

# Pressure Tuning in the Chemical Search for Improved Thermoelectric Materials: $\text{Nd}_x\text{Ce}_{3-x}\text{Pt}_3\text{Sb}_4$

J. F. Meng,<sup>†</sup> D. A. Polvani,<sup>†</sup> C. D. W. Jones,<sup>‡</sup> F. J. DiSalvo,<sup>‡</sup> Y. Fei,<sup>§</sup> and J. V. Badding<sup>\*,†</sup>

*Department of Chemistry, Pennsylvania State University, University Park, Pennsylvania 16802; Department of Chemistry, Cornell University, Ithaca, New York, 14853; and Geophysical Laboratory, Carnegie Institution of Washington, 5251 Broad Branch Rd. NW, Washington D.C. 20015*

*Received August 18, 1999. Revised Manuscript Received October 14, 1999*

The interaction parameters that determine materials properties are generally sensitive to pressure. Thus, pressure tuning provides a means to rapidly explore a material's interaction parameter phase space to increase the rate of discovery of materials with improved properties. Here we report a significant improvement in the thermoelectric properties of the Kondo insulator  $\text{Nd}_x\text{Ce}_{3-x}\text{Pt}_3\text{Sb}_4$  upon pressure tuning to 2 GPa. This result provides a target for synthetic attempts at ambient pressure to duplicate the observed improved high-pressure behavior.

## Introduction

Pressure tuning offers a means to rapidly explore the phase space composed of the interaction parameters (e.g., orbital overlap, orbital energy, magnetic coupling, etc.) that determine materials properties, potentially increasing the rate of discovery of improved materials.<sup>1,2</sup> Most of the interaction parameters that determine materials properties can be rapidly and precisely tuned over a wide range of pressure (additional degrees of freedom are afforded by the possibility of applying stress in a particular direction, potentially altering crystal symmetry). As a result the thermoelectric properties of almost all classes of thermoelectric materials are sensitive to pressure. The band structures of semiconductors, the most important class of thermoelectric materials, can be tuned considerably with pressure. Although the pressure-tuning technique has been applied to understanding the physical properties of semiconductors for over 40 years,<sup>3</sup> little has yet been done to apply this technique to the search for new, improved semiconducting materials, such as thermoelectric materials.

Thermoelectric materials are characterized by a dimensionless figure of merit,  $ZT$ , which determines the fraction of Carnot efficiency attainable in a solid-state thermoelectric cooling device.<sup>4</sup> The expression for  $ZT$  is

$$ZT = \frac{S^2 \sigma}{\kappa} T \quad (1)$$

Here  $S$  is the thermoelectric power ( $\mu\text{V}/\text{K}$ ),  $\sigma$  is the

electrical conductivity (S/cm), and  $\kappa$  is the thermal conductivity (W/cm-K). In the search for high  $ZT$  materials, chemical tuning is often slower than pressure tuning because pressure can be varied much more rapidly than new compounds can be synthesized, at least by traditional methods. Thus, there is reason to believe that higher  $ZT$  may be achieved more rapidly by pressure-tuning methods. Demonstration of  $ZT > 1$  alone, even if only under pressure, would be a significant achievement that would further invigorate the search for improved thermoelectric materials. However, in some materials the effects of pressure tuning can be mimicked chemically, which could allow high  $ZT$  values to be reproduced at ambient pressure after identification at high pressure. In addition, significant stresses in particular crystallographic directions can be achieved by various thin film deposition techniques. A combination of chemical tuning and stress/pressure-tuning techniques is likely to be most effective in finding high  $ZT$  materials.

