_C \approx 0.24$ K. The upper critical field has been determined as $B_{C2}(0\,\mathrm{K}) \approx 0.6$ T, with an initial slope of $B'_{C2} \approx -2.9$ T K^{-1}. From this a coherence length of about 280 Å is

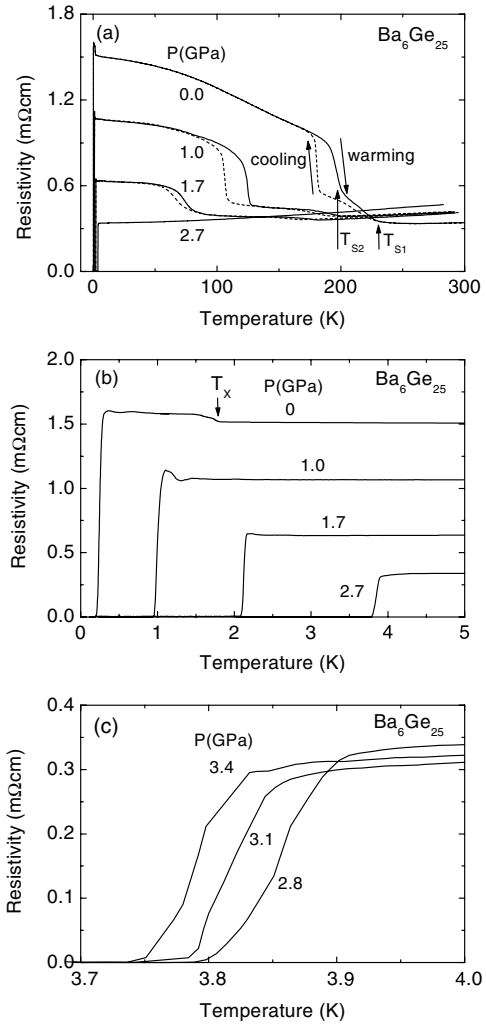

Figure 1. The temperature dependence of the resistivity of Ba_6Ge_{25} at different hydrostatic pressures. (a) The two-step structural transition at T_{S1} and T_{S2} is shifted to lower temperature with increasing pressure. Dashed curves and solid curves respectively describe the cooling-down and warming-up processes, showing a typical thermal hysteresis at the transition. (b) T_C is enhanced drastically when the structural transition is suppressed by pressure. (c) Higher pressures above p_C lead to a slight decrease of T_C.

estimated. By applying hydrostatic pressure, the structural transition is depressed to lower temperature and the high residual resistivity ρ_0 is correspondingly reduced, whereas T_C is enhanced drastically. At a critical pressure of $p_C \approx 2.8$ GPa where the structural distortion is suppressed completely, T_C reaches a maximum value of 3.85 K. Higher pressures above p_C lead to a slight decrease of T_C and the system shows metallic resistivity over the entire temperature range, which resembles the case of $Na_2Ba_4Ge_{25}$ [14]. For $Na_2Ba_4Ge_{25}$, $T_C \approx 1.05$ K ($p = 0$) and no structural distortion was observed. We summarize the pressure dependence of the structural phase transition $T_{S1,S2}$ and T_C in a phase diagram (figure 2). As marked in figure 1(a), T_{S1} (the onset temperature) and T_{S2} (the mid-point of the resistivity jump) are obtained from

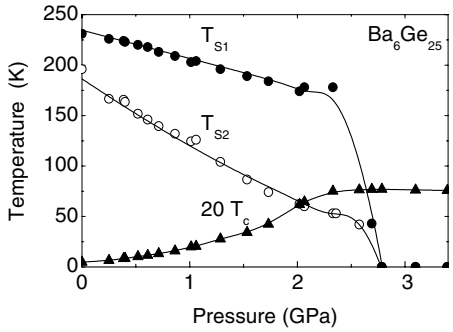

Figure 2. The pressure–temperature phase diagram of Ba_6Ge_{25}. T_{S1} (●, onset temperatures) and T_{S2} (○, mid-point of the resistivity jump), obtained from warming-up data, show that the structural transition is suppressed rapidly by pressure, whereas T_C (▲) is enhanced drastically to a maximum value of 3.85 K at $p_C \approx 2.8$ GPa.

the warming-up data. Obviously, $T_{S1,S2}$ is suppressed rapidly with increasing pressure. On the other hand, T_C undergoes a 16-fold increase as the structural transition disappears at p_C. Moreover, a sample-dependent resistive anomaly T_X appears just prior to T_C at low pressures (see figure 1(b)), but no sign is observed in either magnetic susceptibility or specific heat data. These anomalies might result from the sample inhomogeneity and the grain boundary.

The pressure dependence of the resistivity may be associated with the movement of Ba atoms. In Ba_6Ge_{25}, Ba2 and Ba3 can rattle inside the oversized cages [10–12]. Upon cooling through the phase transition, the strongly displaced atoms are frozen in their split positions, which may be seen as a double-well potential. Moreover, there may even be a tendency toward forming dimers between Ba2 and Ba3 [12]. The resulting disorder causes a strong random scattering, leading to a sharp increase of resistivity at the transition. With increasing pressure, the germanium framework is compressed, changing the potentials in which Ba atoms move and gradually suppressing the structural phase transition. As a critical pressure is approached, Ba atoms can only oscillate in a single potential well, giving rise to a metallic resistivity.

