PHYSICAL REVIEW B **77**, 180504(R) (2008)

Superconductivity in the actinoid-bearing filled skutterudite $ThPt_4Ge_{12}$

D. Kaczorowski and V. H. Tran
Institute of Low Temperature and Structure Research, Polish Academy of Sciences, P.O. Box 1410, 50-950 Wrocław, Poland
(Received 27 March 2008; revised manuscript received 18 April 2008; published 12 May 2008)

$ThPt_4Ge_{12}$ is an actinoid-bearing representative of a recently discovered family of Ge-based skutterudites. Based on magnetization, electrical resistivity, and specific heat data, the compound was characterized as a clean-limit strong-coupling superconductor with T_c=4.62 K. Moreover, some hints are given at a possible non-BCS character of the superconducting state.

DOI: 10.1103/PhysRevB.77.180504 PACS number(s): 74.70.Dd, 74.25.Bt, 82.75.−z

Ternary and higher order compounds crystallizing in a cubic structure of the $LaFe_4P_{12}$ type[1] are commonly referred to as "skutterudites." Until very recently, it was believed that all ternary skutterudites are based on pnicogen atoms (X =P,As,Sb), which together with a transition metal T from the Fe or Co group of the Periodic Table form cagelike frameworks of tilted $[TX_6]$ octahedra. Icosahedral voids in these frameworks are filled or partly filled by an electropositive main group or subgroup element M, which is more or less loosely bound to the host structure. Depending on a particular combination of the constituents that yields the total valence electron count, determines the rigidness of the cage via the T-X and X-X bondings, and controls the interaction between the guest atom M and the $[T_4X_{12}]$ matrix, a great variety of physical properties has been observed ranging from itinerant- or local-moment magnetic ordering, multipolar ordering, half-metallicity, spin and valence fluctuations, heavy fermion behavior, and non-Fermi liquid states to conventional and unconventional superconductivities.[2] Moreover, for some of the $M_xT_4X_{12}$ materials, very large thermal M-atom displacement factors have been found. They correspond to the so-called phonon rattling modes, which give rise to significantly enhanced thermoelectric performance.[3]

Most recently, two research groups have independently communicated discovery of a novel class of ternary compounds with the filled skutterudite structure, in which pnicogen atoms are entirely replaced by the Ge atoms and the T atom is Pt.[4,5] The reported MPt_4Ge_{12} series comprises phases with M=Sr, Ba, La, Ce, Pr, Nd, and Eu. Interestingly, compounds with Sr and Ba have been found to be superconducting below 5.10 and 5.35 K, respectively,[4] whereas those with La and Pr have been characterized as strong-coupling superconductors with T_c=8.3 and 7.9 K, respectively.[5] The superconductivity in $PrPt_4Ge_{12}$ seemed most spectacular as the compound is a Curie–Weiss paramagnet due to the presence of well localized $4f$ magnetic moments. It has been shown, however, that at low temperatures, $PrPt_4Ge_{12}$ is effectively nonmagnetic because of a specific crystal field splitting with a singlet ground state and a nonmagnetic doublet being the first excited level.[5]

In this Rapid Communication, we report on the formation and the superconducting properties of another Ge-based skutterudite, namely, $ThPt_4Ge_{12}$, which is the actinoid-bearing representative of the MPt_4Ge_{12} series. A polycrystalline sample of $ThPt_4Ge_{12}$ was prepared by arc melting stoichiometric amounts of elemental constituents (Th: 99.8 at. %, Pt: 99.99 at. %; and Ge: 99.999 at. %) on a water-cooled copper hearth in high-purity Ar atmosphere gettered by melting Ti ingot. The sample was remelted several times in order to promote homogeneity. Subsequently, it was wrapped in tantalum foil, sealed in an evacuated quartz tube, and annealed at 800 °C for 3 weeks. Quality of the sample was checked by x-ray powder diffraction on a Stoe powder diffractometer with monochromatized Cu $K\alpha$ radiation (λ_0=1.54056 Å) as well as by microprobe analysis using a Phillips 515 scanning electron microscope equipped with an energy dispersive x-ray analysis PV 9800 spectrometer. The measurements showed a single phase of composition close to nominal. The x-ray pattern was resolved with the FULLPROF program[6] yielding a structure with a cubic unit cell of the $LaFe_4P_{12}$ type (space group $Im\bar{3}$) and a lattice parameter a=8.5924(6) Å. This value is similar to those reported for the compounds $LaPt_4Ge_{12}$, $PrPt_4Ge_{12}$, $SrPt_4Ge_{12}$, and $BaPt_4Ge_{12}$ (Refs. 4 and 5), as could be expected from the fact that the unit cell volume of all these phases is mainly determined by the size of the $[Pt_4Ge_{12}]$ polyanion.