The first step in assessing the value of the pressure-tuning approach is to demonstrate a significant enhancement of an important property under pressure. Here we show that the thermoelectric compound  $\text{Nd}_x\text{Ce}_{3-x}\text{Pt}_3\text{Sb}_4$  ( $x = 0.45$ ), which is a Nd-doped Kondo insulator,<sup>5</sup> can be pressure-tuned to  $ZT$  values that could be as much as 10 times its value at ambient pressure ( $ZT = 0.12$ ). These values may exceed the maximum  $ZT$  known at ambient pressure and temperature ( $ZT \approx 1$  for suitably doped antimony bismuth telluride), demonstrating that significant enhancements in thermoelectric properties may be obtained by pres-

\* To whom correspondence should be addressed. E-mail: jvadding@chem.psu.edu.

<sup>†</sup> Pennsylvania State University.

<sup>‡</sup> Cornell University.

<sup>§</sup> Carnegie Institution of Washington.

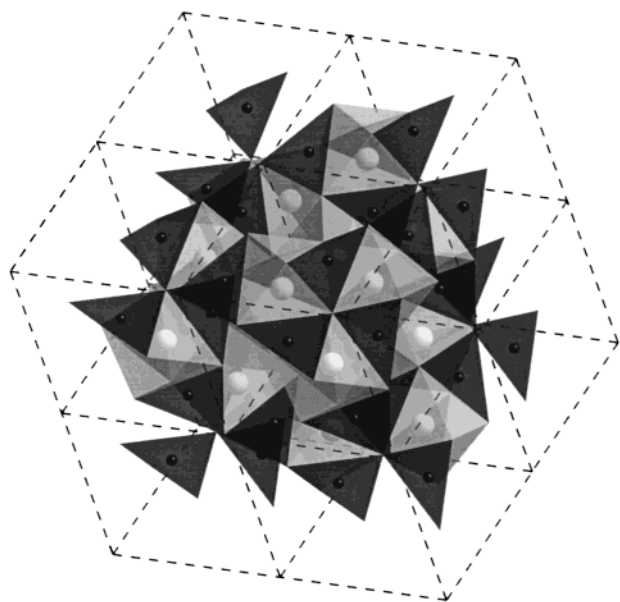
(1) Badding, J. V.; Meng, J. F.; Polvani, D. A. *Chem. Mater.* **1998**, *10*, 2889.

(2) Badding, J. V.; Parker, L. J.; Nesting, D. C. *J. Solid State Chem.* **1995**, *117*, 229.

(3) Paul, W.; Burnett, J. H.; Cheong, H. M. In *High-Pressure Science and Technology-1993*; Schmidt, S. C., Shaner, J. W., Samara, G., Ross, M., Eds.; American Institute of Physics, New York, 1994; p 545.

(4) Barnard, R. D. *Thermoelectricity in metals and alloys*; Taylor & Francis: London, 1972.

(5) Jones, C. D. W.; Regan, K. A.; DiSalvo, F. J. *Phys. Rev. B* **1998**, *58*, 16057.



**Figure 1.** Crystal structure of  $\text{Nd}_x\text{Ce}_{3-x}\text{Pt}_3\text{Sb}_4$ . Nd/Ce atoms are the large spheres, surrounded by distorted dodecahedra of Sb atoms. Pt atoms are represented by the smaller spheres and are surrounded by distorted tetrahedra of Sb atoms.

sure tuning. Furthermore, these results suggest that there is potential to further optimize  $\text{Nd}_x\text{Ce}_{3-x}\text{Pt}_3\text{Sb}_4$  ( $x = 0.27, 0.45$ ) by chemical means.

