

Superconductivity in the Filled Cage Compounds $\text{Ba}_6\text{Ge}_{25}$ and $\text{Ba}_4\text{Na}_2\text{Ge}_{25}$

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(Received 24 July 2001; published 21 November 2001)

The clathrate compound $\text{Ba}_6\text{Ge}_{25}$ 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 $\text{Ba}_6\text{Ge}_{25}$ some of them lock randomly into split positions below $T_S \sim 200$ K. The resulting bad metal undergoes a BCS-like superconducting transition at $T_c \approx 0.24$ K. T_c increases more than 16-fold, as T_S is suppressed by hydrostatic pressure p , but changes only slightly with p from $T_c \approx 0.84$ K in the undistorted sister compound $\text{Ba}_4\text{Na}_2\text{Ge}_{25}$. The large enhancement of T_c in $\text{Ba}_6\text{Ge}_{25}$ may be attributed mainly to the pressure tuning of strong disorder caused by the random displacement of Ba atoms at T_S .

DOI: 10.1103/PhysRevLett.87.247003

PACS numbers: 74.25.Jb, 74.62.Fj, 74.70.Wz

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 can be pushed across the critical point, where the structural distortion vanishes at low temperatures, by applying hydrostatic pressure.

In the recently discovered barium-germanium clathrate compounds, the rigid germanium skeleton provides oversized atomic cages, in which the barium atoms can undergo large anharmonic vibrations. This leads to a complex phonon spectrum consisting of low-lying local (Einstein) modes attributed to the heavy and loosely bound barium atoms in addition to the high-energy modes of the rigid germanium framework.

In this study, we concentrate on the cubic system $\text{Ba}_6\text{Ge}_{25}$ [3–6], in which some barium atoms lock into split positions below about 200 K. This transition, which leaves the cubic space symmetry unchanged, provides to our knowledge the best-studied example of a structural phase change in the barium-germanium clathrate family [7,8]. We report the discovery of bulk superconductivity at ambient pressure in $\text{Ba}_6\text{Ge}_{25}$ below 0.24 K and in its isostructural relative $\text{Ba}_4\text{Na}_2\text{Ge}_{25}$, which lacks the structural transitions of $\text{Ba}_6\text{Ge}_{25}$, below 0.84 K. These low values of T_c contrast with the transition temperatures observed in other barium-germanium/silicon clathrates, which range up to 8 K [9–11]. Under hydrostatic pressure, T_c in $\text{Ba}_6\text{Ge}_{25}$ is found to increase by more than a factor of 16—a remarkable enhancement unique at least among the clathrates—reaching nearly 4 K at the critical pressure, where the structural transitions are completely suppressed. We argue that the underlying change of the

electron-phonon coupling constant λ may be driven by 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 $\text{Ba}_6\text{Ge}_{25}$ approaches the undistorted, low-disorder, high-temperature phase with increasing pressure.

$\text{Ba}_6\text{Ge}_{25}$ [3–6] and $\text{Ba}_4\text{Na}_2\text{Ge}_{25}$ [12] crystallize with the $\text{Ba}_6\text{In}_4\text{Ge}_{21}$ structure type (Pearson symbol $cP124$). The structure is characterized by a 3D chiral framework of condensed Ge_{20} pentagondodecahedra (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 $\text{Ba}3$, where $M = \text{Ba}$ or Na) in the zeolite-like labyrinth. There are two Ba1 and three $M2$ sites as well as one $\text{Ba}3$ site per formula unit. Na atoms randomly replace two of the Ba atoms on the $M2$ sites in $\text{Ba}_6\text{Ge}_{25}$ to form $\text{Ba}_4\text{Na}_2\text{Ge}_{25}$. 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 $\text{Ba}_6\text{Ge}_{25}$ and 2 electrons per formula unit in the case of $\text{Ba}_4\text{Na}_2\text{Ge}_{25}$, 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 $\text{Ba}_6\text{Ge}_{25}$ and $a = 14.4703(2)$ Å for $\text{Ba}_4\text{Na}_2\text{Ge}_{25}$.

