Superconductivity in the Filled Cage Compounds Ba₆Ge₂₅ and Ba₄Na₂Ge₂₅


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The clathrate compound Ba₆Ge₂₅ and its relatives consist of a rigid germanium skeleton, into which barium or other metal atoms are coordinated. These guest atoms can “rattle” freely at high temperatures, but in Ba₆Ge₂₅ some of them lock randomly into split positions below Tₛ ~ 200 K. The resulting bad metal undergoes a BCS-like superconducting transition at T_c = 0.24 K. T_c increases more than 16-fold, as Tₛ is suppressed by hydrostatic pressure $p$, but changes only slightly with $p$ from T_c = 0.84 K in the undistorted sister compound Ba₄Na₂Ge₂₅. The large enhancement of T_c in Ba₆Ge₂₅ may be attributed mainly to the pressure tuning of strong disorder caused by the random displacement of Ba atoms at Tₛ.

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The effect of the lattice and its excitations on the electron liquid in metals provides a lasting source of surprises and discoveries in the study of complex materials. In particular, “conventional” superconductivity is experiencing a revival of interest, motivated largely by the discovery of unexpectedly high superconducting transition temperatures [1] and by the fabrication of field-controlled devices [2]. Especially instructive are cases in which the electronic density of states or the phonon spectrum can be tuned via an external control parameter. Such a scenario may arise naturally in materials close to a structural instability, which leaves the cubic space symmetry unchanged, providing to two effects: an increase of the bare electronic density of states and a softening of an Einstein mode associated with one of the barium atoms (expected when freeing the locked-in Ba atoms from their split positions), as Ba₆Ge₂₅ approaches the undistorted, low-disorder, high-temperature phase with increasing pressure.

Ba₆Ge₂₅ [3–6] and Ba₄Na₂Ge₂₅ [12] crystallize with the Ba₆In₄Ge₂₁ structure type (Pearson symbol $cP12_4$). The structure is characterized by a 3D chiral framework of condensed Geₙ pentagonodecahedra (pdods) forming a 3D channel labyrinth. Each pdod is centered by a barium atom (position Ba1), while the other metal atoms occupy the remaining cavities (M2 and Ba3, where M = Ba or Na) in the zeolite-like labyrinth. There are two Ba1 and three M2 sites as well as one Ba3 site per formula unit. Na atoms randomly replace two of the Ba atoms on the M2 sites in Ba₆Ge₂₅ to form Ba₄Na₂Ge₂₅. Seventeen Ge are fourfold bonded neutral atoms and 8 Ge are threefold bonded ions, giving a nominal concentration of 4 conduction electrons per formula unit for Ba₆Ge₂₅ and 2 electrons per formula unit in the case of Ba₄Na₂Ge₂₅, in order-of-magnitude agreement with low-temperature Hall-effect measurements [7,8]. Four formula units form one cubic unit cell with the lattice parameters $a = 14.5564(2)$ Å in Ba₆Ge₂₅ and $a = 14.4703(2)$ Å for Ba₄Na₂Ge₂₅.

The electrical resistivity at pressures up to about 3.4 GPa (determined from the $T_c$ of Sn) was measured by a low-power ac four-terminal method inside BeCu/Maraging Steel hydrostatic clamp cells filled with a 1:1 mixture of isopentane and n-pentane (see, e.g., [13]). Heat capacity and thermal expansion were determined on small samples ($\approx 0.1$ g) by a thermal relaxation and a high-resolution capacitive method, respectively. Polycrystals of Ba₆Ge₂₅ and Ba₄Na₂Ge₂₅ were prepared by a radio-frequency melting technique in an argon protective atmosphere [4] and have been identified as single phase by microphotography and x-ray diffraction.

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At ambient pressure, the resistivity trace of $\text{Ba}_6\text{Ge}_{25}$ exhibits a narrow range of metallic behavior extending from room temperature down to about 230 K (Fig. 1), followed at lower temperature by a two-step anomaly at $T_{S1,S2} \approx 230$ K, 196 K (on warming), which is accompanied by a dramatic increase of the resistivity to about 1 mΩ cm. Below this jump, the resistivity continues to rise, saturating below 10 K at about $\rho_0 = 1.5$ mΩ cm. At $T_x \approx 1.5$ K, there is a further, smaller anomaly, followed by a superconducting transition with the midpoint of the resistivity jump at $T_c = 0.24$ K. With increasing pressure, the structural transitions are suppressed to lower temperatures and the residual resistivity $\rho_0$ is reduced. The low temperature anomaly disappears and $T_c$ climbs gradually to a maximum of about 3.8 K at 2.7 GPa (Fig. 2), where the resistivity appears metallic, if with a poor residual resistance ratio, over the entire temperature range.