$\text{Nd}_x\text{Ce}_{3-x}\text{Pt}_3\text{Sb}_4$  has a cubic crystal structure (Figure 1) identical to that of the undoped Kondo insulator  $\text{CePt}_3\text{Sb}_4$ .<sup>6</sup> It was chosen for these initial pressure-tuning studies because it has shown promise as a thermoelectric material at ambient pressure, because the high symmetry of its crystal structure simplifies the analysis of its thermoelectric properties, and because it is a ternary compound with a complex crystal structure that might offer significant opportunities for chemical tuning. The stress conditions inside the diamond anvil cells used for some of the measurements reported here often include a substantial uniaxial (directional) component, which can affect the physical properties of a material. For polycrystalline, cubic materials such as  $\text{Nd}_x\text{Ce}_{3-x}\text{Pt}_3\text{Sb}_4$ , it is not necessary to orient samples with respect to this uniaxial stress field or with respect to the thermocouples used for the thermoelectric power measurements. This reduces the experimental challenges involved in thoroughly characterizing the thermoelectric properties (although it is possible to align lower symmetry crystals with respect to stress fields and thermocouples).

### Experimental Section

The  $\text{Nd}_x\text{Ce}_{3-x}\text{Pt}_3\text{Sb}_4$  samples were synthesized by arc melting the elements in a Centorr arc furnace.<sup>5</sup> The temperature dependence of the thermoelectric properties has been previously reported.

Measurement of the thermoelectric power under pressure,<sup>7,8,9</sup> which is necessary to evaluate ZT, is not routine. New techniques were developed to perform thermoelectric power

measurements in high-pressure diamond anvil cells and a large volume octahedral high-pressure apparatus. Details of the experimental approach have been published separately.<sup>10</sup> Briefly, for the diamond anvil cell experiments, samples were cut to dimensions of  $\sim 50 \mu\text{m} \times 50 \mu\text{m}$  in cross section by  $800 \mu\text{m}$  long with a small electrical discharge machine. Samples were loaded into a Mao-Bell diamond anvil apparatus with  $1000\text{-}\mu\text{m}$ -diameter culets.<sup>11</sup> Thermocouple junctions fabricated from  $12.5\text{-}\mu\text{m}$ -diameter chromel–alumel wires were pressed into the samples. The sample media was primarily monoclinic  $\text{ZrO}_2$  with a small amount of CsI surrounding the sample.

After assembly of the diamond cell, a focused Nd:YLF laser beam was used to induce a temperature gradient for the thermoelectric power measurements. A pair of Hewlett-Packard nanovoltmeters interfaced to a Macintosh computer was used to measure the thermoelectric power. For most of the experiments, the laser beam was defocused to a circular spot  $\sim 50 \mu\text{m}$  in diameter. In later experiments, a line focus obtained from a cylindrical lens was used that made alignment of the beam perpendicular to the long axis of the sample less critical. The line focus also reduces the possibility of temperature gradients perpendicular to the long axis of the sample, which could reduce the accuracy of the thermoelectric power measurements. However, both approaches gave accurate results on control samples.

At atmospheric pressure, correct values were obtained for the thermoelectric power of many different samples. At high pressure, controls were consistent with published data for  $\text{CePd}_3$ , Bi, and Ni. Little or no hysteresis was observed for the control samples in the increasing and decreasing pressure directions. Furthermore, the thermoelectric power returned to the correct ambient pressure value after compression, indicating that errors associated with changes in sample dimensions, changes in thermal contact between thermocouples and sample, or motion of the thermocouples under pressure were minimal. On the basis of the precision of the data and experience with standards, we estimate the accuracy of the thermoelectric power measurements to be better than  $\pm 6\%$ . Electrical conductivity measurements in the diamond anvil cell were made by standard four probe dc methods.

The measurements in the octahedral multianvil apparatus<sup>12</sup> were performed on samples  $\sim 1 \text{ mm} \times 1 \text{ mm}$  in cross section and 6–7 mm long. Chromel–alumel thermocouple junctions, together with a suitable heating wire to induce a temperature gradient, were placed onto the samples and the entire assembly was embedded in epoxy. The sample assembly was then loaded into a 7.5-mm-diameter sample chamber in an octahedron with 18-mm truncation. The sample was compressed while measuring the thermoelectric power. Because epoxy has a low strength compared to the inorganic media used for the diamond anvil cell experiments, the pressure conditions inside the multianvil apparatus were considerably more hydrostatic.

