3B2v8.06a/w (Dec 5 2003).51c +model | PHYSB : 307 | Prod.Type:FTP pp.1–2(col.fig.:NIL) | ED:PabitraBoran PAGN:Jay SCAN:

ARTICLE IN PRESS

Available online at www.sciencedirect.com
SCIENCE DIRECT
ELSEVIER
Physica B ▮ (▮▮▮▮) ▮▮▮–▮▮▮
PHYSICA B
www.elsevier.com/locate/physb

Tunneling spectroscopy of single-crystal clathrate $Ba_8Ga_{16}Sn_{30}$

R.A. Ribeiro[a,*], T. Ekino[a], M.A. Avila[b], T. Takabatake[b]

[a]*Faculty of Integrated Arts and Sciences, Hiroshima University, Higashi-Hiroshima 739-8521, Japan*
[b]*Department of Quantum Matter, ADSM, Hiroshima University, Higashi-Hiroshima 739-8530, Japan*

Abstract

Tunneling measurements have been carried out on the $Ba_8Ga_{16}Sn_{30}$. The break-junction was employed to obtain reliable tunneling spectra. The pseudo-gap like feature is obtained as $2\Delta \approx 175$ meV, at 4.2 K, which agrees with thermoelectric power data at low temperature. We have also obtained a small gap $2\Delta \approx 30$–40 meV.

PACS: 74.50.+r; 82.75.−z

Keywords: Tin clathrates; Break-junction; Tunneling; Thermoelectric materials

The thermoelectric properties of $Ba_8Ga_{16}X_{30}$ (X = Ge, Sn) have been the focus of several works [1–3]. These compounds consist of face-shared polyhedral cages, formed by Ge, Sn and Ga, with an enclosed ion (Ba in this case) in each cage that scatters phonons effectively by *rattling*-like vibration. The band structure calculation for $Ba_8Ga_{16}Sn_{30}$ shows a semiconductor gap of 160 meV [4]. This value was used to fit experimental thermoelectric power data, especially at low temperature. Therefore, the existence of a pseudo-gap like feature, where the density of states is suppressed to some extent, is suggested. However, there exists no direct observation of the pseudo-gap structure in this compound. Concerning this matter, tunneling technique provides the most direct probe to investigate the energy gap [5].

In this paper, we present tunneling measurements of $Ba_8Ga_{16}Sn_{30}$ single crystals to see the pseudo-gap in a straightforward way. We have used cryogenic in situ break junction to avoid surface contamination. Tunneling conductance, dI/dV, was measured by an AC-modulation technique with a four probe method [6]. A standard AC technique was used to measure the conductance.

The $Ba_8Ga_{16}X_{30}$ (X = Ge, Sn) single crystals were grown by self-flux method. They present stoichiometry very close to 8:16:30. The $Ba_8Ga_{16}Sn_{30}$ samples used in this work are from the same batch described in previous works [2,3] which possess n-type carriers. The $Ba_8Ga_{16}Ge_{30}$ samples are also n-type and described elsewhere [7].

Before discussing the tunneling data, we show in Fig. 1 the temperature dependence of the resistivity $\rho(T)$ for the sample used in the tunneling measurements. In both samples $\rho(T)$ decreases monotonically with cooling and shows nearly metallic conductivity in the range of a few mΩ cm, indicating that these compounds are heavily doped semiconductors [3].

We show in Fig. 2 a representative tunneling conductance at 4.2 K for a $Ba_8Ga_{16}Sn_{30}$ sample. Although the spectrum shows asymmetry in each bias, a moderate hump structure can be found near 150–200 mV. This asymmetric property may have close relation to an asymmetric junction structure. As shown in the thermoelectric power data [3], this kind of clathrate compound is very sensitive to differences in effective composition. When the tunneling junction is formed by the break junction technique, it can be expected that locally different carrier densities between electrodes cause an asymmetric junction formation. Such a junction could play a similar role of a rectification like pn-diode. The magnitude of peak-to-peak separation (V_{p-p}) in these dI/dV curves is approximately $V_{p-p} = 300-400$ mV, which should correspond to $4\Delta/e$, where 2Δ is the pseudo-gap value.

*Corresponding author. Tel.: +81 824 24 6552; fax: +81 824 24 0757.
E-mail address: ribeiro@hiroshima-u.ac.jp (R.A. Ribeiro).

0921-4526/$ - see front matter © 2006 Published by Elsevier B.V.
doi:10.1016/j.physb.2006.03.075

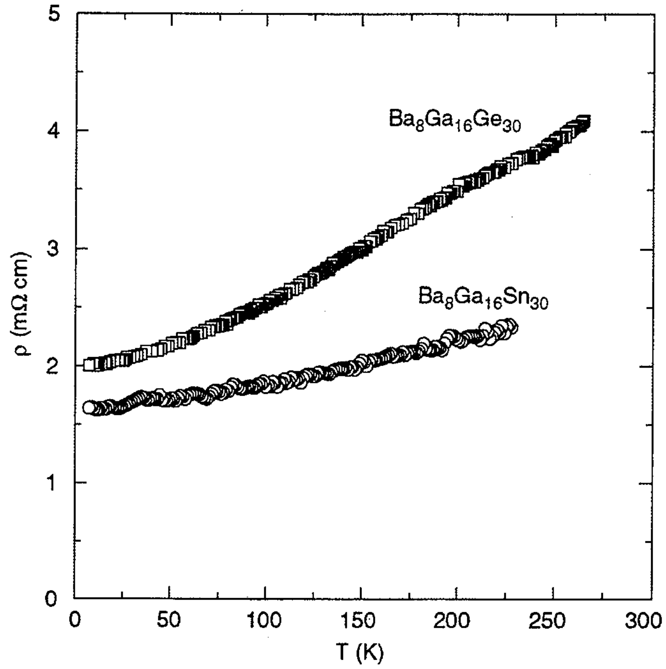

Fig. 1. Electrical resistivity of $Ba_8Ga_{16}X_{30}$ (X = Ge, Sn) single crystals.

