73Ge-NMR study and ab initio calculations on clathrate compound Ba24Ge100

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Abstract. Through 73Ge-NMR measurements and ab initio calculations, we have studied electronic properties of a type-III clathrate compound Ba24Ge100. At ambient pressure, the nuclear spin-lattice relaxation rate 1/T1 has a peak around 200 K followed by an activation type decrease with decreasing temperature and it becomes constant at very low temperatures. Near the peak temperature, the successive structural transformations have been observed at TS1 = 215 K and TS2 = 180 K. The constant value of 1/T1 at low temperatures is considerably smaller than the value at temperatures higher than TS1, which implies that the density of states at the Fermi level D(EF) significantly decreases from the high temperature value at ambient pressure. From ab initio calculations on Ba24Ge100 as well as Ba24Si100, we speculate the phase changes of Ba24Ge100 in the relevant region of the T-P plane. Our results of NMR measurements and D(EF) calculations for the P43m2 and an R3 structures imply that, at high pressures ∼2.8 GPa, there should be increase of D(EF) from the value at ambient pressure and low temperatures. We conclude that this result is predominantly related with the large enhancement of the superconducting transition temperature Tc from 0.24 K (at P = 0) to 3.8 K (at P = 2.7 GPa) observed in Ba24Ge100.

1. Introduction
Clathrate compounds including large cages inside have recently attracted much attention. The local vibration of the guest atoms weakly coupled with their cages surrounding them, which is called "rattling", brings about intriguing physical properties. A type-III clathrate compound Ba24Ge100 exhibits superconductivity at Tc = 0.24 K under ambient pressure. At ambient pressure, two anomalies at TS1 = 215 K and TS2 = 180 K were found in the resistivity measurement of Ba24Ge100[1, 2], which suggests successive structural transformations [3]. Remarkably, the application of the pressure reduces TS1 and TS2, while it increases Tc progressively, reaching Tc = 3.8 K at P = 2.7 GPa. The averaged value of pressure derivative of the Tc, ΔTc/ΔP is about 1.3 K/GPa, which is larger than about 1 K/GPa of the HgBa2Ca2Cu3O6+δ[4], largest value in the superconductors to the best of our knowledge.
These anomalies disappear above \( P = 2.7 \text{ GPa}[1] \). Note that Ba\(_{24}\)Si\(_{100}\) with \( T_c = 1.4 \text{ K} \) does not show any such anomalies[5].

In this paper, we report on electronic properties probed by the nuclear spin-lattice relaxation rate \( 1/T_1 \) in \(^{73}\text{Ge}\)-enriched Ba\(_{24}\)Ge\(_{100}\) through \(^{73}\text{Ge}\)-NMR measurements. We also report on the results by \textit{ab initio} calculations for Ba\(_{24}\)Ge\(_{100}\) and Ba\(_{24}\)Si\(_{100}\).

2. NMR experiments

We synthesized a polycrystalline sample of \(^{73}\text{Ge}\)-enriched Ba\(_{24}\)Ge\(_{100}\) under high pressure [5]. As shown in Figures 1(a) and 1(b), we observed the anomalies in the resistivity and susceptibility measurements at \( T_{S1} \approx 218 \text{ K} \) and \( T_{S2} \approx 182 \text{ K} \), which coincide with the results reported in the earlier studies[2]. We also measured the nuclear spin-lattice relaxation rate \( 1/T_1 \) by the \(^{73}\text{Ge}\)-NMR in a magnetic field \( H = 12 \text{ T} \) at ambient pressure.

Fig.1(c) shows the temperature dependence of \( 1/T_1 T \) normalized by the value at \( T = 4.2 \text{ K} \) on \(^{73}\text{Ge}\)-enriched Ba\(_{24}\)Ge\(_{100}\) at ambient pressure. The value of \( 1/T_1 T \) has a maximum around 200 K near \( T_{S1} \) and \( T_{S2} \). The red line is the fitting curve by a relation of \( 1/T_1 T = A \exp(-E/k_B T) + C \). The activation energy is estimated to be \( E/k_B \approx 330 \text{ K} \), which corresponds to \( \approx 230 \text{ cm}^{-1} \) in wave number. The peak of \( 1/T_1 T \) around 200 K is apparently relevant with the successive transitions at \( T_{S1} \) and \( T_{S2} \) evidenced by the resistivity and susceptibility measurements.

In the temperature range above 250 K and below 20 K, a \( 1/T_1 T = \text{const.} \) behavior holds as is usually seen in normal metals. Notably, the constant value of \( 1/T_1 T \) at low temperatures
is considerably smaller than the value at temperatures higher than $T_{S1}$. Then we expect the density of states at the Fermi level $D(E_F)$ significantly decreases in the low temperature region by structural transformations[3], since the value of $1/T_1T$ is proportional to the square of $D(E_F)$. As a result, the ratio of $D(E_F)_{RT}/D(E_F)_{4.2K} \sim 4$ is estimated from the $1/T_1T$ at ambient pressure.

