

# Hydrostatic high-pressure studies on the ferromagnetic Kondo-lattice compounds CePdSb and CeAg to 16 GPa

A. L. Cornelius,\* A. K. Gangopadhyay, and J. S. Schilling

Department of Physics, Washington University, Campus Box 1105, One Brookings Drive, St. Louis, Missouri 63130-4899

W. Assmus

Physikalisches Institut, Universität Frankfurt, D-60054 Frankfurt, Germany

(Received 2 December 1996)

The dependence of the Curie temperature  $T_c$  of the ferromagnets CeAg and CePdSb on hydrostatic pressure  $P$  to 3.2 and 16 GPa, respectively, has been determined using a diamond-anvil cell loaded with dense helium as pressure medium. For both compounds,  $T_c(P)$  initially increases with applied pressure, followed by a maximum at approximately 1(10) GPa for CeAg(CePdSb). Above 3(15) GPa for CeAg(CePdSb), no ferromagnetic transition could be detected. The present results are compared with earlier studies and discussed within the framework of a phase diagram proposed by Doniach for Kondo lattice systems. CePdSb is the first cerium compound where the dependence of  $T_c$  on  $P$  unequivocally displays the asymmetric peak predicted by this phase diagram. [S0163-1829(97)02421-1]

## I. INTRODUCTION

The Ce-based Kondo lattice compounds CePdSb and CeAg both order ferromagnetically below their Curie temperatures  $T_c$  of 16 and 5.5 K, respectively.<sup>1,2</sup> According to de Gennes scaling, the ordering temperature of a Ce compound should be only approximately 1% of that of its isostructural Gd analog. The value of  $T_c$  for CePdSb, however, lies *higher* than that for GdPdSb.<sup>1</sup> To our knowledge, CePdSb and CeRh<sub>3</sub>B<sub>2</sub> (Ref. 3) are the only Ce compounds to display an ordering temperature higher than that of their Gd analog.

The magnetic behavior of a Kondo lattice system is largely controlled by the product of the exchange coupling strength  $J$  and the density of states at the Fermi energy  $N(E_F)$ . A number of years ago, Doniach<sup>4</sup> examined the one-dimensional Kondo lattice, or ‘‘Kondo necklace,’’ problem in the mean-field approximation and obtained an antiferromagnetic ground state with a simple phase diagram, depicted in Fig. 1, which gives the magnetic ordering temperature  $T_c$  as a function of  $|JN(E_F)|$ . The salient features of this phase diagram were confirmed by a more sophisticated renormalization group calculation by Jullien *et al.*<sup>5</sup> This phase diagram has been shown to give a good qualitative description of the results for many Ce compounds.<sup>3,6</sup> In particular, the asymmetric nature of the phase diagram, where the initial increase of  $T_c$  with increasing  $|JN(E_F)|$  is more gradual than the subsequent rapid drop of  $T_c$  after reaching its maximum value, is a common feature of Ce compounds initially lying to the left of the  $T_c$  maximum in Fig. 1. In the absence of a phase transition, the quantity  $|JN(E_F)|$  is known to increase smoothly with pressure in Ce compounds.<sup>7,8</sup> Because of this, the asymmetry in Fig. 1 should be exhibited in plots of  $T_c$  versus  $P$  as well, as confirmed in combined high-pressure/substitution experiments.<sup>3,6</sup> To date, however, this asymmetry has not been seen in a single Ce compound by the application of pressure alone.<sup>9</sup> It should be noted that CeP and CeAs do

display maxima in  $T_c(P)$ , but do not clearly display any asymmetry about the maxima;<sup>10</sup> it should be noted, however, that these compounds are semimetals where the application of pressure has a drastic effect on  $N(E_F)$ , in contrast to the metallic compounds in the current study.