The resistive upper critical field has been determined as $B_c(0 \text{ K}) = 0.6$ T, with an initial slope of $dB_c/dT = -2.9$ T/K, corresponding to a coherence length of about 280 Å. This value would be small for a conventional metal, but is consistent with a dirty limit calculation following [14]: $dB_c/dT = -(12\pi/\pi^2k_B)\gamma\rho_0V_m^{-1} = -3$ T/K, where $\gamma = C/T$ is the electronic specific heat (Sommerfeld) coefficient and $V_m$ refers to the molar volume. The mean free path can be estimated by standard methods, e.g., [15], as $\ell \approx 1200$ Å $\times$ ($A_F/(4\pi^2\lambda^2)\rho_0/\mu\Omega$ cm)$^{-1}$. Here, $A_F$ refers to the total Fermi surface area and would be minimized for a single spherical Fermi surface, where this expression gives $\ell \approx 3$ Å in $\text{Ba}_6\text{Ge}_{25}$, justifying the use of the dirty limit expression above.

Bulk superconductivity in $\text{Ba}_6\text{Ge}_{25}$ is inferred from measurements of the specific heat (Fig. 3) and magnetic susceptibility (not shown) in addition to the resistive observation shown in Fig. 1. In $\text{Ba}_6\text{Ge}_{25}$, the specific heat results for the normal state yield a Sommerfeld coefficient $\gamma = 21$ mJ/mol K$^2$ above a broadened transition with an onset at 0.27 K, consistent with the onset of the resistive transition, and a bulk transition temperature of about 0.14 K, in agreement with susceptibility data. The ratio of jump height to normal state specific heat, estimated by applying an entropy-balancing geometric construction, is about 1.47, close to the BCS value of 1.43. The discrepancy between the resistive and bulk $T_c$ is attributed to inhomogeneities, resulting in a distribution of $T_c$ across the sample if the transition temperature depends strongly on the precise sample composition. In the isostructural reference compound $\text{Ba}_4\text{Na}_3\text{Ge}_{25}$, which lacks any sharp transitions at high temperatures and displays a metallic resistivity over the entire range down to $T_c$, superconductivity occurs at a higher and only weakly $p$-dependent $T_c$ of $\approx 0.84$ K and from a higher $C/T$ ratio of $\gamma = 33$ mJ/mol K$^2$ (Fig. 3). Again, the jump height is consistent with the weak-coupling BCS value. Following the specific heat of both compounds to higher temperatures, we observe only a small region in which a Debye-like $T^3$ temperature dependence of the specific heat is obeyed (insets of Fig. 3). Above 3 K, the specific heat increases more rapidly, indicating a significant contribution of low-lying localized (Einstein) modes. The additional heat capacity is consistent with the contribution expected from a single Einstein mode per formula unit at

![FIG. 1. The temperature dependence of the resistivity, $\rho(T)$ of $\text{Ba}_6\text{Ge}_{25}$ at different hydrostatic pressures, $p$. At low $p$, a metallic decrease of $\rho(T)$ at high $T$ is interrupted by a strong two-step anomaly at $T_{S1}$ and $T_{S2}$, below which $\rho$ increases dramatically and then saturates at a $p$-dependent low-$T$ value $\rho_0(p)$. The sample-dependent, spurious anomaly at $T_x$ is not yet understood. A full loss of resistivity below a midpoint $T_c = 0.24$ K at ambient pressure is ascribed to a superconducting transition, which rises rapidly with $p$ and reaches 3.8 K at 2.7 GPa, where the resistivity remains metallic from room temperature down to $T_c$.](247003-2)

![FIG. 2. The pressure-temperature phase diagram of $\text{Ba}_6\text{Ge}_{25}$. The resistivity anomalies observed on warming at $T_{S1,S2}$ (closed symbols, onset for $T_{S1}$, midpoint of jump for $T_{S2}$) are associated with the lock-in transitions of Ba 2 and 3 atoms. They are suppressed rapidly with increasing $p$, in step with a dramatic increase of the superconducting transition temperature $T_c$ (open symbols, midpoint of the resistivity drop).](247003-2)
energy $\hbar \Omega = k_B 37.2$ K in Ba$_6$Ge$_{25}$ and at an even lower energy $\hbar \Omega = k_B 32$ K in Ba$_4$Na$_2$Ge$_{25}$. As only the Ba3 position is unique, while there are several Ba1 and M2 positions per formula unit, the lowest Einstein mode is ascribed to the “rattling” of the Ba3 atom. In Ba$_6$Ge$_{25}$, that barium atom assumes an off-symmetry, split position at low temperatures, which is accompanied by a narrowing of the potential well, leading to the increased frequency of oscillation. A qualitatively similar behavior is displayed by the coefficient of thermal expansion, $\alpha = \partial \ln L / \partial T$, where L is the sample length (insets of Fig. 3). However, the low-temperature, $T$-linear contribution to $\alpha$ (offset in $\alpha/T$) is unusually high in Ba$_6$Ge$_{25}$. This may point either at an additional and strongly $p$-dependent contribution to the lattice entropy, for instance from tunneling motion of Ba atoms or from strongly damped vibrational modes, or at an anomalous volume dependence of the electronic density of states at the Fermi level, $N(E_F)$. While $\alpha$ is directly linked to the initial pressure derivative of the total entropy, these findings may have little implication for $N(E_F)$ of Ba$_6$Ge$_{25}$ at high pressure, which plays an important role in determining $T_c(p)$.