Magnetic measurements were carried out in the temperature range from 1.71 to 10 K, in applied magnetic fields of up to 0.3 T, using a Quantum Design superconducting quantum interference device magnetometer. Specific heat and electrical resistivity were measured by the relaxation method and the ac technique, respectively, over the temperature interval of 350 mK—300 K, and in applied fields of up to 0.6 T, employing a Quantum Design physical property measurement system platform.

Figure 1(a) displays the temperature dependence of the electrical resistivity of $ThPt_4Ge_{12}$. At first glance, it seemed of metallic type with the room temperature value $\rho_{300\ K}=7.5\times10^{-7}\ \Omega$ m and very low residual resistivity ρ_0= $6.5\times10^{-9}\ \Omega$ m (just above T_c), i.e., with the residual resistivity ratio being enormously large (RRR ≈100), as for a polycrystalline sample. However, closer inspection of the $\rho(T)$ curve revealed that it does not follow the Bloch–Grüneissen law characteristic of simple metals. Instead, in the entire temperature range studied, except for the region below T_c, it may be very well approximated by the Woodard–Cody (WC) formula,[7] which is appropriate for superconducting materials with significantly strong electron-phonon coupling. Least-squares fit of the experimental data to the WC expression (cf. Fig. 1) yielded the characteristic temperature T_0=142 K that is close to those previously obtained for $SrPt_4Ge_{12}$ and $BaPt_4Ge_{12}$.[4] Below approximately 10 K, the normal-state