To characterize the crystal structure of  $\text{Nd}_{0.45}\text{Ce}_{2.55}\text{Pt}_3\text{Sb}_4$  under pressure, powder diffraction data were collected inside a diamond anvil cell with a focusing diffraction system previously described.<sup>13</sup>

### Results and Discussion

The thermoelectric power for  $\text{Nd}_{0.45}\text{Ce}_{2.55}\text{Pt}_3\text{Sb}_4$  measured in the octahedral multi anvil apparatus is  $80 \mu\text{V/K}$  near ambient pressure at 298 K, in agreement with previous measurements ( $80 \mu\text{V/K}$ ).<sup>5</sup> Upon compression, it increases, reaching a maximum of  $100 \mu\text{V/K}$  at 2 GPa

(6) Kasaya, M.; Katoh, K.; Takegahara, K. *Solid State Commun.* **1991**, *78*, 797.

(7) Singh, A. K.; Ramani, G. *Rev. Sci. Instrum.* **1978**, *49*, 1324.

(8) Zhou, J. S.; Goodenough, J. B. *Phys. Rev. B* **1996**, *53*, 11976.

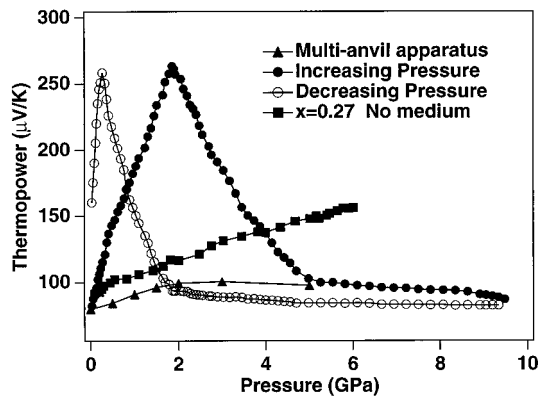
(9) Kraidenov, V. F.; Itskevich, E. S.; Gapotchenko, A. G. *Phys. Solid State* **1995**, *37*, 218.

(10) Polvani, D. A.; Meng, J. F.; Hasegawa, M.; Badding, J. V. *Rev. Sci. Instrum.* **1999**, *70*, 3586. Polvani, D. A.; Fei, Y.; Meng, J. F.; Badding, J. V. submitted to *Rev. Sci. Instrum.*, 1999.

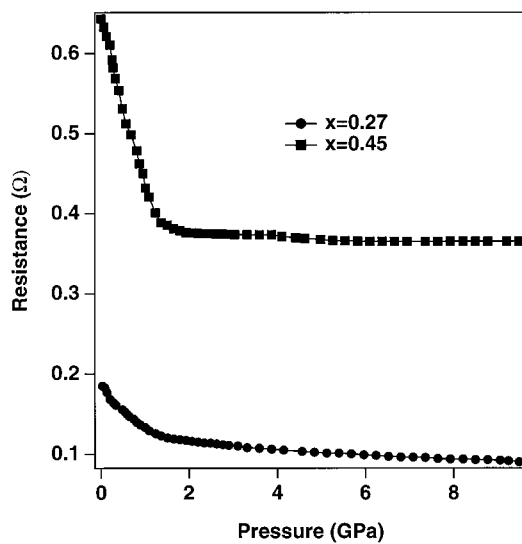
(11) Jephcoat, A. P.; Mao, H. K.; Bell, P. M. In *Hydrothermal Experimental Techniques*; Ulmer, G. C., Barnes, H. L., Eds.; Wiley-Interscience: New York, 1987; p 469.

(12) Bertka, C. M.; Fei, Y. *J. Geophys. Res.* **1997**, *102*, 5251.

(13) Atou, T.; Badding, J. V. *Rev. Sci. Instrum.* **1995**, *66*, 4496.