3. **Ab initio calculations**

Next we show the electronic states studied by the *ab initio* calculations. All the calculations were carried out by the use of VASP code[8] of the pseudo-potential method, where the Vanderbilt ultra-soft pseudo-potentials[9] and the generalized gradient approximation (GGA) for the exchange-correlation were employed. We used the cut-off energy of 350 eV and a k-point mesh of $8 \times 8 \times 8$ for the integration over the Brillouin zone.

| Pressure    | $a$[Å] | Space group          |
|-------------|--------|----------------------|
| Experiment  | ambient| $P4_132$ (cubic)     |
| Calculation | 0      | 14.881               |
|             | 2.8 GPa| 14.560               |

Table 1. The lattice parameter and the space group obtained by the XRD experiment and the results by our calculation for Ba$_{24}$Ge$_{100}$ at $P=0$ and $P=2.8$ GPa.

| Pressure    | $a$[Å] | Space group          |
|-------------|--------|----------------------|
| Experiment  | ambient| $P4_132$ (cubic)     |
| Calculation | 0      | 14.207               |
|             | 3.1 GPa| 13.990               |

Table 2. The lattice parameter and the space group obtained by the XRD experiment and the results by our calculation for Ba$_{24}$Si$_{100}$ at $P=0$ and $P=3.1$ GPa.

At first we have optimized the structures for Ba$_{24}$Ge$_{100}$ and Ba$_{24}$Si$_{100}$. We started the calculations assuming the space group $P4_132$ and the lattice parameters obtained by the X-ray diffraction (XRD) experiments at ambient pressure and room temperature[6, 7] as an initial guess. The cubic structures with the space group $P4_132$ correspond to local minima at the lattice parameters given in Table 1 for Ba$_{24}$Ge$_{100}$ and in Table 2 for Ba$_{24}$Si$_{100}$ at $P = 0$. We have further examined whether other structures with lower symmetries become more stable or not, by setting larger shift to a position of Ba from the center of an open Ge$_{20}$-cage. As a result, we have found that a low-symmetry structure of space group $P1$, which is triclinic, is more stable than the $P4_132$ structure. At $P = 0$ these indicate that the $P4_132$ structure observed at room temperature becomes unstable at low temperatures. The low-symmetry structure, like the $P1$ structure, may be involved in the structural transformations at $T_{S1}$ or $T_{S2}$ upon cooling. When we isotropically pressurized the lattice, the structure has spontaneously changed into an $R3$ structure for both compounds. This structure is robust around the lattice parameters of the $R3$ given in Tables 1 or 2.

Next we calculated the electronic density of states $D(E_F)$ assuming the $P4_132$ as the low pressure room temperature structure and the $R3$ as the high pressure room temperature structure. The $D(E_F)_{P4_132}$ values at $P = 0$ are calculated to be 74[states/eV/Ba$_{24}$IV$_{100}$] for Ba$_{24}$Ge$_{100}$ and 44[states/eV/Ba$_{24}$IV$_{100}$] for Ba$_{24}$Si$_{100}$, as shown in Fig. 2. The $D(E_F)$ values do not show any significant difference between the $R3$ and the $P4_132$ for both compounds. Then, if
Figure 2. Calculated DOS on (a)Ba$_{24}$Ge$_{100}$ and (b)Ba$_{24}$Si$_{100}$. The $D(E_F)^{P4_132}$ at $P=0$ are calculated to be 74[states/eV/Ba$_{24}$IV$_{100}$] for Ba$_{24}$Ge$_{100}$ and 44[states/eV/Ba$_{24}$IV$_{100}$] for Ba$_{24}$Si$_{100}$. In addition, the value do not differ much from that of $R3$ structure at around $P=3$GPa for both compounds. Insets are the magnification of the energy range near the Fermi level.

we assume the $R3$ as the room temperature structure of Ba$_{24}$Ge$_{100}$ at $P=2.8$GPa and assume that it is preserved to low temperature region since no structural transformations was observed experimentally[1, 3], we can expect that $D(E_F)^{P=2.8}$GPa at low temperatures is nearly equal to $D(E_F)^{P=0}$. Taking the ratio $D(E_F)^{P=0}/D(E_F)^{P=0} \sim 4$ obtained from the NMR measurement into consideration, we expect $D(E_F)^{P=2.8}$GPa$/D(E_F)^{P=0} \sim 4$.

In this context, a reason for the dramatic enhancement of the $T_c$ with increasing pressure is expected to be due to the increase of $D(E_F)$. Further investigations of the electronic and superconductive characteristics are now in progress by systematic NMR/NQR measurements under pressure and at low temperatures, along with $ab$ initio calculations.

4. Conclusion

We have investigated the electronic properties of type-III clathrate compound Ba$_{24}$Ge$_{100}$ through the $^{73}$Ge-NMR study at ambient pressure and the $ab$ initio calculations on Ba$_{24}$Ge$_{100}$ and Ba$_{24}$Si$_{100}$. The value of $1/T_1T$ has a maximum around 200 K which is near the temperatures of the successive structural transformations $T_{S1}$ and $T_{S2}$. From the result that a constant value of $1/T_1T$ at low temperatures is considerably smaller than its value at temperatures higher than $T_{S1}$, we speculate that $D(E_F)$ significantly decreases as a result of possible structural transformations. The $ab$ initio calculation on Ba$_{24}$Ge$_{100}$ has revealed that the calculated $D(E_F)$ for the low pressure room temperature $P4_132$ structure shows no significant difference from that of the high pressure $R3$ structure. Incorporating the indication from NMR results in Ba$_{24}$Ge$_{100}$ with the fact of no structural transformation above $P=2.7$GPa, we conclude that the $D(E_F)$ at high pressure phase is higher than that at $P=0$, which is predominantly related with the large enhancement of $T_c$ by applying the pressure in Ba$_{24}$Ge$_{100}$.

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