Magnetocrystalline anisotropy and antiferromagnetic phase transition in $PrRh_2Si_2$

2007 J. Phys.: Condens. Matter 19 506205

(http://iopscience.iop.org/0953-8984/19/50/506205)

IOP PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **19** (2007) 506205 (7pp) doi:10.1088/0953-8984/19/50/506205

Magnetocrystalline anisotropy and antiferromagnetic phase transition in $PrRh_2Si_2$

V K Anand[1], Z Hossain[1], G Behr[2], G Chen[3], M Nicklas[3] and C Geibel[3]

[1] Department of Physics, Indian Institute of Technology, Kanpur 208016, India
[2] Institute for Solid State and Materials Research, Dresden, Germany
[3] Max-Planck Institute for Chemical Physics of Solids, 01187 Dresden, Germany

E-mail: zakir@iitk.ac.in

Received 6 August 2007, in final form 3 October 2007
Published 19 November 2007
Online at stacks.iop.org/JPhysCM/19/506205

Abstract

We present magnetic and transport properties of $PrRh_2Si_2$ single crystals which exhibit antiferromagnetic order below $T_N = 68$ K. Well defined anomalies due to the magnetic phase transition are observed in magnetic susceptibility, resistivity and specific heat data. The T_N of 68 K for $PrRh_2Si_2$ is much higher than the 5.4 K expected on the basis of de Gennes scaling. The magnetic susceptibility data reveal strong uniaxial anisotropy in this compound, similar to that of $PrCo_2Si_2$. With increasing pressure T_N increases monotonically up to $T_N = 71.5$ K at 22.5 kbar.

1. Introduction

$YbRh_2Si_2$ has been widely investigated due to its proximity to a quantum phase transition [1–4]. We show in this paper that its Pr homolog $PrRh_2Si_2$ also presents unique magnetic properties. All the investigated RRh_2Si_2 (R = rare earth) compounds have been found to order antiferromagnetically [1, 5–12]. Among them $GdRh_2Si_2$ has the highest ordering temperature, $T_N \sim 106$ K [6]. $EuRh_2Si_2$ exhibits complex magnetic order with an antiferromagnetic ordering below 25 K [11]. $CeRh_2Si_2$ and $YbRh_2Si_2$ have unusual and interesting magnetic properties, which are discussed below.

The antiferromagnetic ordering temperature $T_N \sim 36$ K in $CeRh_2Si_2$ is very high compared to the de Gennes expected ordering temperature of 1.2 K [12, 13]. One more transition is observed at 24 K. The exact nature (localized versus itinerant) of the magnetism of $CeRh_2Si_2$ is not yet settled. The pressure dependence of T_N and of the magnetic moment indicates an itinerant nature of the magnetism [13]. The itinerant character of magnetism in $CeRh_2Si_2$ has also been suggested from a systematic study of doping at Rh sites in $Ce(Rh_{1-x}Pd_x)_2Si_2$ [14]. However, the dHvA study suggests local moment magnetism in $CeRh_2Si_2$ at ambient pressure. Under the application of pressure the Fermi surface topology changes discontinuously, leading to an itinerant moment magnetism above the critical pressure

of around 1 GPa [15]. Pressure induced superconductivity has been observed around 1 GPa below 0.5 K [16, 17].

Heavy-fermion $YbRh_2Si_2$ has an antiferromagnetic ordering temperature T_N of ∼70 mK [1]. The antiferromagnetic order can be suppressed very easily by application of magnetic field or by substitution of Si by Ge, leading to a quantum critical point [2–4]. Electrical transport, thermodynamic and thermal expansion data reveal that the quantum critical point in $YbRh_2Si_2$ is of local nature, in contrast to the spin density wave type quantum critical point in $CeCu_2Si_2$ [18, 19].

Crystal field effects can have strong influence on the properties of Pr compounds. For example, the low lying crystal field excitations are responsible for the heavy fermion behavior in the unconventional superconductor $PrOs_4Sb_{12}$ [20–22]. Despite numerous investigations of RRh_2Si_2, we did not find any discussion in the literature on the properties of $PrRh_2Si_2$. In this paper we report the magnetization, specific heat, electrical resistivity and magnetoresistance of $PrRh_2Si_2$ single crystals. In addition, we also carried out pressure dependent electrical resistivity measurements.