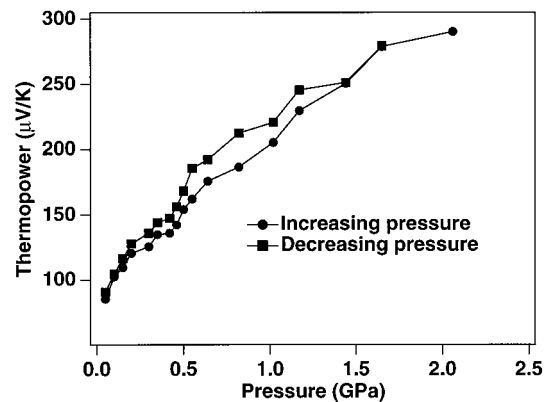


**Figure 2.** Thermoelectric power vs pressure for and  $Nd_xCe_{3-x}Pt_3Sb_4$  under various compression conditions: Multi-anvil apparatus ( $Nd_{0.45}Ce_{2.55}Pt_3Sb_4$ ), diamond anvil cell with  $ZrO_2$  medium between sample/thermocouples and upper diamond ( $Nd_{0.45}Ce_{2.55}Pt_3Sb_4$ ), and no medium between sample/thermocouples and upper diamond ( $Nd_{0.27}Ce_{2.73}Pt_3Sb_4$ ).



**Figure 3.** Resistance vs pressure for  $Nd_{0.45}Ce_{2.55}Pt_3Sb_4$  and  $Nd_{0.27}Ce_{2.73}Pt_3Sb_4$  in a diamond anvil cell.

(Figure 2). This modest increase in the thermoelectric power is likely to lead to a modest increase in ZT. Changes in the thermoelectric power will have the largest effect on ZT because it is squared in eq 1. The electrical conductivity of  $Nd_{0.45}Ce_{2.55}Pt_3Sb_4$  increases by a factor of 1.5–2 times upon compression inside a diamond anvil cell (Figure 3). This may be due to a decrease in the band gap of this material with increasing pressure. It is possible to measure thermal conductivity under pressure, but we have not yet done so, primarily because of several technical challenges. For most materials the thermal conductivity increases with pressure because the frequencies of lattice vibrations generally increase with pressure. Although there are few measurements of thermal conductivity under pressure, materials such as Cs halides increase their thermal conductivity by a factor of  $\sim 1.5$ –2 at pressures up to 2 GPa.<sup>14</sup> If we take this increase as a rough guideline, the increase in the thermal conductivity will be canceled by the increase in the electrical conductivity in the expression for ZT. Because of the increase in the



**Figure 4.** Thermoelectric power vs pressure for  $Nd_{0.45}Ce_{2.55}Pt_3Sb_4$  in a diamond anvil cell. No hysteresis is observed if the pressure is not increased above 2–3 GPa.

thermoelectric power under quasi-hydrostatic compression, ZT will increase by a factor of  $(100/80)^2$  or 1.6 ( $2T = 0.19$ ) a significant increase. However, even this ZT still remains significantly below that of the best thermoelectric materials.

Much more substantial increases in thermoelectric power can be observed under the nonhydrostatic compression conditions inside the diamond anvil cell (Figure 2). The thermoelectric power increases from a value of  $82 \mu V/K$  measured at ambient pressure to a maximum of  $263 \mu V/K$  at 1.9 GPa. The thermoelectric power then decreases upon further increase in pressure. If we again assume that the increases in the thermal and electrical conductivities cancel, ZT is increased by a factor of  $(263/82)^2$  or 10.3. ZT then becomes  $0.12 \times 10.3 = 1.2$ . This value exceeds ZT of doped  $Bi_2Te_3$  at ambient pressure. Even if the increases in the thermal conductivity are larger than we have assumed, the increase in ZT is still substantial. This demonstrates that it is possible to improve the thermoelectric properties of a material by pressure tuning through phase space.