Previous high-pressure studies have been performed on both CePdSb and CeAg.  $T_c(P)$  for CePdSb has been determined to 1.6 GPa using an ac susceptibility technique,<sup>11</sup> yielding  $dT_c/dP \approx +1.7$  K/GPa. As shown in Fig. 1, a positive initial value of  $dT_c/dP$  would imply that CePdSb lies to the left of the maximum in  $T_c(P)$ ;  $T_c$  would be expected to pass through a maximum at higher applied pressures. CeAg

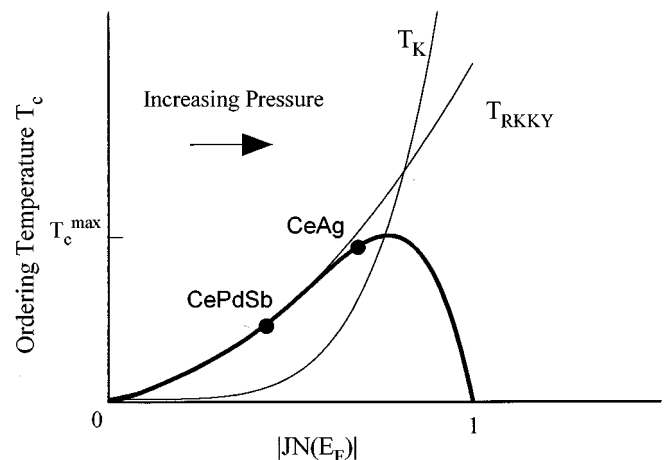


FIG. 1. The phase diagram of the one-dimensional ‘‘Kondo necklace’’ adapted from Ref. 4.  $T_{\text{RKKY}}$  is the temperature associated with the RKKY interaction energy,  $T_K$  the Kondo temperature,  $T_c$  the magnetic ordering temperature,  $J$  the exchange coupling strength, and  $N(E_F)$  the density of states at the Fermi energy. The approximate locations of CePdSb and CeAg are displayed. The position of a given Ce system in this diagram moves to the right as pressure is applied.

was one of the first compounds that was shown to exhibit the expected behavior of a Kondo lattice, with two studies finding a maximum in  $T_c(P)$  near 0.7 GPa.<sup>12–14</sup> From this pressure behavior, CeAg lies to the left of the maximum in Fig. 1, but to the right of CePdSb, as displayed. The first study on CeAg, with a maximum pressure of 3.5 GPa, found that  $T_c(P)$  continued to drop with increasing pressure after reaching its maximum value;<sup>12</sup> but a subsequent study to 4 GPa found a significantly different  $T_c(P)$  behavior,<sup>13,14</sup> with  $T_c(P)$  passing through a minimum at higher pressures. Since both of these studies used a resistivity technique which can lead to difficulties in accurately determining  $T_c(P)$ , we have chosen to determine  $T_c(P)$  directly from the magnetic properties (ac susceptibility), in an effort to resolve the discrepancy between the two reports.

We have measured the Curie temperatures of CePdSb(CeAg) in a diamond-anvil cell as a function of hydrostatic pressure to 16(3.2) GPa. With increasing pressure, the value of  $T_c$  initially increases for both compounds, passing through a maximum near 1(10) GPa for CeAg(CePdSb), in agreement with the Doniach phase diagram of Fig. 1. CePdSb is the first Ce compound to unequivocally display the anticipated asymmetry by the application of pressure alone.

## II. EXPERIMENT

Polycrystalline samples of CePdSb were prepared by melting a 1:1:1 stoichiometric ratio of Ce (99.99%), Pd (99.995%), and Sb (99.999%), all from Johnson-Matthey, in an argon arc melter. The samples were estimated to be more than 95% phase pure from x-ray powder diffraction. The lattice constants were determined to be  $a = 4.5955(5)$  Å and  $c = 7.917(2)$  Å, in good agreement with previous reports.<sup>1,15</sup> The dc susceptibility was measured in a Quantum Design superconducting quantum interference device (SQUID) magnetometer in a field of 1 kOe at temperatures between 5 and 300 K. Curie-Weiss behavior is exhibited above 150 K with a value of  $\mu_{\text{eff}} \approx 2.8\mu_B/\text{Ce}$ . The saturation moment measured at 5 K was found to be  $\mu_s \approx 0.9\mu_B/\text{Ce}$ . The measured values of  $\mu_{\text{eff}}$  and  $\mu_s$  agree well with previous experiments.<sup>1,15</sup> In particular, the results are characteristic of a Kondo lattice compound with  $\mu_{\text{eff}}$  near the value expected for  $\text{Ce}^{3+}$  ( $2.54\mu_B/\text{Ce}$ ) but  $\mu_s$  considerably reduced from the expected  $\text{Ce}^{3+}$  value of  $2.14\mu_B/\text{Ce}$  due to Kondo compensation of the 4f moments by the conduction electron spins.