Bulk superconductivity of Ba_6Ge_{25} is further inferred from the measurements of specific heat and susceptibility at ambient pressure [13]. It is shown that the specific heat discontinuity at T_C ($\Delta C/\gamma T_C = 1.47$) is in accordance with the weak-coupling BCS value of 1.43. The sharp reduction of the magnetic susceptibility and the smooth decrease of the Hall coefficient through the transition $T_{S1,S2}$ [10, 11] may suggest that the density of states at the Fermi level $N(E_F)$ is modified but the total number of conduction electrons stays constant. The reduction of $N(E_F)$ at the transition $T_{S1,S2}$ is evident as well on comparing the resistive pressure dependence of Ba_6Ge_{25} and its isostructural relative $Na_2Ba_4Ge_{25}$ [14]. At ambient pressure, both T_C and the low-temperature specific heat show a much lower value for Ba_6Ge_{25} than for $Na_2Ba_4Ge_{25}$ despite the higher nominal concentration of conduction electrons in the former. However, once the structural distortion of Ba_6Ge_{25} is removed by pressure, both systems exhibit metallic resistivity and Ba_6Ge_{25} now has a much *higher* value of T_C. The origin of the low $N(E_F)$ in Ba_6Ge_{25} at low pressures may lie in the strong disorder scattering, which smears out any fine structure of $N(E_F)$. In summary, $N(E_F)$ for Ba_6Ge_{25} appears to undergo a sharp reduction due to the structural distortion, which is lifted as the structural instability is suppressed by pressure, leading to a drastic increase of T_C.

In conclusion, we have investigated the low-temperature properties of a new type of clathrate, Ba_6Ge_{25}, by tuning the material with hydrostatic pressure. Some interesting features have been observed:

(1) a first-order structural phase transition from metal to semiconductor takes place at a relatively high temperature, which is associated with the random 'locking-in' of Ba atoms to split positions in the oversized cavities;
(2) a BCS-like superconducting state occurs out of the dirty metal;
(3) T_C is strongly enhanced upon removing the structural instability by pressure;
(4) as the structural phase transition is suppressed at p_C, Ba_6Ge_{25} shows similar behaviour to the conventional metallic superconductors.

We recently measured the upper critical field of Ba_6Ge_{25}. The results indicate that the density of state $N(E_F)$ increases by a factor of 4 when the structural phase transition is suppressed by pressure [15].

References

[1] Nolas G S, Slack G A and Schujman S B 2001 *Semiconductors and Semimetals* vol 69, ed T M Tritt (San Diego: Academic Press) p 255
[2] Kawaji H, Horie H, Yamanaka S and Ishikawa M 1995 *Phys. Rev. Lett.* **74** 1427
[3] Nolas G S, Cohn J L, Slack G A and Schujman S B 1998 *Appl. Phys. Lett.* **73** 178
Cohn J L, Nolas G S, Fessatidis V, Metcalf T H and Slack G A 1999 *Phys. Rev. Lett.* **82** 779
[4] Slack G A 1995 *CRC Handbook of Thermoelectrics* ed D M Rowe (Boca Raton, FL: Chemical Rubber Company Press) p 407
[5] Adams G B, Keeffe M O, Demkov A A, Sankey O F and Huang Y M 1994 *Phys. Rev.* B **49** 8048
Demkov A A, Sankey O F, Schmidt K E, Adams G B and O'Keeffe M 1994 *Phys. Rev.* B **50** 17 001
[6] San-Miguel A, Kéghélian P, Blase X, Mélinon P, Perez A, Itié J P, Polian A, Reny E, Cros C and Pouchard M 1999 *Phys. Rev. Lett.* **83** 5290
[7] Carrillo-Cabrera W, Curda J, von Schnering H G, Paschen S and Grin Yu 2000 *Z. Kristallogr.* **215** 207
[8] Fukuoka H, Iwai K, Yamanaka S, Abe H, Yoza K and Häming L 2000 *J. Solid State Chem.* **151** 127
Kim S J, Hu S, Uher C, Hogan T, Huang B, Corbett J D and Kanatzidis M G 2000 *J. Solid State Chem.* **153** 321
[9] von Schnering H G, Kröner R, Carrillo-Cabrera W, Peters K and Nesper R 1998 *Z. Kristallogr.* **213** 665
[10] Paschen S, Tran V H, Baenitz M, Carrillo-Cabrera W, Michlck R, Grin Yu and Steglich F 2000 The new clathrate Ba_6Ge_{25} *Proc. 19th ICT* ed D M Rowe (Cardiff: Babrow) p 374
[11] Paschen S, Tran V H, Baenitz M, Carrillo-Cabrera W, Grin Yu and Steglich F 2002 *Phys. Rev.* B **65** 134435
[12] Carrillo-Cabrera W 2002 unpublished results
[13] Grosche F M, Yuan H Q, Carrillo-Cabrera W, Paschen S, Langhammer C, Kromer F, Sparn G, Baenitz M, Grin Yu and Steglich F 2001 *Phys. Rev. Lett.* **87** 247003
[14] Yuan H Q, Grosche F M, Carrillo-Cabrera W, Paschen S, Sparn G, Baenitz M, Grin Yu and Steglich F 2002 *High Pressure Res.* **22** 147
[15] Yuan H Q *et al* 2002 unpublished results