Upon decreasing the pressure in the diamond anvil cell, there was considerable hysteresis observed (Figure 2). The hysteresis is likely due to irreversible changes in crystallinity, defect concentration, etc. induced by compression to a pressure as high as 9.5 GPa. If the pressure is increased only to where the thermoelectric power is at a maximum, no significant hysteresis is observed (Figure 4).

It is important to consider potential sources of error in the thermoelectric power measurements. Because the thermoelectric power returns to the correct, ambient pressure value after the release of pressure (for pressures up to  $\sim 2$  GPa), it can be concluded that changes in the thermal contact between sample and thermocouples or movement of the thermocouples did not affect the measurements. Changes in the measured temperature gradient due to the proximity of the diamonds, which have a very high thermal conductivity, was considered as a source of error. A layer of  $\sim 50 \mu m$  of monoclinic  $ZrO_2$  separates the sample from the diamond anvils. Mahan has performed calculations that show that even when a diamond is contacting the sample, the relationship between thermoelectric voltage and temperature is not altered.<sup>15</sup> Experimentally, little change

(14) Gerlich, D.; Andersson, P. *J Phys. C* **1982**, *15*, 5211.

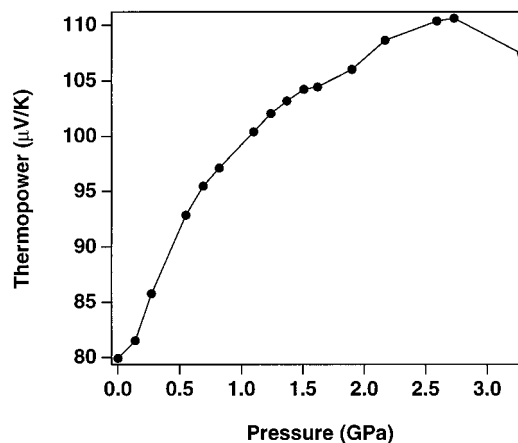
(15) Mahan, G. D. personal communication.

is observed in the measured thermoelectric power at ambient pressure even when the diamond anvil is in direct contact with the sample (Figure 2).<sup>10</sup> As mentioned previously, the large increases in thermoelectric power observed for  $\text{Nd}_x\text{Ce}_{3-x}\text{Pt}_3\text{Sb}_4$  were not seen in several control samples.

Two different mechanisms, for which the relevant phase space parameters are different, could be important to the observed increase in the thermoelectric power under nonhydrostatic compression. In semiconductors, such as  $\text{Ce}_3\text{Pt}_3\text{Sb}_4$ , the details of the band structure determine the thermoelectric power.<sup>16</sup> In particular, a rapid change in the density of states at the Fermi energy gives rise to a large thermoelectric power. This can be achieved by having the Fermi energy near one or more band extrema. The relevant phase space parameters for optimizing the thermoelectric power are then the band energies. It is possible that the pressure tuning of  $\text{Nd}_x\text{Ce}_{3-x}\text{Pt}_3\text{Sb}_4$  shifts the band extrema to a region of phase space that results in a larger thermoelectric power. Another potential contribution to the observed increase in the thermoelectric power could be changes in electronic structure due to the Kondo effect, which is important in intermediate valence metals and Kondo insulators. Here the relevant phase space parameters are the energies of the *f* electrons and the degree of hybridization between the *f* orbitals and other, more delocalized orbitals.<sup>1</sup> The Kondo effect is related to the phenomena of intermediate valence, in which rare earth ions can exhibit an effective valence intermediate between two integral values.<sup>17,18</sup>

