(P, T) Phase Diagram of Clathrate Superconductor 
\( \text{Ba}_{24}\text{Ge}_{100} \)

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Abstract. Precise electrical resistivity and ac calorimetry measurements under pressures have revealed (P, T) phase diagram of superconducting clathrate Ba\(_{24}\)Ge\(_{100}\). Following conventional superconducting theory, the pressure dependence of the density of state at Fermi energy, \( N(E_F) \), estimated by the electronic specific heat \( C/T \) has been discussed with the \( T_c(P) \). Up to \( P = 2.1 \) GPa, where \( T_c(P) \) starts to saturate, \( C/T \) increases with \( T_c \) in agreement with the theory. On further compression, \( C/T \) is strongly suppressed while \( T_c \) slightly decreases. Across \( P_c \approx 2.9 \) GPa, where structural deforming transitions at \( T_{s1(s2)} \) are suppressed, pressure variation of \( C/T \) becomes smaller. In addition to the enhancement of the \( N(E_F) \), other changes in crystal and/or electrical structure may play important roles to pressure dependence of \( T_c \) in Ba\(_{24}\)Ge\(_{100}\).

Oversized-cage compounds including atoms or molecules, such as skutterudites, pyrochlores and clathrates, have been attracted much attention for not only scientific interests but their thermoelectric potential. Clathrate Ba\(_{24}\)Ge\(_{100}\) is a superconductor below \( T_c = 240 \) mK at ambient pressure \([1]\). Well above \( T_c \), two successive structure deforming phase transitions have been observed at \( T_{s1} = 215 \) K and \( T_{s2} = 180 \) K accompanied by a pronounced thermal hysteresis \([2]\). The two-step increases in the electrical resistivity \( \rho \) on cooling suggests the reduction of the electronic density of state at Fermi energy, \( N(E_F) \), at low temperature. It is also indicated by the soft X-ray spectroscopy \([3]\). With increasing pressure, \( T_{s1} \) and \( T_{s2} \) are shifted to lower temperature, but \( T_c \) increases remarkably to 3.8 K at \( P_c = 2.8 \) GPa where the structural transitions are suppressed \([1]\). From the \( \rho(P) \) at low temperature, \( dH_c/dT|_{T_c} \) \([4]\) and NMR results \([5]\), the obtained \( N(E_F) \) is strongly enhanced under pressure, and thus, the superconductivity in Ba\(_{24}\)Ge\(_{100}\) are concluded as a conventional one, namely \( T_c \) varies with \( N(E_F) \). Because of the few number of precise experiments around \( P_c \), it is still not revealed the detail of the change of electronic state, e.g. how \( N(E_F) \) and crystal structure varies across \( P_c \). Here, we have studied the pressure temperature phase diagram of Ba\(_{24}\)Ge\(_{100}\) via the simultaneous \( \rho \) and ac calorimetry \( C_{ac} \) measurements under pressure with special focus on the vicinity of the structural instability at \( P_c \). The \( N(E_F) \) estimated by the electronic specific heat coefficient \( C/T \) increases up to \( P \approx 2.1 \) GPa, where \( T_c(P) \) starts to saturate. Interestingly, \( C/T \) strongly decreases on further compression, although \( T_c(P) \) keeps constant or slightly decreases. These results indicate that the modification of crystal structure and/or Fermi surface, which does not strongly affect \( T_c \), seems to occur around \( P_c \).

The simultaneous \( \rho \) and \( C_{ac} \) have been measured as a function of temperature between 1.8 K
and room temperature and pressures up to 4 GPa. Two Au-AuFe (0.07%) thermocouples (TC) are welded to the both ends of sample, and two Au wires are also attached in between them for ρ measurement. For C_{ac} measurement, a modulating heat was applied by current through the sample or TC, and the oscillating temperature was measured by another TC. Pressure was applied by a diamond anvil pressure cell filled with glycerin as a pressure medium and estimated by a ruby fluorescence method at low temperature. Additional signal on C_{ac} from pressure medium shows a clear liquid to glass transition anomaly. The pressure dependence of the anomaly indicates the glycerin solidifies around P = 4 GPa at room temperature, in good agreement with the previously reported phase diagram of glycerin [6]. From these facts, at least room temperature and the pressure region discussing here, pressure is tuned and applied homogeneously.

Figure 1. Pressure-temperature phase diagram of Ba_{24}Ge_{100}. Open and closed symbols are phase boundaries determined by ρ and C_{ac}, respectively. For T_{s2}, the downward and upward triangles are obtained on cooling and warming processes. T_{c} is multiplied by 5 for clear view. The lines are guides for eyes.

