

# Improvement in the thermoelectric properties of pressure-tuned $\beta$ -K<sub>2</sub>Bi<sub>8</sub>Se<sub>13</sub>

J. F. Meng<sup>a)</sup> and N. V. Chandra Shekar<sup>a)</sup>

*Department of Chemistry, Pennsylvania State University, University Park, Pennsylvania 16802*

D.-Y. Chung and M. Kanatzidis

*Department of Chemistry and Center for Fundamental Materials Research, Michigan State University, East Lansing, Michigan 48824*

J. V. Badding<sup>b)</sup>

*Department of Chemistry, Pennsylvania State University, University Park, Pennsylvania 16802*

(Received 31 January 2003; accepted 18 June 2003)

The thermoelectric power, electrical conductivity, crystal structure, and Raman active phonon modes of the semiconductor  $\beta$ -K<sub>2</sub>Bi<sub>8</sub>Se<sub>13</sub> have been studied under pressure. There is a large increase in the electrical conductivity in the pressure range 0–1 GPa and a sharp maximum in the magnitude of the thermoelectric power at  $\sim 1.4$  GPa. X-ray diffraction studies revealed no structural change upon compression. The Raman active vibrational modes did not shift substantially with pressure, suggesting that the pressure induced changes in the phonon thermal conductivity may not be large. The thermoelectric figure of merit,  $ZT$ , likely increases by a factor of at least 2 from its ambient pressure value of 0.23. This is the first  $n$ -doped material for which we have observed a peak in the thermoelectric power suggestive of an electronic topological transition upon compression. © 2003 American Institute of Physics. [DOI: 10.1063/1.1599049]

## INTRODUCTION

Several approaches have been adopted in the search for improved thermoelectric materials, ranging from the synthesis of bulk materials<sup>1,2</sup> and quantum-well structures<sup>3</sup> that may exhibit improved thermoelectric figure of merit,  $ZT$  ( $T$  is the temperature and  $Z=S^2\sigma/\kappa$ ,  $S$  is the thermoelectric power,  $\sigma$  is the electrical conductivity, and  $\kappa$  is the thermal conductivity), to combinatorial synthesis techniques that rapidly screen materials for desirable thermoelectric properties.<sup>4</sup> Pressure tuning may offer a means to guide the search for higher  $ZT$  thermoelectric materials.<sup>5,6</sup> Observation of improved properties under pressure can provide targets for synthesis at ambient pressure and a valuable “proof of principle” finding. Pressure can be changed more rapidly than new materials can generally be synthesized, allowing the phase space of interaction parameters that determine materials properties such as thermoelectric power to be explored more rapidly.<sup>5</sup> Thus far we have observed substantial increases in the thermoelectric power and thus  $ZT$  upon pressure tuning semiconductors such as Nd<sub>x</sub>Ce<sub>3-x</sub>Pt<sub>3</sub>Sb<sub>4</sub>,<sup>6</sup> Sb<sub>1.5</sub>Bi<sub>0.5</sub>Te<sub>3</sub>,<sup>7</sup> BaBiTe<sub>3</sub>,<sup>8</sup> and Sr<sub>8</sub>Ga<sub>16</sub>Ge<sub>30</sub>.<sup>9</sup> Pressure tuned Sb<sub>1.5</sub>Bi<sub>0.5</sub>Te<sub>3</sub>, in particular, is observed to exhibit  $ZT$  in excess of 2, substantially higher than that observed for any bulk thermoelectric material at ambient pressure.