2. Sample preparation and measurements

Single crystals of $PrRh_2Si_2$ were grown from indium flux as well as using the floating zone method in a mirror furnace (CSI Japan). Appropriate amounts of high purity elements (Pr 99.99%, La 99.9%, Rh 99.999% and Si 99.9999%) were arc melted several times on a water cooled copper hearth under argon atmosphere. The arc melted polycrystalline $PrRh_2Si_2$ and indium were taken in a molar ratio of 1:20 in an alumina crucible, which was then sealed inside a tantalum crucible with a partial pressure of argon gas. The sealed tantalum crucible was heated to 1450 °C under argon atmosphere for 2 h and then cooled down to 900 °C at a rate of 5 °C h^{-1}. Below 900 °C the rate of cooling was increased to 300 °C h^{-1}. Indium flux was removed by etching with dilute hydrochloric acid. We obtained single crystals of about 2.5 mm × 1.5 mm × 0.4 mm by this method. We also succeeded in growing a $PrRh_2Si_2$ single crystal using a float zone mirror furnace with 10 mm h^{-1} growth rate and counter-rotation of seed and feed rods. The diameter of the float zone grown crystal was about 6 mm.

Samples were characterized by Cu Kα x-ray diffraction and scanning electron microscope (SEM) equipped with energy dispersive x-ray analysis (EDAX). The Laue method was used to orient the single crystals. A commercial SQUID magnetometer was used to measure magnetization. Specific heat was measured using the relaxation method in a physical property measurement system (PPMS—Quantum Design). Electrical resistivity was measured by the standard ac four probe technique using the AC-transport option of the PPMS. Pressure studies of the electrical resistivity up to 2.3 GPa and in the temperature range 3 K $< T <$ 300 K were carried out utilizing a clamp-type double-layer pressure cell consisting of an inner cylinder made of NiCrAl and an outer body of Cu:Be. Silicone oil served as the pressure transmitting medium. The pressure inside the cell was determined at low temperature by the inductively measured shift of the superconducting transition temperature of lead.

3. Results and discussion

From the analysis of powder x-ray diffraction data of the crushed single crystals (figure 1), we find that $PrRh_2Si_2$ crystallizes in the $ThCr_2Si_2$-type tetragonal structure (space group $I4/mmm$) with the lattice parameters $a = 0.4079$ nm, $c = 1.0138$ nm, and the unit cell volume = 0.168 76 nm^3 for the flux grown sample, and $a = 0.4078$ nm, $c = 1.0138$ nm, and unit cell volume = 0.168 58 nm^3 for the float zone grown sample. The x-ray diffraction

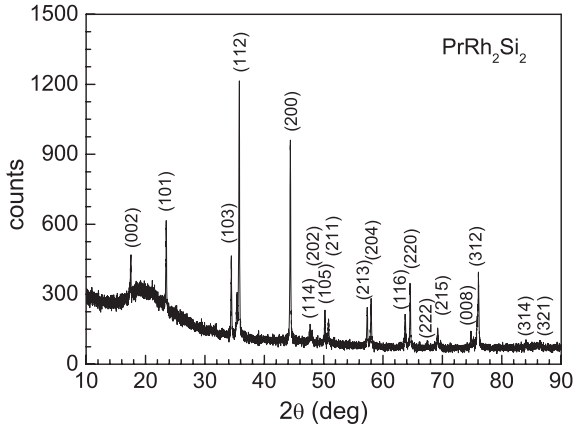

Figure 1. Indexed powder x-ray diffraction pattern of $ThCr_2Si_2$-type body-centered-tetragonal pulverized $PrRh_2Si_2$ single crystal (flux grown).

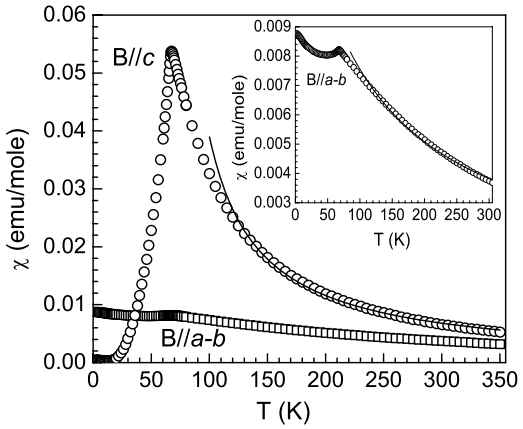

Figure 2. Temperature dependence of magnetic susceptibility of $PrRh_2Si_2$ single crystal (flux grown) measured in a field of 3.0 T. The inset shows the enlarged view of $B \parallel a$–b data. The solid lines represent the fit to Curie–Weiss behavior.

and SEM image confirmed the samples to be single phase. The EDAX composition analysis confirmed the desired stoichiometric composition of 1:2:2.