The single crystal of CeAg in the present study was grown using a Czochralski technique out of a levitated melt out of a cold crucible.<sup>2</sup> Stoichiometric amounts of cerium (99.99% purity) and silver (99.999% purity) were prereacted in an argon arc furnace. The prereacted material was subsequently melted and levitated for at least one hour to ensure homogeneity. The crystals were then pulled from the melt by a tungsten rod at a speed of 3 mm/h. The crystal had a cylindrical shape with a diameter of 5–7 mm and a length of 20–100 mm. The cylindrical crystal from which the samples used in the current study were cut had the crystallographic (001) direction  $5^\circ$  from the cylindrical axis. It was found that CeAg reacted rapidly with air and formed a nonmagnetic compound. For this reason, the samples used for the high-pressure experiments were coated with a thin layer of poly-

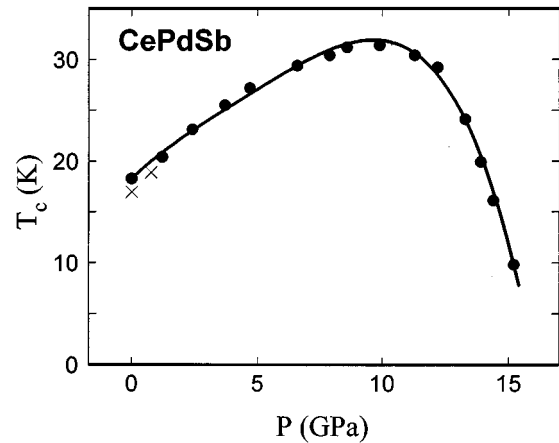


FIG. 2. The dependence of the Curie temperature  $T_c$  of CePdSb on increasing hydrostatic pressure: (●) present experiment; (×) data from Ref. 11. No ferromagnetic transition was detected above 15 GPa. The solid line is a guide to the eye.

vinyl toluene inside a glovebox before loading into the diamond-anvil cell.

The high-pressure apparatus consists of a copper-beryllium diamond-anvil clamp. A complete discussion of the high-pressure apparatus can be found elsewhere.<sup>3,16</sup> The magnitude of the pressure in the cell is determined by the standard ruby fluorescence technique<sup>17</sup> to an accuracy of 0.15 GPa. The good hydrostaticity of the pressure, even at pressures well above the melting curve of He, is indicated by the fact that the ruby fluorescence line remains sharp. A primary/secondary coil system that is sensitive enough to detect ferromagnetic transitions in samples with mass  $\leq 1$   $\mu\text{g}$  was employed to measure the ac susceptibility  $\chi_{\text{ac}}(T)$  using a PAR 124 lock-in amplifier.

## III. RESULTS

The results of the present high-pressure experiment on CePdSb are shown in Fig. 2. As can be seen,  $T_c(P)$  initially increases with pressure from  $T_c(0) = 18$  K at a rate of  $+1.6$  K/GPa, in excellent agreement with previous studies.<sup>11</sup> At  $\sim 10$  GPa,  $T_c$  passes through its maximum value of  $\sim 31$  K. Increasing pressure above 10 GPa leads to a rapid drop in  $T_c$ ; above 15 GPa, no ferromagnetic transition could be detected down to 2 K. After the pressure was released from 16 to 0 GPa, the ferromagnetic transition was found to return to its initial ambient pressure value. As can be seen in Fig. 2, the  $T_c(P)$  curve is asymmetrical about the maximum in  $T_c$ ; this result is consistent with the Kondo lattice model where CePdSb is initially positioned on the phase diagram as displayed in Fig. 1.

The results of the high-pressure experiments on CeAg are shown in Fig. 3. The ambient pressure value of  $T_c = 5.7$  K, the initial pressure derivative  $dT_c/dP \approx +3.5$  K/GPa and the maximum in  $T_c(P)$  at  $\sim 1$  GPa all agree well with the resistivity results.<sup>12–14</sup> Above 1 GPa,  $T_c(P)$  is seen to be a decreasing function of pressure, in agreement with Eiling and Schilling,<sup>12</sup> but in sharp contrast to the results of Fujiwara *et al.*<sup>13,14</sup> Above 3 GPa, no ferromagnetic transition could be detected down to 2 K. When pressure was released from 3 to