Chung *et al.* have reported synthesis of  $\beta$ -K<sub>2</sub>Bi<sub>8</sub>Se<sub>13</sub> which has a complex monoclinic structure (Fig. 1).<sup>10</sup> It is attractive as a thermoelectric material because of its low

thermal conductivity (1.28 W/mK) and high thermoelectric power ( $-200 \mu\text{V/K}$ ). When doped appropriately, its electrical conductivity at ambient pressure can be as high as 250 S/cm, resulting in a  $ZT$  of 0.23. Here we report a substantial increase in the thermoelectric power of pressure tuned  $n$ -type K<sub>2</sub>Bi<sub>8</sub>Se<sub>13</sub>. This is the first  $n$ -type material we have found to exhibit a large increase in thermoelectric power upon pressure tuning under nonhydrostatic conditions at pressures as low as 2 GPa. We also have investigated the effect of pressure on the electrical conductivity, low frequency Raman modes, and crystal structure of K<sub>2</sub>Bi<sub>8</sub>Se<sub>13</sub>.

## EXPERIMENT

The experimental technique for the measurement of the thermoelectric power under pressure and an error analysis of this technique have been reported previously.<sup>11</sup> Briefly, samples are compressed in a Mao–Bell diamond anvil cell at pressures between ambient and 10 GPa. A culet size of about 1 mm and gasket hole of the same size are used. Typical rectangular sample dimensions are  $700 \mu\text{m} \times 50 \mu\text{m} \times 50 \mu\text{m}$ . Monoclinic ZrO<sub>2</sub> is used as the pressure transmitting medium. Type  $K$  thermocouple junctions with  $12.5 \mu\text{m}$  leads are deeply embedded into the sample for the thermoelectric power measurements. A temperature gradient is induced by means of an infrared laser focused to a narrow line. During the thermoelectric power measurements, four lead-two probe resistance measurements are also performed by passing current through two of the thermocouple leads while measuring the voltage between the other two leads. This resistance measurement includes the contact resistances between the sample and the thermocouple leads, allowing an upper bound to be placed this resistance, which was a few

<sup>a)</sup>On leave from Indira Gandhi Center for Atomic Research, Kalpakam 603 102, Tamil Nadu, India.

<sup>b)</sup>Author to whom correspondence should be addressed; electronic mail: jvadding@chem.psu.edu

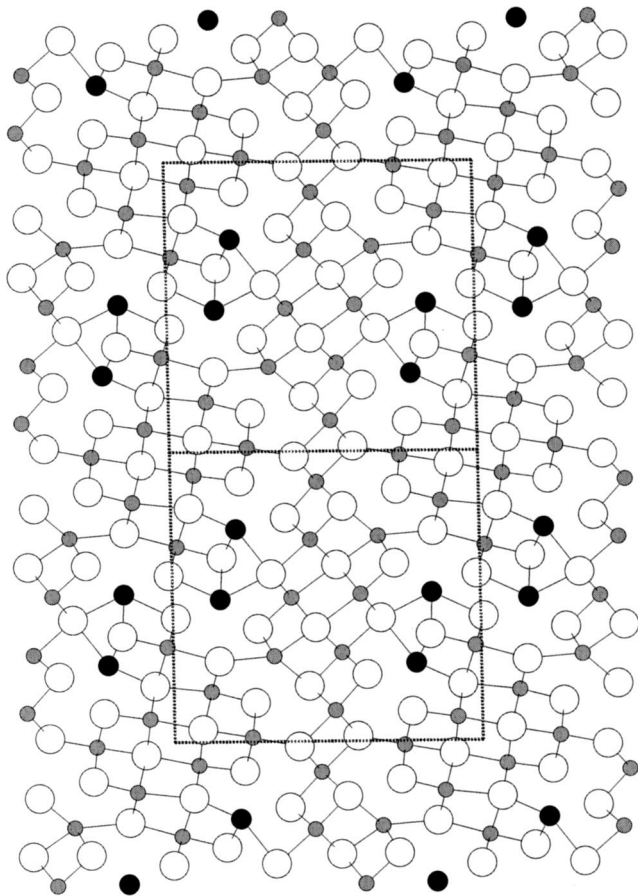


FIG. 1. Crystal structure of  $\beta$ - $\text{K}_2\text{Bi}_8\text{Se}_{13}$ . Small dark atoms are potassium, small lightly shaded atoms are bismuth, and large unfilled atoms are selenium.

