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Optical Reflection Spectra of Silicon Clathrate Compounds $Ba_8Ag_xSi_{46-x}$

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Optical Reflection Spectra of Silicon Clathrate Compounds $Ba_8Ag_xSi_{46-x}$

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Optical reflection spectra are measured for $Ba_8Ag_xSi_{46-x}$ ($0 \le x \le 6$) at room temperature. A systematic decrease in the plasmon energy is found with increasing x, indicating that the carrier concentration decreases with increasing x. When x increases, the superconducting transition temperature T_c decreases. An origin of the decrease in T_c is assigned to the decrease in the density of states at the Fermi level due to the decrease in the carrier concentration.

Keywords: silicon clathrate; superconductivity; reflection spectrum

INTRODUCTION

A discovery of superconductivity in silicon clathrate compounds $Ba_6Na_2Si_{46}$[1] has attracted a deep interest from the viewpoint of the cage structured materials as well as new superconducting silicon compounds. The cage structured materials with the inclusion of guest atoms, such as clathrate[2] and zeolite[3], has the wide controllability in the chemical composition for the doping without changing the basic structure.

In $Ba_6Na_2Si_{46}$, the superconducting phase transition is observed at the temperature $T_c \sim 4$ K[1], although no superconductivity is observed in Na_8Si_{46}. The origin of the superconductivity is understood in the BCS regime. Electrons of Na and Ba atoms are transferred to the Si_{46} network. The Fermi level is located at the narrow energy band which is constructed by the hybridization of 5*d* orbital of Ba atom and the Si network conduction band[4]. Hence, the high density of states at the Fermi level is expected. NMR

experiments imply that Ba 5*d* states significantly contribute to the state density at the Fermi level[5]. The high state density is ascribed to the main origin of the high T_c. In Ba_8Si_{46}, the superconducting phase transition is observed at $T_c = 8$ K[6]. The origin of such a high T_c is assigned to the much larger contribution of Ba-5*d* hybridized state. When Ag is mixed with Ba_8Si_{46}, Ag atoms are introduced at the replace site of Si network as shown in Fig. 1. With increasing Ag content, T_c decreases drastically, and the superconductivity is not observed for $x > 4$ within the measurement temperature range down to 1.8 K[6], although Ag content is less than 10 % of Si network. The origin of the decrease in T_c is not well known yet. In the present paper, the optical reflection spectrum is measured for $Ba_8Ag_xSi_{46-x}$ ($0 \leq x \leq 6$) at room temperature, and the systematic decrease is found in the plasmon energy, indicating that the carrier concentration decreases with increasing x. It is proposed that the decrease in T_c is ascribed mainly to the decrease in the carrier concentration, because the decrease in the carrier concentration may cause the decrease in the state density of the Fermi level at the Ba-5*d* hybridized band.

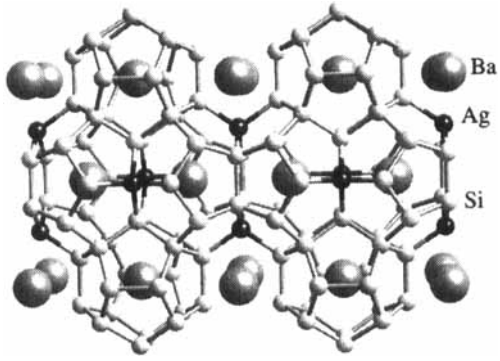

FIGURE 1. Schematic illustration of $Ba_8Ag_6Si_{40}$.

EXPERIMENTAL

Samples $Ba_8Ag_xSi_{46-x}$ (x = 0, 0.5, 1, 2, 3, 6) were prepared under high pressure[6]. $BaSi_2$, Si and Ag were mixed at the given composition, and melted in an arc furnace under an Ar atmosphere. The melted mixtures were ground and compressed in an h-BN container by using a cubic anvil press at 3 GPa and 800 °C. Samples were cut into a plate form to measure the optical

reflection spectrum. Sample surface is not smooth but has many small flat terraces with the size of several ten μm. Some part of reflected light escapes from the optical alignment. In order to improve this, parabolic mirrors were used to collect a reflected light as much as possible, and the observed reflectance was gained up to about one half of the true value. Some part of incident light is far from the normal condition to the sample surface, because of the large solid angle. Nicolet Magna 550 and Varian Cary 5G spectrometers were used for the infrared and visible spectral regions, respectively.

RESULTS AND DISCUSSTIONS

Figure 2 shows the reflection spectra of $Ba_8Ag_xSi_{46-x}$, where x is shown in the figure. The origin of ordinate is shifted in each curve to see them easily. The absolute value of reflectance is normalized to unity at the lower energy limit, because the reflectance of metal is known to approach unity at the zero energy. The Drude-like high reflectance region is seen in each curve at near infrared to mid infrared regions. This is characteristic of metallic specimens. The higher energy shoulder corresponds to the plasmon energy as marked by vertical lines.

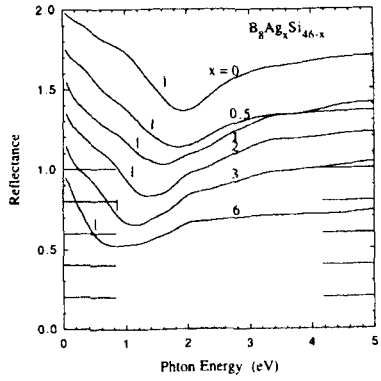

FIGURE 2 Reflection spectrum of $Ba_8Ag_xSi_{46-x}$ at room temperature.