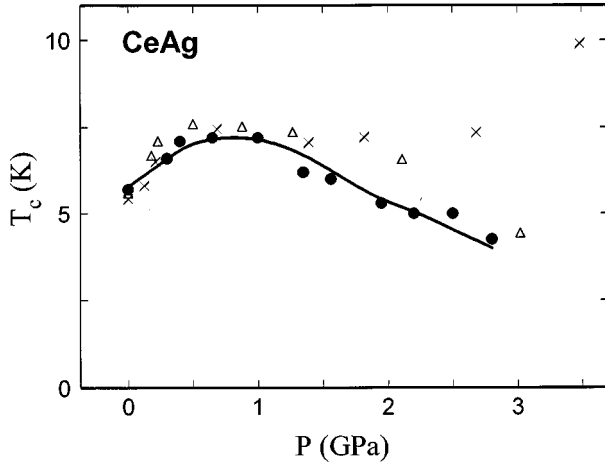


FIG. 3. The dependence of the Curie temperature  $T_c$  of CeAg on increasing hydrostatic pressure: (●) present experiment; (△) data from Ref. 12, (×) Ref. 13. No ferromagnetic transition was detected above 3 GPa in the present studies. Solid line is a guide to the eye.

0 GPa, no ferromagnetic transition could be detected above 2 K. This loss of ferromagnetism could arise from a strongly hysteretic phase transition near 3 GPa or from possible exposure of the sample to air following the release of pressure. The results on CeAg are in good agreement with what is expected of a Kondo lattice compound positioned on the phase diagram as displayed in Fig. 1.

#### IV. DISCUSSION

Kondo lattice systems are characterized by a competition between the magnetic ordering of local moments through Ruderman-Kittel-Kasuya-Yosida (RKKY) interactions and the eventual destruction of the local moments by the Kondo effect. The energies of the competing phenomena are characterized by  $kT_K \propto \exp[-1/|JN(E_F)|]$ , the binding energy of the Kondo singlet, and  $kT_{\text{RKKY}} \propto J^2 N(E_F)$ , the energy of the RKKY interaction. For small values of  $|JN(E_F)|$ , the RKKY term dominates and magnetic ordering will occur. For large values of  $|JN(E_F)|$ , the Kondo term dominates and the magnetic ordering is destroyed due to Kondo compensation. In Doniach's solution<sup>4</sup> for the one-dimensional "Kondo necklace," as displayed in Fig. 1, it can be seen that these competing interactions give rise to a maximum in  $T_c$  and an asymmetric  $T_c$  curve with respect to the maximum due to the rapid increase in  $T_K$  as it overtakes  $T_{\text{RKKY}}$ , ultimately leading to a nonmagnetic ground state. As hypothesized by Doniach,<sup>4</sup> this general behavior should also hold for three-dimensional systems. In fact, the phase diagram in Fig. 1 has been used to account for the behavior of many Ce compounds that display a well-defined maximum in  $T_c$ .<sup>3,6,12,18-22</sup>

When comparing data from systems with different bulk moduli, it is more suitable to plot  $T_c$  versus the change in relative sample volume  $V/V_m$ . In Fig. 4 we show the dependence of  $T_c$  on  $V/V_m$  for CePdSb and CeAg and the selected Ce compounds  $\text{CeRh}_3(\text{B}_{1-x}\text{Si}_x)_2$ ,<sup>3,23</sup>  $\text{CeRh}_2(\text{Si}_{1-x}\text{Ge}_x)_2$ ,<sup>18,20</sup> and  $\text{CePd}_2(\text{Si}_{1-x}\text{Ge}_x)_2$ .<sup>19,20</sup> The