tenths of an ohm or less. We assume that if the contact resistance is low, the thermocouples and the sample are in good thermal contact as well. The thermoelectric power as a function of pressure measured by this technique for various standards such as bismuth (Fig. 2), which undergoes several phase transition up to 8 GPa,<sup>12</sup> and several other materials is reproducible and in good agreement with previous reports.<sup>11</sup>

At ambient pressure with both diamonds in contact with the  $\text{ZrO}_2$  media, the thermoelectric power measured for  $\beta$ - $\text{K}_2\text{Bi}_8\text{Se}_{13}$  in the diamond cell is  $-196 \mu\text{V/K}$ , in excellent agreement with the value of  $-200 \mu\text{V/K}$  measured on bulk samples by standard techniques.<sup>10</sup> Similar to the behavior observed for  $\text{Nd}_x\text{Ce}_{3-x}\text{Pt}_3\text{Sb}_4$ ,<sup>6</sup>  $\text{Sb}_{1.5}\text{Bi}_0\text{Te}_3$ , and  $\text{BaBiTe}_3$ ,<sup>8</sup> the thermoelectric power versus pressure curves are virtually identical in the increasing and decreasing pressure directions as long as the pressure is not increased above 2–3 GPa. The reversibility of this measurement indicates that, at least up to these pressures, systematic errors associated with changes in thermocouple configuration, etc., are not significant. In contrast to the behavior observed for  $\text{K}_2\text{Bi}_8\text{Se}_{13}$ , most of the semiconductors we compressed in the diamond anvil cell did not exhibit sharp increases in the thermoelectric power. Separate electrical conductivity measurements are made in the standard configuration with four independent leads and four independent probes. Pressure is measured by ruby fluorescence method.<sup>13</sup> Raman spectra are

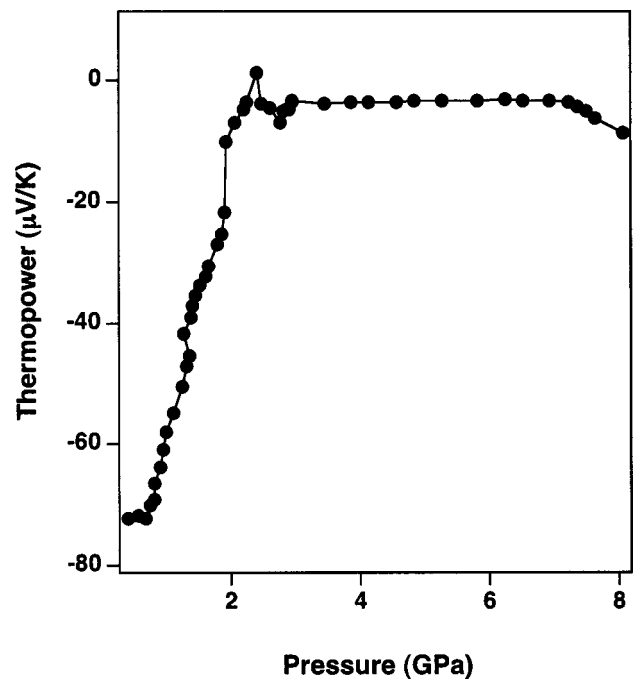


FIG. 2. Thermoelectric power of Bi standard vs pressure. Features in the thermoelectric power at 2.4, 2.7, and 7.2 GPa are associated with phase transitions. The magnitude of the thermoelectric power at ambient pressure and between the phase transitions is in good agreement with a previous report (see Ref. 12). There are slight differences from the reported transition pressures (2.5, 2.7, and 7.7 GPa) and the shape of curve near the transitions which are likely due to differences in nonhydrostatic stress.

collected using a Dilor XY microfocus Raman spectrometer with 514.5 nm excitation.