Fig. 1 shows pressure temperature phase diagram obtained by temperature dependence of ρ and C_{ac}. It is almost consistent with previous report [1]. A clear anomaly around T_{s2} with thermal hysteresis (downward and upward triangles) is observed in both curves of ρ(T) and C_{ac}(T), indicating a first-order phase transition. With increasing pressure, T_{s1(s2)} is shifted to lower temperature, but T_{c} is enhanced drastically accompanied with the reduction of ρ at low temperature, as seen in Fig. 2(a). ρ(T) around T_{s2} above 2 GPa shows two step anomalies as plotted in Fig. 1, although any C_{ac} anomalies are not detected. Because of a strong smearing of the ρ(T) and C_{ac} anomalies above 2 GPa, it is not unambiguously determined P_{c}. However, our obtained P_{c} ~ 2.9 GPa is very close to a previously reported value of P_{c} = 2.8 GPa [1].

In our experimental region above T = 1.8 K, the superconducting transition was observed above P = 1.5 GPa as shown in Fig. 2. The ρ(T) at low temperature has a large value and weakly depends on temperature reflecting the random scattering from disordered phase [2, 7]. A clear λ-like anomaly in specific heat at T_{c} under pressure is firstly observed, indicating that the superconductivity in Ba_{24}Ge_{100} is bulk nature even in the higher temperature superconducting region. T_{c} is defined as a midpoint of the resistive drop and of the C_{ac} jump and is plotted in Fig. 1 and 3. T_{c} strongly increases with pressure up to P ~ 2.2 GPa and slightly varies on further compression.

As argued by the previous experiments [4, 5], we will discuss how the N(E_F) varies with T_{c}. Assuming that the pressure dependence of specific heat of pressure medium glycerin at
Figure 2. Temperature dependence of (a) $\rho$ and (b) $C_{ac}/T$ of $\text{Ba}_{24}\text{Ge}_{100}$ under several pressures.

Figure 3. Pressure dependence of $T_c$ (closed circle) and the normal state $C_{ac}/T$ at 4 K (open circle) corresponding to the electronic specific heat coefficient.

Low temperature is negligibly small, we estimated the electronic specific heat at normal state as the $C_{ac}/T$ at 4 K. Pressure dependence of $C_{ac}/T(\propto N(E_F))$ as well as $T_c$ are represented in Fig. 3. $C_{ac}/T$ increases accompanied with the increase of $T_c$ up to $P \sim 2.1$ GPa. It is in good agreement with the previous suggestions that the $N(E_F)$ is strongly enhanced with $T_c$ [4, 5]. It is in agreement with the conventional BCS theory that $T_c$ varies with the $N(E_F)$ as follows, $T_c \propto \Theta_D \exp[-1/N(E_F)V]$, where $\Theta_D$ is the Debye temperature, $V$ is the electron-phonon coupling constant. Pressure collapse of the structural transitions may reduce the random scattering leading to a drastic enhancement of $T_c$. At higher pressures than $P = 2.2$ GPa, $T_c$ weakly depends on pressure, although the $N(E_F)$ is strongly suppressed. Above $P_c \sim 2.9$ GPa, where the structural phase transitions at $T_{s1(s2)}$ are suppressed, the $C/T$ seems to be weak pressure dependence. Between 2.2 GPa and $P_c$, the low and high pressure phase may coexist arising from the first-order transition at $T_{s2}$. Moreover, Raman scattering experiment revealed pressure-induced structural phase transition at room temperature and $P=3.2$ GPa, which seems
to be due to the structural distortion combined with the enhanced guest-host interactions [8]. Up to 2.2 GPa, the pressure evolution of $T_c$ seems strongly correlated the enhancement of $N(E_F)$. Above 2.2 GPa, a probable intermediated phase makes it difficult to simply discuss the relation between $T_c$ and $C_{ac}/T$. However, it seems not rule out the conventional superconducting scenario. For first-order phase transition, the volume discontinuity across $P_c$ is expected. It is important to take into account for the pressure variation of the volume to discuss the density of state. Thermal expansion measurements under pressure can directly determine pressure variance of the volume and is desired.

In conclusion, we have thermodynamically determined pressure temperature phase diagram of Ba$_{24}$Ge$_{100}$ through the precise electrical resistivity and specific heat measurements. We revealed that the $N(E_F)$ increases with $T_c$ up to $P \sim 2.2$ GPa and decreases at higher pressure while $T_c$ doesn't vary. In addition to the enhancement of the $N(E_F)$, other changes in crystal and/or electrical structure play important roles to the strong pressure variation of $T_c$.

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