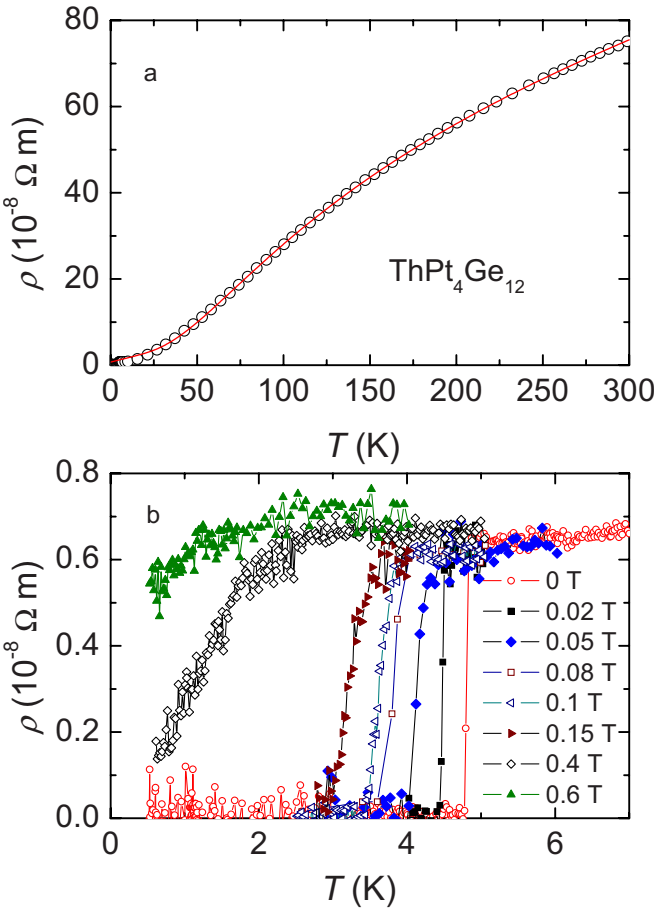

FIG. 1. (Color online) (a) Temperature dependence of the electrical resistivity of $ThPt_4Ge_{12}$. For the sake of clarity, only every 15th experimental point is displayed. The solid line is the WC fit described in the text. (b) Low-temperature resistivity measured in zero and several nonzero applied magnetic fields.

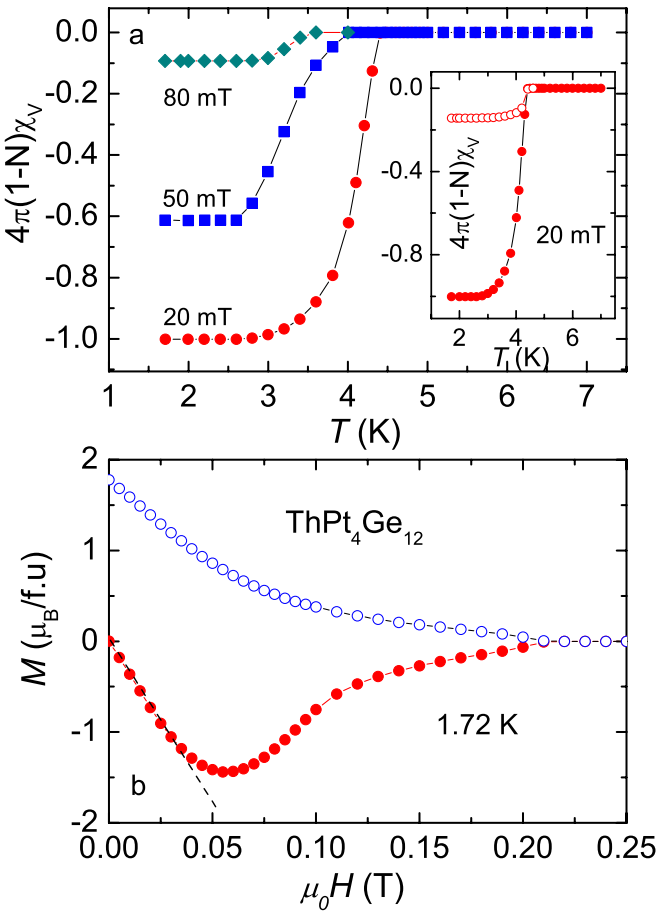

FIG. 2. (Color online) (a) Temperature dependence of the dc magnetic susceptibility of $ThPt_4Ge_{12}$ measured in several different magnetic fields after cooling the specimen in zero field. The inset shows the temperature dependence of the magnetic susceptibility taken in a field of 20 mT after cooling the specimen in zero (ZFC; full circles) and applied (FC; open circles) fields. (b) Magnetic field dependence of the magnetization in $ThPt_4Ge_{12}$ measured at 1.72 K with increasing (full circles) and decreasing (open circles) field.

resistivity exhibits a T^5 dependence expected for electron-phonon interactions in clean metallic systems.

Shown in Fig. 1(b) is the low-temperature region of the resistivity of $ThPt_4Ge_{12}$. Despite the large noise in experimental data, one unambiguously observes a transition to superconducting state that takes place at $T_c=4.8(1)$ K in zero magnetic field. The critical temperature gradually diminishes with rising field strength and already in a field of 0.4 T drops below 0.35 K (the terminal low temperature in this study).