Although a full understanding of why there is a difference between the results observed in the octahedral apparatus (hydrostatic compression) and the diamond cell (nonhydrostatic compression) will require additional investigation, we believe that the different pressure conditions in the two types of apparatus are important. Nonhydrostatic compression, even on polycrystalline materials, can induce significant changes in materials properties. For example, the superconducting  $T_c$  of  $\text{La}_{1.9}\text{Sr}_{0.1}\text{Cu}_3\text{O}_4$  can be doubled by application of epitaxial nonhydrostatic stress.<sup>19</sup> It exhibits only a small increase upon application of hydrostatic pressure. The superconducting  $T_c$  of Nb decreases under hydrostatic compression, but increases upon nonhydrostatic compression.<sup>20</sup> Unfortunately, relatively little is yet known about the effects of nonhydrostatic stress on physical properties such as the thermoelectric power or superconducting  $T_c$ , principally because of challenges associated with an accurate characterization of the nonhydrostatic stress conditions. To fully understand the effect of nonhydrostatic stress, it will be necessary to characterize the stress and temperature gradients inside the diamond anvil cell.

The magnitude of the observed increase in the thermoelectric power of  $\text{Nd}_x\text{Ce}_{3-x}\text{Pt}_3\text{Sb}_4$  varied. A large



**Figure 5.** Thermoelectric power vs pressure for  $\text{Nd}_{0.45}\text{Ce}_{2.55}\text{Pt}_3\text{Sb}_4$  in a diamond anvil cell. Although a large increase in the thermoelectric power to similar values was observed many times in the diamond anvil cell (Figure 4), sometimes more modest increases were observed.

increase to  $\sim 250\text{--}300 \mu\text{V/K}$  was observed many times for both  $x = 0.27$  and  $x = 0.45$ , with both line and heating spot foci. At other times, the increases in the thermoelectric power were more modest (Figure 5), similar to that observed under hydrostatic compression conditions. We attribute this behavior to differences in the degree of nonhydrostatic compression from sample to sample. Because the sample assembly contains both a relatively soft media, CsI, and a stronger media, monoclinic  $\text{ZrO}_2$ , it would not be surprising to find large differences in stress conditions from sample run to sample run, depending on the relative proportions of the two media and how they flow during compression.

Further evidence for the importance of nonhydrostatic stress comes from experiments in which there was no medium between the upper diamond anvil and the sample. Under these conditions, the amount of nonhydrostatic stress that can be supported is considerably greater. A smaller, but still substantial, increase in the thermoelectric power of a  $\text{Nd}_{0.27}\text{Ce}_{2.73}\text{Pt}_3\text{Sb}_4$  sample (which also exhibited increases in thermoelectric power up to  $300 \mu\text{V/K}$  under similar pressure conditions to that of the  $\text{Nd}_{0.45}\text{Ce}_{2.55}\text{Pt}_3\text{Sb}_4$  sample) is observed (Figure 2). Although for clarity it is not shown in Figure 2, upon release of pressure no hysteresis was observed and the thermoelectric power returned to the same ambient pressure value. This again rules out several errors associated with movement of the thermocouples etc.

Figure 6 shows the changes in lattice parameter upon compression of  $\text{Nd}_{0.45}\text{Ce}_{2.55}\text{Pt}_3\text{Sb}_4$  to 4 GPa inside the diamond anvil cell, with the sample surrounded by the same  $\text{ZrO}_2$  medium used for thermoelectric power measurements. There was no change in crystal structure up to this pressure. The diffraction geometry utilized has the incident X-ray beam parallel to the uniaxial axis of compression. Because the diffraction experiment samples diffraction planes that are nearly parallel to the incident beam, these planes are also nearly parallel to the uniaxial axis of compression. The interplanar spacings used to determine the lattice parameter are thus perpendicular to the axis of compression. The stress experienced by the sample in this direction is considerably less than the stress parallel to the axis. As a result, there is little change in lattice