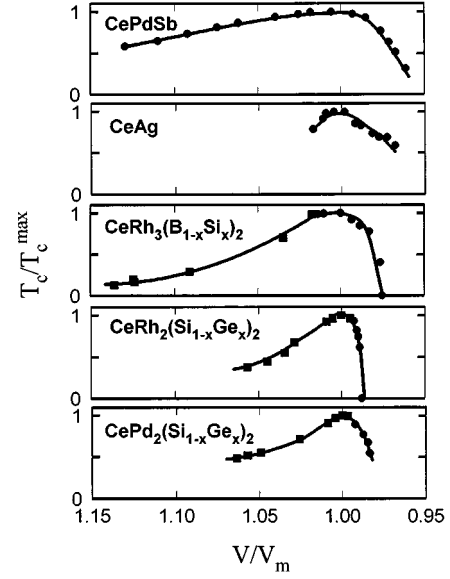


FIG. 4. The relative ordering temperature  $T_c/T_c^{\text{max}}$  for CePdSb ( $T_c^{\text{max}} \approx 31$  K),  $\text{CeRh}_3(\text{B}_{1-x}\text{Si}_x)_2$  ( $T_c^{\text{max}} \approx 120$  K),  $\text{CeRh}_2(\text{Si}_{1-x}\text{Ge}_x)_2$  ( $T_c^{\text{max}} \approx 38$  K), and  $\text{CePd}_2(\text{Si}_{1-x}\text{Ge}_x)_2$  ( $T_c^{\text{max}} \approx 11$  K) versus relative volume  $V/V_m$ , where  $V_m$  is volume at which  $T_c = T_c^{\text{max}}$ . Value of  $V$  at given pressure is estimated as discussed in Ref. 24. Filled circles (●) give results of high-pressure experiment for  $x=0$ , squares (■) for substitution experiments at ambient pressure (see Ref. 3 for details). Solid lines are guides for the eye.

latter compounds were chosen because data for them are available over a large portion of the Doniach phase diagram either from hydrostatic pressure experiments for  $x=0$  or from substitution experiments<sup>24</sup> with variable  $x$ . For all of the Ce systems the dependence of  $T_c$  on  $V/V_m$  bears a close resemblance to the phase diagram in Fig. 1. The marked asymmetry in  $T_c(V)$  about  $V=V_m$  is apparent for all data in Fig. 4. In all cases, less than a 5% volume reduction is necessary to force  $T_c$  to pass from its maximum value  $T_c^{\text{max}}$  to 0 K. That this asymmetry is real, and not due to an inequivalence of changing  $V/V_m$  through high pressure or chemical substitution experiments, is indicated by the fact that for  $\text{CeRh}_2\text{Ge}_2$ ,  $d\ln T_K/d\ln V \approx -12$  to  $-15$  in both types of experiments.<sup>25,18</sup> Indeed, since  $J \propto |V_{df}|^2$ , where  $V_{df}$  gives the hybridization strength between the  $f$  and  $d$  orbitals, the substitution of Si for B or Ge for Si in the above compounds should not change the local environment of the  $d$  or  $f$  orbitals, but be equivalent to a negative pressure, where  $V_{df}$  changes in a gradual manner as the spacing between atoms increases.

In conclusion, we have shown that the magnetic behavior of the Kondo lattice compound CePdSb can be explained quite well by the Doniach phase diagram where applied pressure increases the quantity  $|JN(E_F)|$ . In particular, the asymmetry in the  $T_c(P)$  dependence predicted by this diagram has for the first time been observed in a Ce compound by the application of high pressure alone. In addition, in contrast to a previously published paper, we find the compound CeAg to behave in a manner consistent with the Doniach phase diagram.