In the normal state, $ThPt_4Ge_{12}$ is a weak diamagnet with the magnetic susceptiblity of about 1.3×10^{-7} cm^3 g^{-1}. As displayed in Fig. 2(a), in a field of 20 mT, an onset of the superconducting state occurs at 4.4 K. The strong diamagnetic signal observed at 1.75 K upon cooling the sample in zero field (ZFC) corresponds to the perfect shielding of the total volume of the sample by supercurrents if the demagnetization factor N of 0.21 is assumed.[8] The Meissner–Ochsenfeld effect [field-cooled (FC) condition] is only 1.8% of the theoretical value of $-1/4\pi$ expected for a perfect diamagnet. This feature implies very strong pinning in a type-II superconductor. With rising magnetic field strength, the critical temperature T_c gradually decreases, and the superconductivity becomes hardly observable by means of $\chi(T)$ measurement already in fields above 0.15 T. Shown in Fig. 2(b) is the field dependence of the magnetization $M(H)$ in $ThPt_4Ge_{12}$ measured at 1.72 K. This $M(H)$ loop clearly exhibits a behavior characteristic of type-II superconductor. The lower critical field μ_0H_{c1}, determined from the point where the magnetization deviates from the linearity, amounts to approximately 3 mT. The upper critical field μ_0H_{c2} at this temperature is about 0.2 T.

The low-temperature specific heat data of $ThPt_4Ge_{12}$, which were measured in fields of 0 and 0.5 T, are shown in Fig. 3(a) as C_p/T versus T^2. A distinct jump observed in zero magnetic field indicates the onset of superconductivity at $T_c=4.62(1)$ K. This value, which is derived from entropy balance construction, is slightly lower than that revealed from the resistivity measurements. In a field of 0.5 T, the superconductivity is totally suppressed. The normal-state specific heat can be approximated in the range of 0.35–7 K with the function $C_{pn}(T)=\gamma_n+C_{ph}$, where $C_{ph}=\beta T^3+\delta T^5$.[9] The limiting value of the Debye temperature estimated from the value of β is about 217 K, i.e., very similar to those

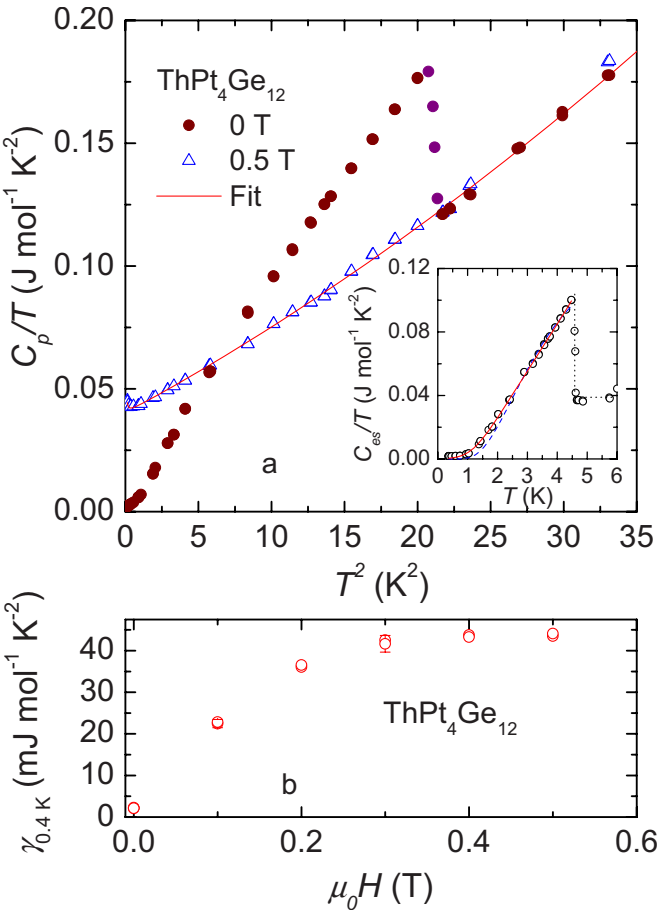

FIG. 3. (Color online) (a) Temperature dependence of the specific heat of $ThPt_4Ge_{12}$ measured in zero magnetic field and in 0.5 T, which is plotted as C_p/T versus T^2. Solid line is a fit discussed in the text. The inset shows the electronic specific heat in the superconducting state in the form of C_{es}/T versus T. Dashed and solid lines are the theoretical descriptions analyzed in the text. Dotted line is a guide for the eyes. (b) Magnetic field dependence of the Sommerfeld ratio $\gamma = C_p/T$ measured at $T = 0.4$ K. Experimental error bars are of the size of the symbols.