## RESULTS AND DISCUSSION

Similar to several other small band gap semiconductors that exhibit increases in thermoelectric power upon pressure tuning, the electrical conductivity of  $\text{K}_2\text{Bi}_8\text{Se}_{13}$  increases rapidly as a function of increasing pressure (Fig. 3) at modest pressures. The magnitude of the thermoelectric power increases rapidly with pressure (Fig. 4), exhibiting a maxima at

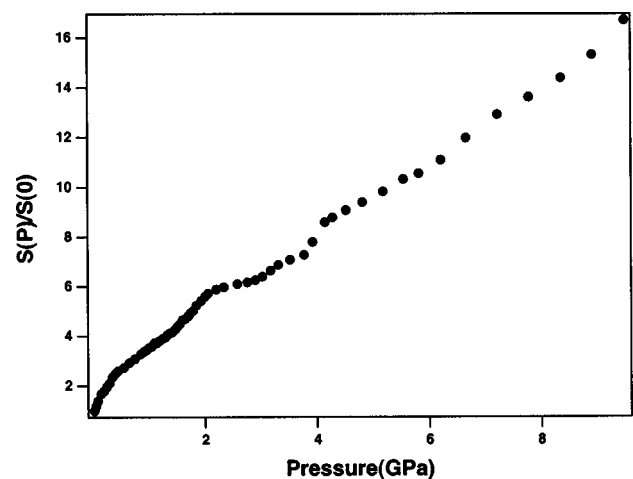


FIG. 3. Electrical conductivity of  $\text{K}_2\text{Bi}_8\text{Se}_{13}$  vs pressure normalized by the ambient pressure conductivity.

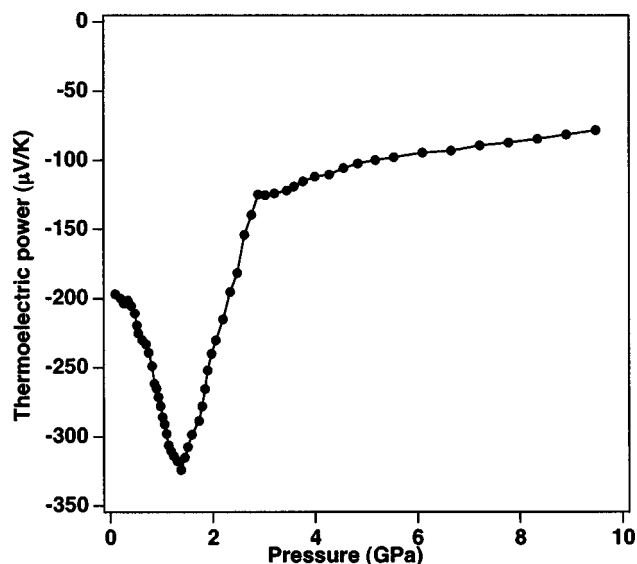


FIG. 4. Thermoelectric power of  $K_2Bi_8Se_{13}$  vs pressure up to 10 GPa.

1.38 GPa, where  $S = -324 \mu V/K$ . At higher pressures the magnitude of the thermoelectric power decreases. Three independent measurements on different samples confirmed the reproducibility of the maximum in the thermoelectric power at 1.38 GPa. The behavior observed for  $K_2Bi_8Se_{13}$  is qualitatively similar to that of  $p$ -type  $Nd_xCe_{3-x}Pt_3Sb_4$ ,<sup>6</sup>  $Sb_{1.5}Bi_{0.5}Te_3$ ,<sup>7</sup> and  $BaBiTe_3$ .<sup>8</sup>

It is important to ascertain whether the large change in the thermoelectric power is associated with a structural transition. High pressure x-ray diffraction studies in a Mao–Bell cell<sup>14</sup> under the same compression conditions used for the thermoelectric power measurements revealed no structural changes in the pressure range of interest.