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 (≈ 0.1 g) by a thermal relaxation and a high-resolution capacitive method, respectively. Polycrystals of $\text{Ba}_6\text{Ge}_{25}$ and $\text{Ba}_4\text{Na}_2\text{Ge}_{25}$ 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.

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 m Ω cm. Below this jump, the resistivity continues to rise, saturating below 10 K at about $\rho_0 \approx 1.5$ m Ω 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 $T_c \approx 0.24$ K. With increasing pressure, the structural transitions are suppressed to lower temperatures and the residual resistivity ρ_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 $B_{c2}(0 \text{ K}) \approx 0.6$ T, with an initial slope of $dB_{c2}/dT \approx -2.9$ 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]: $dB_{c2}/dT = -(12e/\pi^3 k_B) \gamma \rho_0 V_m^{-1} \approx -3$ 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 $\ell \approx 1200 \text{ Å} \times [A_F/(4\pi \text{ Å}^2) \rho_0/\mu\Omega \text{ cm}]^{-1}$. Here, A_F refers to the total Fermi surface area and would be minimized for a single spherical Fermi surface, where this expression gives

$\ell \sim 3 \text{ Å}$ 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 $\gamma \approx 21$ mJ/molK² 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 $\text{Ba}_4\text{Na}_2\text{Ge}_{25}$, 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 ≈ 0.84 K and from a higher C/T ratio of $\gamma \approx 33$ mJ/molK² (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

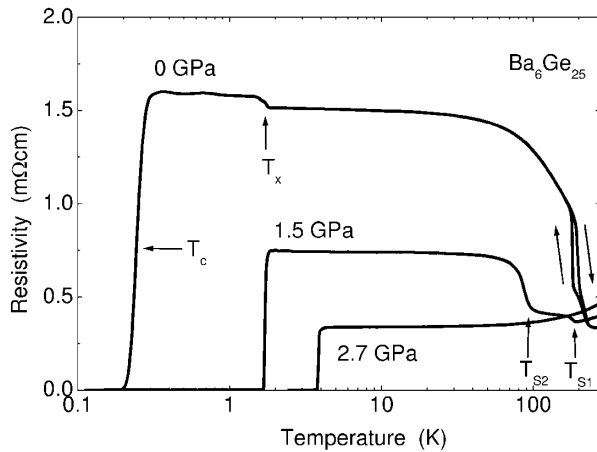


FIG. 1. The temperature dependence of the resistivity, $\rho(T)$ of $\text{Ba}_6\text{Ge}_{25}$ at different hydrostatic pressures, p . At low p , a metallic decrease of $\rho(T)$ at high T is interrupted by a strong two-step anomaly at T_{S1} and T_{S2} , below which ρ increases dramatically and then 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 $T_c \approx 0.24$ 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 .

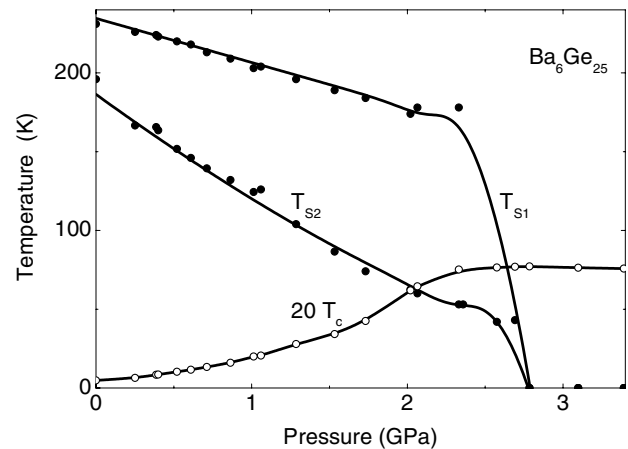


FIG. 2. The pressure-temperature phase diagram of $\text{Ba}_6\text{Ge}_{25}$. The resistivity anomalies observed on warming at $T_{S1,S2}$ (closed symbols, onset for T_{S1} , midpoint of jump for T_{S2}) are associated with the lock-in transitions of Ba 2 and 3 atoms. They are suppressed rapidly with increasing p , in step with a dramatic increase of the superconducting transition temperature T_c (open symbols, midpoint of the resistivity drop).