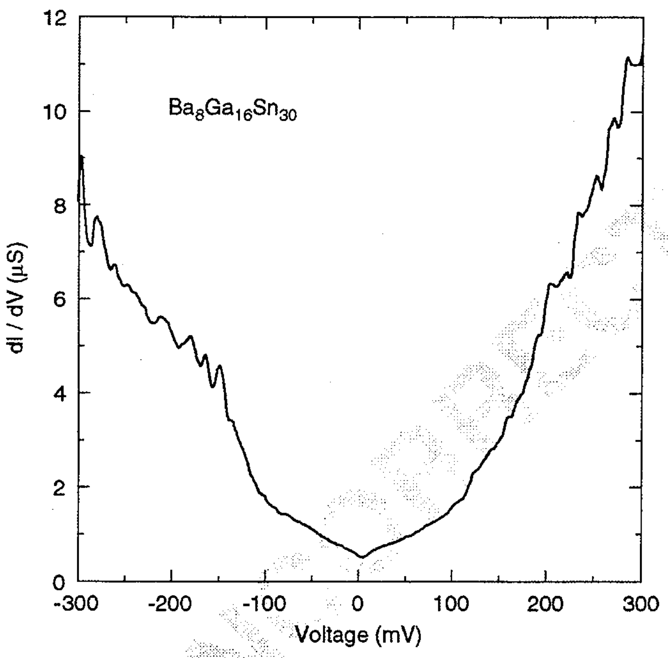

Fig. 2. Tunnel differential conductance dI/dV at 4.2 K for $Ba_8Ga_{16}Sn_{30}$ in high bias.

Fig. 3 shows the tunneling conductance at 4.2 K in $Ba_8Ga_{16}Sn_{30}$ samples with the gap like feature at a lower bias region. The dI/dV on the bottom of the Fig. 3 has the broad conductance overshoots. This is associated with weakly accumulated spectral weight at the gap edge due to pseudo-gap phenomena. We have often observed this kind of behavior around the zero bias. The curve on the top of Fig. 3 is the normalized conductance of the bottom dI/dV after dividing by the background conductance (dotted curve), estimated by fitting a 4th degree polynomial function to the higher bias conductance. This type of background feature always appears in such measurements. The gap peaks are clearly visible at $\approx$30–40 meV after eliminating the effect of the background conductance. If we consider an SIS junction, the gap value is $2\Delta \approx 30$–40 meV.

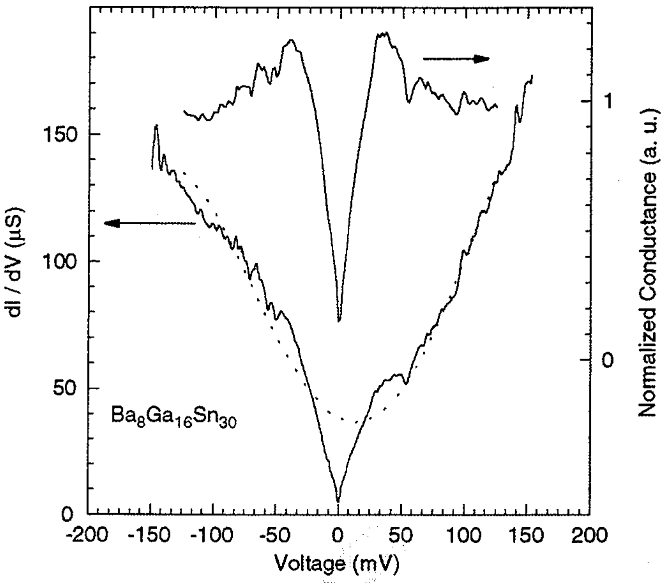

Fig. 3. Typical dI/dV at 4.2 K for $Ba_8Ga_{16}Sn_{30}$ at lower bias.

In summary, we have carried out break-junction tunneling measurements on $Ba_8Ga_{16}Sn_{30}$ single crystals, where we detected a pseudo-gap of $2\Delta \approx 150$–200 meV. This value agrees with the value estimated using the thermoelectric power data [4]. We also demonstrate very reproducible gap with $2\Delta \approx 30$–40 meV. Further study is needed to clarify the gap-closing temperature in these materials.

We thank T. Takasaki for fruitful discussions. This work was supported in part by Japan Society for the Promotion of Science (JSPS- Grant ID No. P03658) and by a Grant-in-aid for COE research (No. 13CE2002) and for Scientific research (No. 15540346) of the Ministry of Education, Culture, Sports and Technology of Japan.

References

[1] G.S. Nolas, J.L. Cohn, J.S. Dyck, C. Uher, G.A. Jamberton, T.M. Tritt, J. Mater. Res. 19 (2004) 3556.
[2] D. Huo, T. Sakata, M.A. Avila, M. Tsubota, F. Iga, H. Fukuoka, S. Yamanaka, S. Aoyagi, T. Takabatake, Phys. Rev. B 71 (2005) 075113.
[3] M.A. Avila, D. Huo, T. Sakata, K. Suekuni, Takabatake, cond-mat/0505095.
[4] K. Koga, T. Kamai, K. Oshiro, M. Matsuura, pre-print.
[5] E.L. Wolf, Principles of Electron Tunneling Spectroscopy, Oxford, New York, 1985.
[6] T. Ekino, T. Takabatake, H. Tanaka, H. Fujii, Phys. Rev. Lett. 75 (1995) 4262.
[7] M.A. Avila, et al., in these proceedings.