Pressure and stress can in general introduce significant changes in electronic structure that have a major impact on transport properties.<sup>15–21</sup> Sharp maxima in the thermoelectric power as a function of pressure have been observed for semiconductors undergoing an electronic topological or Lifshitz transition (ETT).<sup>22,23</sup> Similar to the behavior observed for pressure tuned  $Sb_{1.5}Bi_{0.5}Te_3$ ,<sup>7,22</sup> the thermoelectric power versus pressure curve (Fig. 4) for  $K_2Bi_8Se_{13}$  is suggestive of the presence of an ETT. Such transitions occur when the topology of the Fermi surface changes due to a perturbation such as compression or alloying.<sup>24</sup> A band extremum, which is associated with a Van Hove singularity in the density of states, crosses the Fermi energy, resulting in a change in the topology of the Fermi surface and a strong energy dependence to the electronic density of states near the Fermi energy.  $K_2Bi_8Se_{13}$  is the first  $n$ -type semiconductor for which we have observed a maximum in the thermoelectric power suggestive of an ETT. We note that because an ETT can be induced by alloying as well as pressure, it may be possible to reproduce the improved behavior observed at high pressure at ambient pressure.

To determine the thermoelectric figure of merit,  $ZT$ , it is important to have the thermal conductivity and the electrical conductivity in addition to the thermoelectric power. We did not measure the thermal conductivity under pressure, al-

though it is generally possible to place bounds on it.<sup>6,7</sup> Because there were variations in the electrical conductivity of various  $K_2Bi_8Se_{13}$  samples, presumably due to adventitious variations in doping level, and it is technically difficult to measure the electrical conductivity and thermoelectric power simultaneously under pressure in a diamond cell, there are uncertainties in estimating  $ZT$  at high pressure. Both the thermoelectric power and the electrical conductivity vary with the doping level.  $K_2Bi_8Se_{13}$  samples which exhibit a thermoelectric power of  $\sim -200 \mu V/K$ , such as those compressed in the diamond cell, typically have an electrical conductivity near 250 S/cm and a  $ZT$  of 0.23. Because the thermoelectric power is squared in the expression for  $ZT$ , increases in it tend to have a large effect on  $ZT$ . For  $K_2Bi_8Se_{13}$  the ratio squared of the maximum in the thermoelectric power at 1.38 GPa to the thermoelectric power at ambient pressure is  $(-324/-196)^2$  or 2.7.

The electronic contribution to the thermal conductivity ( $\kappa_e$ ) for  $K_2Bi_8Se_{13}$  is only at most 10% of the total thermal conductivity ( $\kappa = \kappa_e + \kappa_p$ ).<sup>10</sup> Thus the phonon contribution ( $\kappa_p$ ) to the thermal conductivity dominates at ambient pressure.  $\kappa_p$  typically increases with pressure, but not likely by more than a factor of 2 for semiconductors at pressures less than 2 GPa.<sup>6,7</sup> If the electrical conductivity of the samples compressed in the diamond cell for thermoelectric power measurements increases by the factor of 4 (at 1.38 GPa) observed for those samples compressed for electrical conductivity measurements, it is likely that the decrease in  $ZT$  due to increases in the thermal conductivity will be at least counterbalanced by the increase due to the electrical conductivity (the electronic contribution to the thermal conductivity will also increase with the increase in the electrical conductivity according to the Wiedemann–Franz law,<sup>25,26</sup> but will still not dominate). Thus although it is difficult to quantitatively estimate  $ZT$  at high pressure, it appears that it will increase by a factor of 2 or more due to the increase in the thermoelectric power, but may not approach values in excess of 1 observed for materials such as pressure tuned  $Nd_xCe_{3-x}Pt_3Sb_4$ ,<sup>6</sup> and  $Sb_{1.5}Bi_{0.5}Te_3$ .<sup>7</sup>