The temperature dependence of the magnetic susceptibility of the $PrRh_2Si_2$ single crystal is shown in figure 2 for magnetic field applied along the a–b plane and the c axis. A large anisotropy in the magnetic susceptibility $\chi(T)$ is observed. The susceptibility data have much larger values for $B \parallel c$ compared to that for $B \parallel a$–b, implying the easy axis to be the c axis. This anisotropic behavior is similar to the strong uniaxial anisotropy along the c axis in $CeRh_2Si_2$ [10] but different from the easy plane behavior observed in $YbRh_2Si_2$ [1]. Within a series of R–T–X compounds, the change of the magnetic anisotropy on changing the R element is governed by the change in the α_J second order Stevens factor within the CEF Hamiltonian [23]. A change from a uniaxial behavior in $CeRh_2Si_2$ and $PrRh_2Si_2$ to an easy plane behavior in $YbRh_2Si_2$ is in full accordance with $\alpha_J < 0$ for the Ce and Pr while $\alpha_J > 0$ for the Yb compound. Since in all three cases the anisotropy is very pronounced, it indicates a very large and positive A_2^0 CEF parameter in the whole RRh_2Si_2 series. An

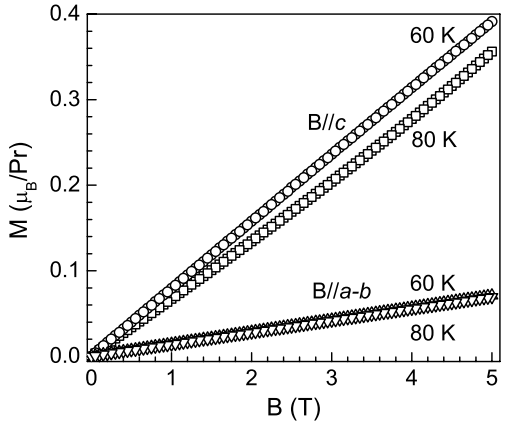

Figure 3. Field dependence of isothermal magnetization of $PrRh_2Si_2$ single crystal (flux grown) at 60 and 80 K along $B \parallel c$ and $B \parallel a$–b.

antiferromagnetic transition is observed in the susceptibility data at 68 K for both $B \parallel a$–b and $B \parallel c$. As expected for an antiferromagnet, T_N decreases with increasing magnetic field ($T_N = 66.5$ K at $B = 5$ T). The susceptibility data exhibit a slight deviation from the Curie–Weiss behavior $\chi(T) = C/(T - \theta_p)$ for both $B \parallel a$–b and $B \parallel c$ due to the effect of crystal fields. From the linear fit of inverse susceptibility data (100–300 K) at 3 T we obtain the effective magnetic moment $\mu_{eff} = 3.48\ \mu_B$ (very close to the theoretical value of 3.58 μ_B for Pr^{3+} ions) and the Curie–Weiss temperature $\theta_p^a = -103.2$ K for $B \parallel a$–b, and $\mu_{eff} = 3.63\ \mu_B$ and $\theta_p^c = +57.9$ K for $B \parallel c$. Further, we note a very pronounced peak and a rapid decrease of magnetic susceptibility to essentially zero value below 20 K for $B \parallel c$ and a much weaker temperature dependence for $B \parallel a$–b, which suggests strongly anisotropic Ising-type antiferromagnetism in $PrRh_2Si_2$ similar to that of $PrCo_2Si_2$ [24].

The isothermal magnetization data exhibit a linear dependence on field at 60 K (magnetically ordered state) and 80 K (paramagnetic state) for both $B \parallel a$–b and $B \parallel c$ (figure 3). The magnetic moments at 5 T are very small in both the directions (0.07 μ_B/Pr for $B \parallel a$–b and 0.39 μ_B/Pr for $B \parallel c$) and the maximum value attained is only 12% of the saturation magnetization for the Pr^{3+} ion (3.2 μ_B/Pr). Measurements at higher fields are required to observe the metamagnetic transitions which are expected in antiferromagnets with strong magneto-crystalline anisotropy.