To unravel the strong pressure dependence of $T_c$ in Ba$_6$Ge$_{25}$, we consider first the impact of the high-temperature phase transitions on the electronic structure. The anomalies at $T_{S1,S2}$ are caused by a first order (as evidenced by the strong thermal hysteresis) structural transformation, which has been studied in detail [7,8,16]. They coincide with a sharp reduction of the magnetic susceptibility by roughly the expected Pauli contribution in a free-electron picture, while the Hall coefficient is continuous through the transition, indicating that — while the density of states at the Fermi level may change at $T_{S1,S2}$ — the total number of conduction electrons is unaffected. Strikingly, the resulting low temperature specific heat is significantly lower in Ba$_6$Ge$_{25}$ than in Ba$_4$Na$_2$Ge$_{25}$, despite the higher nominal electron density in the former. Taken together, the jump of the susceptibility on crossing $T_{S1,S2}$ [7,8] and the low value of the Sommerfeld coefficient when compared to the reference compound Ba$_4$Na$_2$Ge$_{25}$, suggest that the effective density of states at the Fermi level in Ba$_6$Ge$_{25}$ undergoes a sharp reduction at the structural phase transition.

The resulting differences between the low-$T$ electronic density of states of the two compounds are expected to have a significant effect on their superconducting properties. Within the conventional BCS/McMillan formalism [17], we can estimate the electron-phonon coupling constant $\lambda$ from $T_c$, obtaining values around 0.3 – 0.4 (Table I), in rough agreement with electron-phonon coupling parameters observed in polyvalent metals. These values may be used to estimate the bare (band structure) electronic density of states at the Fermi level, $N(\epsilon_F)$ (see Table I) and hence to disentangle the effects of band structure and phonon spectrum on $\lambda$. The resulting values for $N(\epsilon_F)$ indicate that the distorted low-temperature phase of Ba$_6$Ge$_{25}$ is accompanied by an anomalously low bare density of states, despite its nominally larger electron count.

To understand this effect, we consider the large random displacement of the barium atoms on sites 2 and 3 at the structural transition by as much as 0.5 Å, as determined by detailed x-ray diffraction studies [16]. We stress that in contrast to the superstructure observed at the formation of a charge density wave (e.g., [18]), no intercell correlations were found in Ba$_6$Ge$_{25}$ despite the large atomic displacements. The resulting disorder leads to strong random scattering and hence to the observed jump in the resistivity. Moreover, the short mean free path of order 3 Å.

![Figure 3](image-url)

**FIG. 3.** The specific heat coefficient $C/T$, open symbols, of Ba$_6$Ge$_{25}$ (a) and Ba$_4$Na$_2$Ge$_{25}$ (b) at low $T$ (main figures) and plotted vs $T^2$ up to about 5 K (insets). The low-$T$ data show bulk superconducting transitions with normalized jump heights $\Delta C/\gamma T_c$ of 1.47 and 1.49 in Ba$_6$Ge$_{25}$ and Ba$_4$Na$_2$Ge$_{25}$, respectively. Above about 3 K, $C/T$ is no longer well described by a Debye $T^2$ law (straight lines in insets, obtained by fitting $C/T = \gamma + \beta T^2$ to the low-temperature data, with $\beta = 3.8$ mJ/mol K$^2$ (Debye temperature $\Theta_D = 250$ K) in both compounds and $\gamma = 21$ mJ/mol K$^2$ in Ba$_6$Ge$_{25}$ and $\gamma = 33$ mJ/mol K$^2$ in Ba$_4$Na$_2$Ge$_{25}$). A single additional Einstein mode at energy $\hbar \Omega$ is sufficient in either case to obtain satisfactory agreement (lines through points in insets), with $h \Omega (\text{Ba}_6\text{Ge}_{25})/k_B = 37.2$ K and $h \Omega (\text{Ba}_4\text{Na}_2\text{Ge}_{25})/k_B = 32$ K. In addition, the insets show the coefficient of linear thermal expansion over $T$, $\alpha/T$, for both compounds (closed symbols).
TABLE I. Normal state and superconducting parameters of Ba₆Ge₂₅ and Ba₄Na₂Ge₂₅. Z is the nominal number of conduction electrons per unit cell and \( \gamma = C/T \) extrapolated to \( T = 0 \). Using [17] with a Coulomb repulsion parameter \( \mu^* = 0.1 \) and \( t_D = 250 \) K (cf. Fig. 3), \( \lambda \) is estimated from the bulk \( T_c \). Factoring out the mass-renormalization \( 1 + \lambda \), a band-structure density of states per formula unit is calculated as \( N_{\text{th}}(E_F) = \frac{3\gamma}{\pi^2k_B^2(1 + \lambda)} \). The frequency \( \Omega \) of the lowest Einstein mode is obtained from an analysis of the low-\( T \) specific heat (cf. Fig. 3) and the low-\( T \) Gr"uneisen parameter, \( \Gamma_0 = \frac{3N_{\text{th}}\alpha}{\kappa_T C} \) where the isothermal compressibility \( \kappa_T = (47 \text{ GPa})^{-1} \) is determined from high-\( p \), room-\( T \) x-ray diffraction [16] is found by extrapolation to \( T = 0 \).