The Kramers-Kronig (KK) analysis is performed to estimate the plasmon energy of these samples, as follows. An example form of the typical dielectric function ε in a metallic sample is given by

$$\varepsilon = \varepsilon_0 \left\{ 1 - \frac{\omega_p^2}{\omega(\omega + i\gamma)} \right\}, \tag{1}$$

where ε_0, ω_p, γ are the non-resonant part of dielectric function, the plasmon energy and the damping energy, respectively. At $\omega = \omega_p$, ε approaches zero, but it is not so reliable to estimate ω_p from this relation, because of the complex value of ε. On the other hand, a dielectric function is known to have the peak at $\omega = \omega_p$ in the function $-\mathrm{Im}\left(\frac{1}{\varepsilon}\right)$. This function is known to be proportional to the energy loss rate of an electron beam. Indeed, this function should have the clear peak at $\omega = \omega_p$, as seen in an example form of eq. (1):

$$-\mathrm{Im}\left(\frac{1}{\varepsilon}\right) = \frac{\omega\omega_p^2\gamma}{\varepsilon_0[(\omega^2 - \omega_p^2)^2 + \gamma^2\omega^2]}. \tag{2}$$

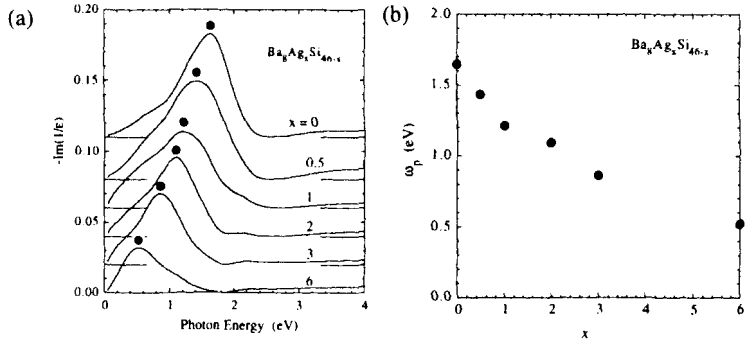

FIGURE 3 (a)Spectrum of $-\mathrm{Im}(1/\varepsilon)$ in $Ba_8Ag_xSi_{46-x}$, (b) the plasmon energy as a function of x.

We can calculate the value of eq. (2) by using ε which is obtained from the KK analysis of the reflection spectra in Fig. 2. The result is shown in Fig 3(a). A clear peak is seen in each curve. In Fig. 3(b), the plasmon energy is plotted

as a function of Ag content x.

Generally, the plasmon energy is given by $\omega_p = \sqrt{\frac{4\pi e^2 n}{\varepsilon_0 m}}$, where e, n and m are the elementary charge of electron, the carrier concentration and the effective mass of carrier, respectively. If we assume that $\varepsilon_0 = 10$, $m = m_0$, and each Ba atom supplies two electrons as carriers in the conduction band, the plasmon energy is estimated to be 1.4 eV. This value has a good correspondence with the observed plasmon energy in Ba_8Si_{46}, 1.65 eV.

The reason why the carrier concentration decreases with increasing Ag content is explained qualitatively as follows. In n-type Si crystal with a diamond structure, the concentration of electrons decreases by the doping of Ag[7]. Ag atom acts as the ionized acceptor just below the conduction band at –0.29 eV. The local electronic state of Ag atom in Si_{46} network seems to be rather similar to that in Si crystal. Hence, if we assume the similar behavior as seen in Si crystal, Ag atoms can act as the acceptor in $Ba_8Ag_xSi_{46-x}$. The carriers supplied by Ba atoms may be trapped at acceptor sites around Ag atoms in Si_{46} network.

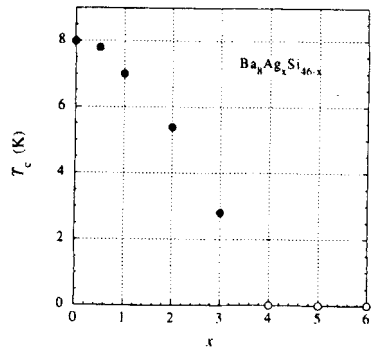

FIGURE 4 Superconducting phase transition temperature in $Ba_8Ag_xSi_{46-x}$[6]. The values smaller than 1.8 K are marked at 0K.

The temperature of superconducting phase transition T_c in $Ba_8Ag_xSi_{46-x}$ is shown in Fig. 4[6]. The value of T_c decreases with increasing x. If the carrier concentration decreases with increasing Ag content, the Fermi level decreases in the energy. In Ba_8Si_{46}, the Fermi level is located at the very high

density of states of the hybridized energy band of Ba-5*d* and Si_{46} network. Hence, the density of states at the Fermi level is expected to decrease with increasing Ag content. Another supplementary origin may be possible, such as the change in the lattice vibration mode[8], *etc.*

CONCLUSION

Optical reflection spectra are measured for $Ba_8Ag_xSi_{46-x}$ ($0 \leq x \leq 6$) at room temperature. A systematic decrease in the plasmon energy is found with increasing x, indicating that the carrier concentration decreases with increasing x. The main origin of the decrease in T_c is assigned to the decease in the carrier concentration followed by the decrease in the density of states at the Fermi level.

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