energy $\hbar\Omega \approx k_B 37.2$ K in $\text{Ba}_6\text{Ge}_{25}$ and at an even lower energy $\hbar\Omega \approx k_B 32$ K in $\text{Ba}_4\text{Na}_2\text{Ge}_{25}$. 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 $\text{Ba}_6\text{Ge}_{25}$, 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, $\alpha \equiv \partial \ln L / \partial T$, where L is the sample length (insets of Fig. 3). However, the low-temperature, T -linear contribution to α (offset in α/T) is unusually high in $\text{Ba}_6\text{Ge}_{25}$. 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 α is directly linked to the *initial* pressure derivative of the total entropy, these findings may have little implication for $N(E_F)$ of $\text{Ba}_6\text{Ge}_{25}$ at *high* pressure, which plays an important role in determining $T_c(p)$.

To unravel the strong pressure dependence of T_c in $\text{Ba}_6\text{Ge}_{25}$, 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 $\text{Ba}_6\text{Ge}_{25}$ than in $\text{Ba}_4\text{Na}_2\text{Ge}_{25}$, 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 $\text{Ba}_4\text{Na}_2\text{Ge}_{25}$, suggest that the effective density of states at the Fermi level in $\text{Ba}_6\text{Ge}_{25}$ 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 λ 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_{bs} (see Table I) and hence to disentangle the effects of band structure and phonon spectrum on λ . The resulting values for N_{bs} indicate that the distorted low-temperature phase of $\text{Ba}_6\text{Ge}_{25}$ 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 $\text{Ba}_6\text{Ge}_{25}$ 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