<table>
<thead>
<tr>
<th></th>
<th>( \gamma )</th>
<th>( T_c ) (( p = 0 ))</th>
<th>( N_{\text{th}} )</th>
<th>( \hbar\Omega/k_B )</th>
<th>( \Gamma_0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba₄Na₂Ge₂₅</td>
<td>2</td>
<td>33</td>
<td>0.84</td>
<td>0.40</td>
<td>10.0</td>
</tr>
<tr>
<td>Ba₆Ge₂₅</td>
<td>4</td>
<td>21</td>
<td>0.14</td>
<td>0.31</td>
<td>6.8</td>
</tr>
</tbody>
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brings the material close to the bad metal regime where \( k_F \ell \sim 1 \), indicating that localization effects may become important. In first approximation, the high level of disorder effectively smears out, via collision-time broadening, any structure in reciprocal space on a scale finer than \( 1/\ell \) and hence smooths \( N(E) \) over \( \delta E = \hbar v_F/\ell \), where \( v_F \) refers to the Fermi velocity. In the present case, where \( E_F \) lies close to the band edge [19], a significant reduction of the density of states can result, if \( \hbar v_F/\ell > E_F \), which is automatically satisfied in the bad metal limit. Other mechanisms, e.g., changes to the band structure corresponding to the formation of (virtual) Ba-Ba bonds [8,16,19], may contribute further to a reduction of \( N(E_F) \) on entering the distorted low-\( T \) state.

The central result of this study, the dramatic enhancement of superconductivity in Ba₆Ge₂₅ under hydrostatic pressure (Fig. 2), is consistent with a simple picture emerging from the preceding comparison of Ba₆Ge₂₅ and Ba₄Na₂Ge₂₅: as Ba₆Ge₂₅ approaches the undistorted high-pressure structure, the combined effect of an increase in the bare density of states and of a shift of phononic spectral weight to lower energies enhances \( \lambda \) and increases \( T_c \). Both mechanisms can be more effective, if pressure is applied instead of chemical substitution: the ultimate density of states in undistorted Ba₆Ge₂₅ is expected to be higher than that of Ba₄Na₂Ge₂₅ because of the higher electron count, and the phonon spectrum at \( p_c \) can be softer (smaller \( \Omega \)) than that of the reference compound, which is at ambient pressure far away from the lattice instability. However, the anomalously large low-temperature Gr"uneisen parameter \( \Gamma_0 \) in Ba₆Ge₂₅ (Table I) indicates an initial decrease of the total entropy with pressure at low \( T \). Although at high enough \( p \), \( N(E_F) \) may nevertheless be increasing with \( p \), as postulated above, this may point at additional and strongly \( p \)-dependent contributions to the lattice entropy, or could even require an altogether different explanation for the strong variation of \( T_c \) with \( p \).

In the clathrate compound Ba₄Ge₂₅, pressure can be used to control strong disorder. By suppressing high-temperature structural phase transitions at which barium atoms are displaced randomly into split positions, the electronic properties and phonon spectrum can be tuned over an unusually wide range, leading to a more than 16-fold enhancement of \( T_c \). Filled cage compounds form an increasingly active branch of novel materials research. The mechanisms discussed for Ba₆Ge₂₅ and Ba₄Na₂Ge₂₅ may be relevant to other complex structures outside the clathrate family.

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[19] I. Zerec et al. (to be published).