Finally, we note that there is a slight softening of one of the Raman modes of  $K_2Bi_8Se_{13}$  under pressure (Fig. 5). One mode at  $221 \text{ cm}^{-1}$  at 0.68 GPa, softens by  $11 \text{ cm}^{-1}$  at 2.1 GPa. Near an electronic topological transition phonon modes often soften.<sup>27</sup> The crystal structure of  $K_2Bi_8Se_{13}$  does not change up to 2.1 GPa, so the shift in intensities and peak positions upon compression is not due to altered crystal symmetry. The change in the Raman spectrum observed between 0.08 and 0.68 GPa is reversible. None of the mode positions changes very much up to 2.1 GPa, suggesting that the changes in phonon frequencies and phonon thermal conductivity in this pressure range may not be very large.

## SUMMARY

In summary,  $\beta$ - $K_2Bi_8Se_{13}$  is an  $n$ -type thermoelectric material for which we have found a substantial maximum in the magnitude of the thermoelectric power upon compression. The peak in the thermoelectric power is suggestive of an electronic topological transition.  $ZT$  likely increases by a

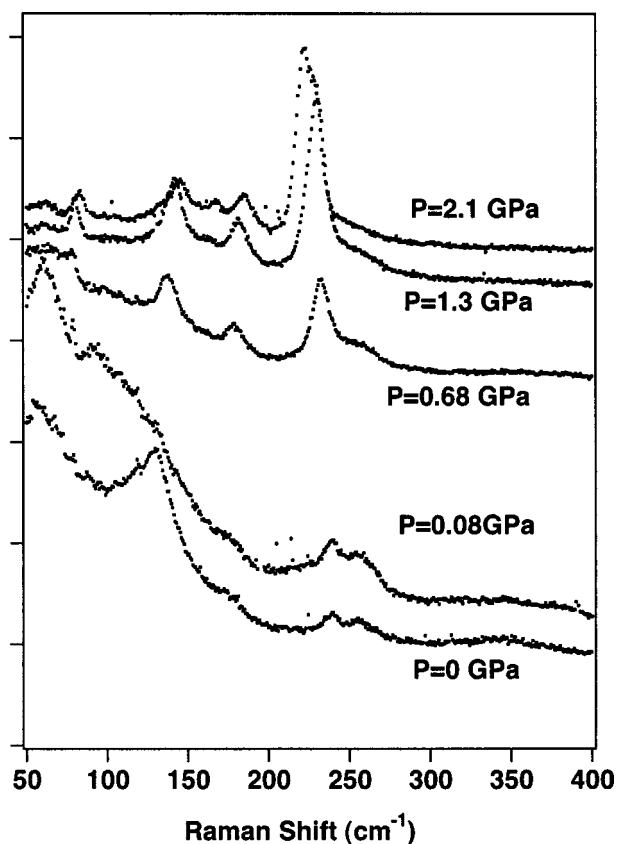


FIG. 5. Raman spectra of  $K_2Bi_8Se_{13}$  at 0, 0.08, 0.68, 1.3, and 2.1 GPa.

factor of at least 2 from its ambient pressure value of 0.24. These results suggest that there is further potential for optimizing the ambient pressure thermoelectric properties of  $\beta$ - $K_2Bi_8Se_{13}$ .

<sup>1</sup>B. C. Sales, D. Mandrus, and R. K. Williams, *Science* **272**, 1325 (1996).

<sup>2</sup>D. Y. Chung, T. Hogan, P. Brazis, M. Rocci-Lane, C. Kannerwulf, M.