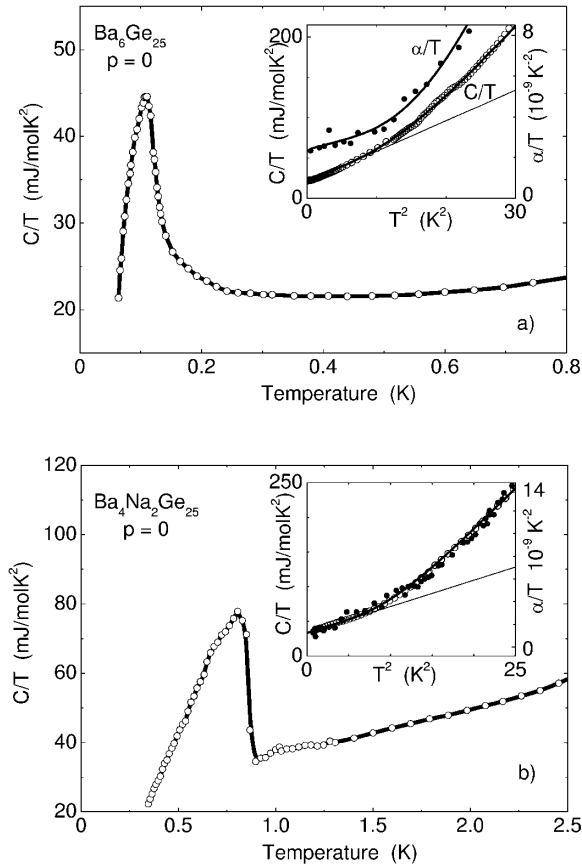


FIG. 3. The specific heat coefficient C/T , open symbols, of $\text{Ba}_6\text{Ge}_{25}$ (a) and $\text{Ba}_4\text{Na}_2\text{Ge}_{25}$ (b) at low T (main figures) and plotted vs T^2 up to about 5 K (insets). The low- T data show bulk superconducting transitions with normalized jump heights $\Delta C/\gamma T_c$ of 1.47 and 1.49 in $\text{Ba}_6\text{Ge}_{25}$ and $\text{Ba}_4\text{Na}_2\text{Ge}_{25}$, respectively. Above about 3 K, $C(T)$ is no longer well described by a Debye T^3 law (straight lines in insets, obtained by fitting $C/T = \gamma + \beta T^2$ to the low-temperature data, with $\beta = 3.8 \text{ mJ/molK}^4$ (Debye temperature $\Theta_D \approx 250$ K) in both compounds and $\gamma \approx 21 \text{ mJ/molK}^2$ in $\text{Ba}_6\text{Ge}_{25}$ and $\approx 33 \text{ mJ/molK}^2$ in $\text{Ba}_4\text{Na}_2\text{Ge}_{25}$). A single additional Einstein mode at energy $\hbar\Omega$ is sufficient in either case to obtain satisfactory agreement (lines through points in insets), with $\hbar\Omega(\text{Ba}_6\text{Ge}_{25})/k_B = 37.2$ K and $\hbar\Omega(\text{Ba}_4\text{Na}_2\text{Ge}_{25})/k_B = 32$ K. In addition, the insets show the coefficient of linear thermal expansion over T , α/T , for both compounds (closed symbols).

TABLE I. Normal state and superconducting parameters of $\text{Ba}_6\text{Ge}_{25}$ and $\text{Ba}_4\text{Na}_2\text{Ge}_{25}$. 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 $\Theta_D \approx 250$ K (cf. Fig. 3), λ 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 $N_{bs}(E_F) = 3\gamma/[\pi^2 k_B^2(1 + \lambda)]$. The frequency Ω of the lowest Einstein mode is obtained from an analysis of the low- T specific heat (cf. Fig. 3) and the low- T Grüneisen parameter, $\Gamma_0 = (3V_m\alpha)/(\kappa_T C)$ [where the isothermal compressibility $\kappa_T \approx (47 \text{ GPa})^{-1}$ is determined from high- p , room- T x-ray diffraction [16]] is found by extrapolation to $T = 0$.

	$Z/4$	γ $\frac{\text{mJ}}{\text{molK}^2}$	T_c ($p = 0$) K	λ	N_{bs} eV^{-1}	$\hbar\Omega/k_B$ K	Γ_0
$\text{Ba}_4\text{Na}_2\text{Ge}_{25}$	2	33	0.84	0.40	10.0	32	1.4
$\text{Ba}_6\text{Ge}_{25}$	4	21	0.14	0.31	6.8	37.2	7.9

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 smoothes $N(E)$ over $\delta E \approx \hbar v_F/\ell$, 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 $\text{Ba}_6\text{Ge}_{25}$ under hydrostatic pressure (Fig. 2), is consistent with a simple picture emerging from the preceding comparison of $\text{Ba}_6\text{Ge}_{25}$ and $\text{Ba}_4\text{Na}_2\text{Ge}_{25}$: as $\text{Ba}_6\text{Ge}_{25}$ 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 λ 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 $\text{Ba}_6\text{Ge}_{25}$ is expected to be higher than that of $\text{Ba}_4\text{Na}_2\text{Ge}_{25}$ because of the higher electron count, and the phonon spectrum at p_c can be softer (smaller Ω) than that of the reference compound, which is at ambient pressure far away from the lattice instability. However, the anomalously large low-temperature Grüneisen parameter Γ_0 in $\text{Ba}_6\text{Ge}_{25}$ (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 $\text{Ba}_6\text{Ge}_{25}$, 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 $\text{Ba}_6\text{Ge}_{25}$ and $\text{Ba}_4\text{Na}_2\text{Ge}_{25}$ may be relevant to other complex structures outside the clathrate family.

We wish to thank, in particular, S. Ramakrishnan, G. G. Lonzarich, I. Zerec, O. Yaresko, and P. Thalmeier.

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