The specific heat data of single-crystal $PrRh_2Si_2$ (indium flux grown) together with those of the nonmagnetic reference compound $LaRh_2Si_2$ are shown in figure 4. The specific heat of $PrRh_2Si_2$ exhibits a pronounced λ-type anomaly at 68 K, which confirms the intrinsic nature of antiferromagnetic ordering in this compound. The float zone grown single crystal of $PrRh_2Si_2$ also exhibits a similar well defined anomaly at 68 K due to antiferromagnetic order. The specific heat data of $PrRh_2Si_2$ and $LaRh_2Si_2$ hardly differ from each other below 20 K, showing that the magnetic excitations have vanished exponentially below 20 K. This indicates a large gap in the magnetic excitation spectra in the ordered state, which can obviously be attributed to the strong Ising-type anisotropy observed in the magnetic susceptibility data. The linear coefficient to the specific heat is $\gamma \sim 18$ mJ mol^{-1} K^{-2}. The temperature dependence of the magnetic entropy is shown as an inset in figure 4. At 70 K the magnetic entropy attains a value of 7.85 J mol^{-1} K^{-1}, which is 36% more than $R \ln 2$ and 14% lower than $R \ln 3$. Thus, either three singlets or one

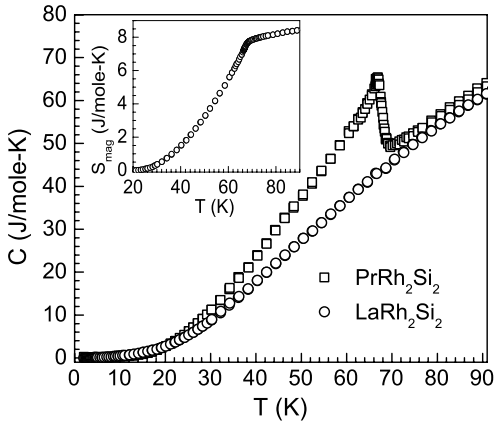

Figure 4. Temperature dependence of the specific heat of single-crystal $PrRh_2Si_2$ (flux grown) and polycrystalline $LaRh_2Si_2$ in the temperature range 2–90 K. The inset shows the magnetic contribution to the entropy of $PrRh_2Si_2$.

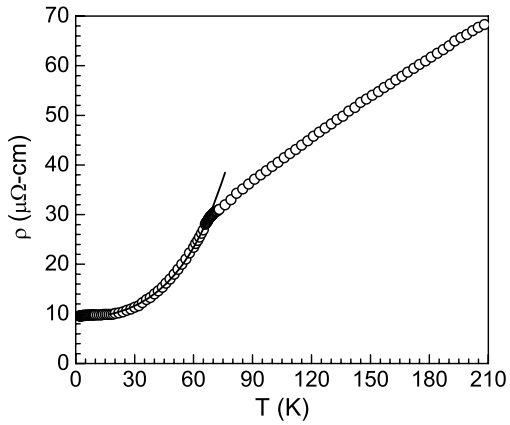

Figure 5. Temperature dependence of electrical resistivity ($I \parallel a$–b) of flux grown $PrRh_2Si_2$ single crystal in the temperature range 1.8–210 K. The solid line shows the fit to gapped magnon characteristics in the ordered state, i.e. $\rho(T) = \rho_0 + AT^2 + C\{\frac{1}{5}T^5 + \Delta T^4 + \frac{5}{3}\Delta^2 T^3\}\exp(-\Delta/T)$.

singlet and one doublet CEF levels are in the energy range below 80 K and involved in the magnetic ordering. Because of the huge uniaxial anisotropy and the general trend of the CEF parameters within the RRh_2Si_2 series, one can suspect that these lowest CEF levels are the two Γ_1 singlets and either the Γ_2 singlet or the Γ_5 doublet [25].