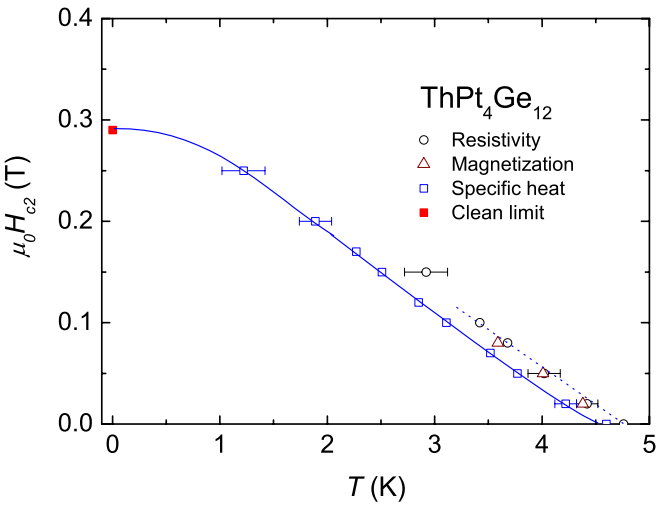

FIG. 4. (Color online) Upper critical field versus temperature determined for $ThPt_4Ge_{12}$ from the resistivity (circles), magnetization (triangles), and specific heat (squares) data. Filled square represents the calculated value of $H_{c2}(0)$ in the clean limit. Solid line emphasizes a linear variation of H_{c2} with temperature.

reported for the other MPt_4Ge_{12} compounds.[4,5] This result supports the specific lattice vibration model developed for skutterudites in which vibrations of the polyanion are described by the Debye term and those of the guest cation by the Einstein term.[10] The normal-state electronic specific heat coefficient γ_n was found to be 40 mJ mol^{-1} K^{-2}, i.e., nearly identical to that derived for $SrPt_4Ge_{12}$ and $BaPt_4Ge_{12}$ (Ref. 4 and 5) but about two times smaller than the values reported for $LaPt_4Ge_{12}$ and $PrPt_4Ge_{12}$.[5]

In the inset of Fig. 3(a), the temperature dependence of the electronic specific heat is shown, which is calculated as the difference $C_{es} = C_p - C_{ph}$. The dimensionless specific heat jump at the critical temperature $\Delta C_{es}/\gamma_n T_c$ amounts to 1.7. This value is considerably larger than the BCS value of 1.426 and also distinctly different from those found for the other Ge-based skutterudites.[4,5] Hence, in contrast to the other MPt_4Ge_{12} compounds, with a possible exception of that with M=Pr,[5] $ThPt_4Ge_{12}$ is clearly a strong-coupling superconductor. This conclusion is corroborated by the value of the electron-phonon coupling constant λ of about 0.57, which is calculated from the relation $\Delta C_{es}/\gamma_n T_c = 1.43 + 0.942\lambda^2 - 0.195\lambda^3$.[11] Another estimate for λ may be obtained from the McMillan formula,[12] which yields similar value of about 0.62, for a typical magnitude of the Coulomb pseudopotential $\mu^* = 0.1$.