- \*Present address: Materials Science and Technology Division, Los Alamos National Laboratory, MS K764, Los Alamos, NM 87545.
- <sup>1</sup>S. K. Malik and D. T. Adroja, *Phys. Rev. B* **43**, 6295 (1991).
  - <sup>2</sup>R. Takke, N. Dolezal, W. Assmus, and B. Lüthi, *J. Magn. Magn. Mater.* **23**, 247 (1981).
  - <sup>3</sup>A. L. Cornelius and J. S. Schilling, *Phys. Rev. B* **49**, 3955 (1994).
  - <sup>4</sup>S. Doniach, in *Valence Instability and Related Narrow Band Phenomena*, edited by R. D. Parks (Plenum, New York, 1977).
  - <sup>5</sup>R. Jullien, J. N. Fields, and S. Doniach, *Phys. Rev. B* **16**, 4889 (1977).
  - <sup>6</sup>A. L. Cornelius, J. S. Schilling, D. Mandrus, and J. D. Thompson, *Phys. Rev. B* **52**, R15 699 (1995).
  - <sup>7</sup>J. S. Schilling, *Adv. Phys.* **28**, 657 (1979).
  - <sup>8</sup>J. D. Thompson, *Physica B* **190**, 61 (1993).
  - <sup>9</sup>J. D. Thompson and J. M. Lawrence, in *Handbook on the Physics and Chemistry of Rare Earths*, edited by K. A. Gschneidner, Jr., L. Eyring, G. H. Lander, and G. R. Choppin (North-Holland, Amsterdam, 1994), p. 383.
  - <sup>10</sup>N. Môri, Y. Okayama, H. Takahashi, Y. Haga, and T. Suzuki, *Physica B* **186-188**, 444 (1993).
  - <sup>11</sup>P. C. Riedi, J. G. M. Armitage, J. S. Lord, D. T. Adroja, B. D. Rainford, and D. Fort, *Physica B* **199-200**, 558 (1994).
  - <sup>12</sup>A. Eiling and J. S. Schilling, *Phys. Rev. Lett.* **46**, 364 (1981).
  - <sup>13</sup>H. Fujiwara, M. Kurisu, and H. Kadomatsu, *J. Magn. Magn. Mater.* **70**, 369 (1987).
  - <sup>14</sup>M. Kurisu, *J. Phys. Soc. Jpn.* **56**, 4064 (1987).
  - <sup>15</sup>O. Trovarelli, J. G. Sereni, G. Schmerber, and J. P. Kappler, *Phys. Rev. B* **49**, 15 179 (1994).
  - <sup>16</sup>S. Klotz, J. S. Schilling, and P. Müller, in *Frontiers of High-Pressure Research*, edited by H. D. Hochheimer and E. D. Etters (Plenum, New York, 1991).
  - <sup>17</sup>G. J. Piermarini, S. Block, J. D. Barnett, and R. A. Forman, *J. Appl. Phys.* **46**, 2774 (1975).
  - <sup>18</sup>C. Godart, L. C. Gupta, C. V. Tomy, J. D. Thompson, and R. Vijayaraghavan, *Europhys. Lett.* **8**, 375 (1989).
  - <sup>19</sup>I. Das and E. V. Sampathkumaran, *Phys. Rev. B* **44**, 9711 (1991).
  - <sup>20</sup>J. D. Thompson, R. D. Parks, and H. Borges, *J. Magn. Magn. Mater.* **54-57**, 377 (1986).
  - <sup>21</sup>D. Gignoux and J. Voiron, *J. Magn. Magn. Mater.* **54-57**, 363 (1986).
  - <sup>22</sup>S. A. Shaheen, J. S. Schilling, M. Abd-Elmeguid, H. Micklitz, P. Klavins, and R. N. Shelton, *Physica B* **139-140**, 410 (1986).
  - <sup>23</sup>S. K. Malik, G. K. Shenoy, S. K. Dhar, P. L. Paulose, and R. Vijayaraghavan, *Phys. Rev. B* **34**, 8196 (1986).
  - <sup>24</sup>The volumes are estimated using the Birch equation of state  $V/V_0 = (1 + B'P/B)^{-1/B'}$ . For CeRh<sub>3</sub>B<sub>2</sub>, the value of  $B = 141$  GPa taken from Athreya, Ph.D. thesis, Iowa State University, 1986, and an estimated  $B' = 4$  were used. For CeAg, the measured values of  $B = 53$  GPa taken from Ref. 14, and an estimated  $B' = 4$  were used; this value of  $B$  agrees well with that (52.5 GPa) at 5 K from the elastic constants in Ref. 2. Since the bulk modulus for CeRh<sub>2</sub>Si<sub>2</sub>, CePd<sub>2</sub>Si<sub>2</sub>, and CePdSb have not as yet been measured, the relationship  $BV_0 = \text{constant}$  as determined for the RAl<sub>2</sub> series from Penney *et al.*, *Solid State Commun.* **44**, 1199 (1982) was used to estimate  $B$  from a measured compound. The values used are 117 GPa for CeRh<sub>2</sub>Si<sub>2</sub> and 112 GPa for CePd<sub>2</sub>Si<sub>2</sub> and  $B' = 4.6$  for both are estimated using the values for isostructural CeCu<sub>2</sub>Si<sub>2</sub> of  $B = 120$  GPa and  $B' = 4.6$  from Spain *et al.*, *Physica B* **130-140**, 449 (1986). For CePdSb an estimated  $B' = 4$  and  $B = 72$  GPa, scaled from the values for RAl<sub>2</sub> of Penney *et al.*, are used.
  - <sup>25</sup>J. D. Thompson, Y. Uwatoko, T. Graf, M. F. Hundley, D. Mandrus, C. Godart, L. C. Gupta, P. C. Canfield, A. Migliori, and H. A. Borges, *Physica B* **199-200**, 589 (1994).