- Bastea, C. Uher, and M. G. Kanatzidis, *Science* **287**, 1024 (2000).
- <sup>3</sup>L. D. Hicks and M. S. Dresselhaus, *Phys. Rev. B* **47**, 12727 (1993).
- <sup>4</sup>X. D. Xiang, X. D. Sun, G. Briceno, Y. L. Lou, K. A. Wang, H. Y. Chang, W. G. Wallacefreedman, S. W. Chen, and P. G. Schultz, *Science* **268**, 1738 (1995).
- <sup>5</sup>J. V. Badding, J. F. Meng, and D. A. Polvani, *Chem. Mater.* **10**, 2889 (1998).
- <sup>6</sup>J. F. Meng, D. A. Polvani, C. D. W. Jones, F. J. DiSalvo, Y. Fei, and J. V. Badding, *Chem. Mater.* **12**, 197 (2000).
- <sup>7</sup>D. A. Polvani, J. F. Meng, N. V. C. Shekar, J. Sharp, and J. V. Badding, *Chem. Mater.* **13**, 2068 (2001).
- <sup>8</sup>J. F. Meng, N. V. C. Shekar, J. V. Badding, D. Y. Chung, and M. G. Kanatzidis, *J. Appl. Phys.* **90**, 2836 (2001).
- <sup>9</sup>J. F. Meng, N. V. C. Shekar, J. V. Badding, and G. S. Nolas, *J. Appl. Phys.* **89**, 1730 (2001).
- <sup>10</sup>D. Y. Chung *et al.*, *Chem. Mater.* **9**, 3060 (1997).
- <sup>11</sup>D. A. Polvani, J. F. Meng, M. Hasegawa, and J. V. Badding, *Rev. Sci. Instrum.* **70**, 3586 (1999).
- <sup>12</sup>B. T. Ferdin, N. V. Jaya, K. Anbukumar, and S. Natarajan, *Rev. Sci. Instrum.* **66**, 5636 (1995).
- <sup>13</sup>G. J. Piermarini, S. Block, J. Barnett, and R. A. Foreman, *J. Appl. Phys.* **46**, 2774 (1975).
- <sup>14</sup>T. Atou and J. V. Badding, *Rev. Sci. Instrum.* **66**, 4496 (1995).
- <sup>15</sup>N. B. Brandt, M. Yu Lavrenyuk, N. Ya Minina, and A. M. Savin, *Zh. Eksp. Teor. Fiz.* **94**, 235 (1988).
- <sup>16</sup>N. B. Brandt, M. Yu Lavrenyuk, N. Ya Minina, A. M. Savin, W. Kraak, and R. Herrmann, *Phys. Status Solidi B* **143**, 601 (1987).
- <sup>17</sup>X. F. Chen, G. X. Tessema, and M. J. Skove, *Phys. Rev. B* **48**, 13141 (1993).
- <sup>18</sup>T. A. Davis, W. Schaffer, M. J. Skove, and E. P. Stillwell, *Phys. Rev. B* **39**, 10094 (1989).
- <sup>19</sup>T. M. Tritt, E. P. Stillwell, and M. J. Skove, *Phys. Rev. B* **34**, 6799 (1986).
- <sup>20</sup>Y. T. Tseng, G. X. Tessema, and M. J. Skove, *Solid State Commun.* **82**, 841 (1992).
- <sup>21</sup>Y. T. Tseng, G. X. Tessema, and M. J. Skove, *Solid State Commun.* **94**, 867 (1995).
- <sup>22</sup>E. S. Itskevich, L. M. Kashirskay, and V. F. Kraidenov, *Semiconductors* **31**, 276 (1996).
- <sup>23</sup>I. M. Lifshitz, *Sov. Phys. JETP* **11**, 1130 (1960).
- <sup>24</sup>Ya. M. Blanter, M. I. Kaganov, A. V. Pantsulaya, and A. A. Varlamov, *Phys. Rep.* **245**, 159 (1994).
- <sup>25</sup>H. J. Goldsmid, *Electronic Refrigeration*. (Pion Ltd., London, 1986).
- <sup>26</sup>N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Holt, Rinehart, and Winston, 1976).
- <sup>27</sup>L. Dagens, *J. Phys. F: Met. Phys.* **8**, 2093 (1978).