Fitting the experimental $C_{es}(T)$ data in terms of the BCS-type formula, $C_{es,BCS} \sim \exp(-\alpha T_c/T)$, where the parameter α is related to the superconducting gap, yields $\alpha = 1.7$ that is larger than the BCS value of 1.44. However, as is apparent from the inset of Fig. 3(a), this description (marked by the dashed line) notably deviates from the experimental curve at temperatures below 2.5 K. Instead, the experimental data can be very well fitted by the sum $C_{es} = C_{es,BCS} + cT^3$ [note the solid line in the inset of Fig. 3(a)], with $\alpha = 1.44$ and the coefficient $c = 3$ mJ mol^{-1} K^{-4}. The presence of the T^3 term in the temperature dependence of the C_{es} may imply the existence of point-node energy gap structure, but this hypothesis needs further investigation. It is tempting to explore a possibility that the superconductivity in $ThPt_4Ge_{12}$ is unconventional. In this context it is worth noting that the magnetic field dependence of the Sommerfeld ratio $\gamma = C_p/T$, which was measured at 0.4 K [see Fig. 3(b)], is strongly nonlinear, i.e., at variance with the behavior expected for a classical BCS-type superconductor. One may recall that a nonlinear dependence of $\gamma(T)$ has been observed for the point-nodal superconductor YNi_2B_2C.[13]

The thermodynamic critical field $\mu_0 H_{c2}$ can be calculated by an integration of the specific heat data in the superconducting state according to the equation $\frac{1}{2}\mu_0 V_M H_{c0}^2(T) = \Delta U(T) - T\Delta S$, where $\Delta U = \int_T^{T_c}(C_{es} - \gamma_n T')dT'$ is the internal energy difference and $\Delta S = \int_T^{T_c}\frac{C_{es} - \gamma_n T'}{T'}$ is the entropy difference. For $ThPt_4Ge_{12}$, an extrapolation $H_{c0}(T)$ to zero temperature yields a value of 42 mT that is close to $\mu_0 H_{c0}(0)$ derived for the Sr- and Ba-containing counterparts.[4]

The temperature dependence of the upper critical field

$\mu_0 H_{c2}$ in $ThPt_4Ge_{12}$, which is derived from the electrical resistivity, magnetization, and specific heat data, is shown in Fig. 4. Similar to the case of the La- and Pr-containing analogs,[5] $\mu_0 H_{c2}$ varies linearly with T. The slope $-d\mu_0 H_{c2}/dT$ is 0.085 T K^{-1}, being a few times smaller than the initial slope near T_c reported for $SrPt_4Ge_{12}$ and $BaPt_4Ge_{12}$.[4] By using formulas given in Refs. 14 and 15, one may calculate the Fermi wave number $k_F \approx 6.3 \times 10^9$ m^{-1}. Then, in the framework of the model developed by Orlando *et al.*,[15] this estimate of k_F, together with the experimental values of T_c, ρ_0, and γ, yields the Fermi velocity $v_F \approx 1.3 \times 10^5$ m s^{-1}, the effective mass $m^* \approx 5.6 m_o$, the electronic mean free path of the quasiparticles $l \approx 435$ nm, and the BCS coherence length $\xi_0 \approx 37$ nm. The so-derived relation $l \gg \xi_0$ clearly corroborates the previously formulated hypothesis that $ThPt_4Ge_{12}$ exhibits the clean-limit superconductivity. According to the formula $\mu_0 H_{c2}(0) = -0.73 T_c (d\mu_0 H_{c2}/dT)|_{T_c}$, which is appropriate for the clean limit,[16] the upper critical field at zero temperature amounts to about 0.29 T (indicated by the solid square in Fig. 4). This value is in fairly good agreement with the experimental data, yet almost an order of magnitude lower than those reported for the other MPt_4Ge_{12} compounds.[4,5] From the values of $\mu_0 H_{c2}$ and $\mu_0 H_{c1}$, one can determine the Ginzburg–Landau coherence length ξ_{LG} and the penetration depth λ_{GL} to be equal to $\approx$35 and $\approx$150 nm, respectively.[17] Hence, the Ginzburg–Landau parameter κ_{LG} for $ThPt_4Ge_{12}$ is estimated to be about 4.5, which is well within the range for type-II superconductivity. This result may be compared to $\kappa_{LG}=14$, which is obtained for $SrPt_4Ge_{12}$, and $\kappa_{LG}=24$, which is found for $BaPt_4Ge_{12}$.[4]