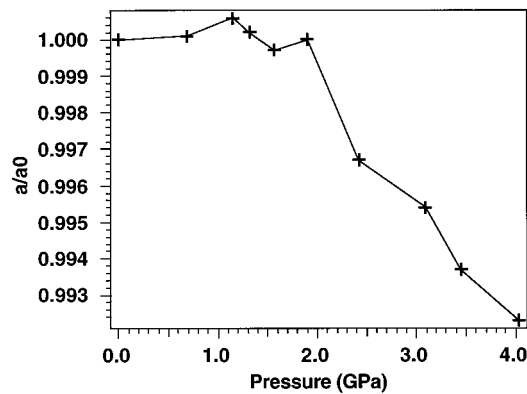
(16) *CRC handbook of thermoelectrics*; Rowe, D. M.; CRC Press: Boca Raton, FL, 1995.

(17) Wachter, P. In *Handbook on the Chemistry and Physics of the Rare Earths*; Gschneidner, K. A., Jr., Eyring, L., Lander, G. H., Choppin, G. R., Eds.; Elsevier: New York, 1994; p 177.

(18) Mahan, G. D. *Many-Particle Physics*; Plenum: New York, 1990.

(19) Locquet, J.-P.; Perret, J.; Fompeyrine, J.; Mächler, E.; Seo, J. W.; Van Tendeloo, G. *Nature* **1998**, *394*, 453.

(20) Struzhkin, V. V.; Timofeev, Y. A.; Hemley, R. J.; Mao, H.-K. *Phys. Rev. Lett.* **1997**, *79*, 4262.



**Figure 6.** Changes in the lattice parameter of cubic  $Nd_{0.45}Ce_{2.55}Pt_3Sb_4$  upon compression. Lattice parameter has been normalized to the value at ambient pressure. Small fluctuations in lattice parameter are due to experimental errors, which are less than 0.1%.

parameter (Figure 6) upon compression to 2 GPa, considerably less than would be expected upon hydrostatic compression.<sup>21</sup> If a diffraction experiment were performed in a perpendicular direction through the sample gasket, a larger decrease in lattice parameter would be expected, more than would be observed upon hydrostatic compression. Once the strength of the medium or sample is exceeded (above 2 GPa), the sample begins to flow and the lattice parameter decreases, although it remains larger than would be expected for hydrostatic compression. The pressure at which the lattice parameter begins to decrease correlates with the observed maximum in the thermoelectric power, again emphasizing the importance of non-hydrostatic uniaxial stress. These observations also

provide a plausible explanation for the observed irreversibility in the thermoelectric power upon compression to pressures in excess of 2 GPa, which is where irreversible flow of the sample begins to occur.

Substituting smaller atoms into a chemical structure is a common means of mimicking the effects of pressure tuning. The compound SmS, for example, can be pressure tuned into a region of phase space that exhibits an intermediate valence state (for which the Kondo effect is important) by means of pressure or by substituting smaller rare earth ions into the structure.<sup>22</sup> Nd and Ce have nearly the same atomic radii. We are currently undertaking efforts to substitute smaller rare earth ions into  $Nd_xCe_{3-x}Pt_3Sb_4$  to determine whether effect of pressure can be reproduced by chemically tuning. In addition, once the effects of nonhydrostatic stress are better understood, it may be possible to mimic them at ambient pressure with various film deposition techniques, which can induce significant uniaxial or biaxial stress components.

**Acknowledgment.** This research was supported by ONR and DARPA.

**Note Added in Proof.** Recently, N. V. Chandrashekar and J. V. Badding have proposed that the large increases in thermoelectric power observed under non-hydrostatic compression may be explained by the presence of an electronic topological (or Lifshitz) transition, which can occur when a band extremum crosses the Fermi energy. Peaks in the thermoelectric power associated with these transitions have been observed in other materials.

CM990540Z

(21) Hemley, R. J.; Mao, H.-k.; Shen, G.; Badro, J.; Gillet, P.; Hanfland, M.; Häusermann, D. *Science* **1997**, *276*, 1242.

(22) Jayaraman, A. *Rev. Mod. Phys.* **1983**, *55*, 65.