In conclusion, $ThPt_4Ge_{12}$ is another representative of the recently discovered family of MPt_4Ge_{12} intermetallics crystallizing in the filled skutterudite structure. Like the compounds with M=Sr, Ba, La, and Pr, it exhibits type-II superconductivity at low temperatures (T_c=4.62 K). However, in contrast to the other phases, $ThPt_4Ge_{12}$ can be classified as a clean-limit superconductor. Its characteristic thermodynamic features indicate strong electron-phonon coupling. Most interestingly, some properties in the superconducting state (the temperature dependence of the electronic specific heat C_{es} and the magnetic field dependence of the Sommerfeld coefficient γ) deviate from the predictions of the BCS theory. Taken together these findings provoke an intriguing conjecture that the superconductivity in $ThPt_4Ge_{12}$ may be unconventional.

The work was supported by the Ministry of Science and Higher Education through the research Grants No. N202 116 32/3270 and No. N202 082/0449.

[1] W. Jeitschko and D. J. Braun, Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem. **33**, 3401 (1977).

[2] B. C. Sales, in *Handbook on the Physics and Chemistry of Rare Earths*, edited by K. A. Gschneidner, Jr., J.-C. G. Bünzli, and V. K. Pecharsky (Elsevier, Amsterdam, 2003), Vol. 33, Chap. 211, pp. 1–34.

[3] C. Uher, in *Chemistry, Physics and Materials Science of Thermoelectric Materials: Beyond Bismuth Telluride*, edited by M. G. Kanatzidis, S. D. Mahanti, and T. P. Hogan (Kluwer, Dordrecht, 2003), pp. 121–146.

[4] E. Bauer, A. Grytsiv, Xing-Qiu Chen, N. Melnychenko-Koblyuk, G. Hilscher, H. Kaldarar, H. Michor, E. Royanian, G. Giester, M. Rotter, R. Podloucky, and P. Rogl, Phys. Rev. Lett. **99**, 217001 (2007).

[5] R. Gumeniuk, W. Schnelle, H. Rosner, M. Nicklas, A. Leithe-Jasper, and Yu. Grin, Phys. Rev. Lett. **100**, 017002 (2008).

[6] J. Rodriguez-Carvajal, Physica B **192**, 55 (1992).

[7] D. W. Woodard and G. D. Cody, Phys. Rev. **136**, A166 (1964).

[8] The accuracy of this estimation is limited by experimental uncertainty in determining the material density of the specimen measured.

[9] This formula corresponds to the Debye model in which the low-frequency expansion of the density of phonon modes $D(\omega)$ is cut on the ω^4 term.

[10] V. Keppens, D. Mandrus, B. C. Sales, B. C. Chakoumakos, P. Dai, R. Coldea, M. B. Maple, D. A. Gajewski, E. J. Freeman, and S. Bennington, Nature (London) **395**, 876 (1998).

[11] V. Z. Kresin and V. P. Parkhomenko, Sov. Phys. Solid State **16**, 2180 (1975).

[12] W. L. McMillan, Phys. Rev. **167**, 331 (1968).

[13] C. L. Huang, J.-Y. Lin, C. P. Sun, T. K. Lee, J. D. Kim, E. M. Choi, S. I. Lee, and H. D. Yang, Phys. Rev. B **73**, 012502 (2006).

[14] U. Rauchschwalbe, W. Lieke, C. D. Bredl, F. Steglich, J. Aarts, K. M. Martini, and A. C. Mota, Phys. Rev. Lett. **49**, 1448 (1982).

[15] T. P. Orlando, E. J. McNiff, Jr., S. Foner, and M. R. Beasley, Phys. Rev. B **19**, 4545 (1979).

[16] E. Helfand and N. R. Werthamer, Phys. Rev. **147**, 288 (1966).

[17] V. L. Ginzburg and L. D. Landau, Zh. Eksp. Teor. Fiz. **20**, 1064 (1950).