The electrical resistivity measured with ac current flowing in the a–b plane is shown in figure 5. The resistivity shows typical metallic behavior with room temperature resistivity $\rho_{300\ \mathrm{K}}$ of 85 $\mu\Omega$ cm, residual resistivity $\rho_0 \sim 9.6$ $\mu\Omega$ cm and residual resistivity ratio (RRR) ~ 9. A linear decrease of resistivity is observed with decreasing temperature until it meets the antiferromagnetic transition at 68 K, below which the resistivity shows a large decrease. In the ordered state the resistivity data present gapped magnon characteristics and fit well to the relation [26]

$$\rho(T) = \rho_0 + AT^2 + C\{\tfrac{1}{5}T^5 + \Delta T^4 + \tfrac{5}{3}\Delta^2 T^3\}\exp(-\Delta/T)$$

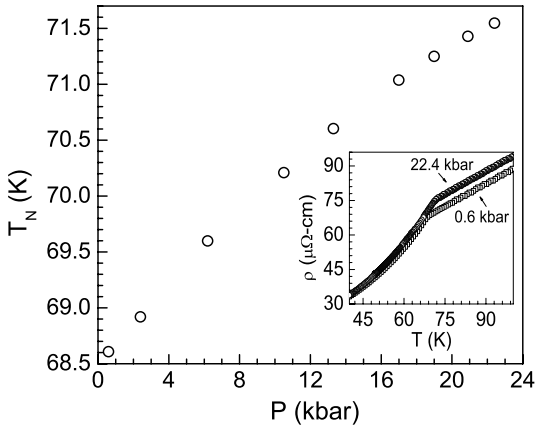

Figure 6. T_N of $PrRh_2Si_2$ as a function of externally applied pressure. The inset shows the temperature dependence of resistivity under pressure.

below 65 K (see figure 5) where $\rho_0 = 9.8\ \mu\Omega$ cm is the residual resistivity, $A = 0.002\,41\ \mu\Omega$ cm K^{-2} is the coefficient to the Fermi liquid term, $C = 8.96 \times 10^{-9}\ \mu\Omega$ cm K^{-5} is the prefactor to the magnon contribution and $\Delta = 37.8$ K is the magnon energy gap.

As both $CeRh_2Si_2$ and $YbRh_2Si_2$ exhibit strong pressure dependence in the electrical resistivity we have performed resistivity measurements on $PrRh_2Si_2$ under externally applied pressure. Up to 22.5 kbar there is no pronounced effect of externally applied pressure on the resistivity except an increase of T_N from 68.5 K at $p = 0$ to 71.5 K at $p = 22.5$ kbar (figure 6). A similar weak effect of pressure on the magnetically ordered state was also found in $PrCo_2Si_2$ [27].

From the de Gennes scaling in the family of RRh_2Si_2 (R = rare earths), one would expect an ordering temperature of 5.4 K in $PrRh_2Si_2$. While in $CeRh_2Si_2$ the anomalously high T_N might be a result of the mixture of localized and itinerant character of the magnetic order, we can not offer any clear reason for the high T_N of $PrRh_2Si_2$. Enhanced density of states as in the case of $GdRh_2Si_2$ and large value of exchange constant (as evidenced by large θ_p) definitely contribute to a higher value of T_N. It is also found that RRh_2Si_2 compounds which have higher values of T_N than expected on the basis of de Gennes scaling have their moments aligned along the c axis below T_N. $PrRh_2Si_2$ also has higher T_N than expected and the magnetic susceptibility data suggest that Pr moments lie along the c axis in this case also. We suspect the uniaxial anisotropy which forces the moment to lie along the c axis is also responsible for the high T_N in $PrRh_2Si_2$. A system with uniaxial anisotropy has much larger value of magnetic susceptibility for $B \parallel$ (easy-axis), which helps in the process of magnetic ordering. Thus T_N for a system with uniaxial anisotropy will be higher than that of an isotropic system or a weakly anisotropic system.

4. Conclusion

We succeeded in growing single crystals of $PrRh_2Si_2$, which forms in a $ThCr_2Si_2$-type body-centered tetragonal structure. Temperature dependent magnetic susceptibility, electrical resistivity, and specific heat data reveal strongly anisotropic Ising-type antiferromagnetic order below 68 K in this compound. Application of pressure up to 22.5 kbar does not stabilize any new ordered phase but T_N increases from 68 to 71.5 K.

Acknowledgment

Technical assistance from Mr Jochen Werner is gratefully acknowledged.

References

[1] Trovarelli O, Geibel C, Mederle S, Langhammer C, Grosche F M, Gegenwart P, Lang M, Sparn G and Steglich F 2000 *Phys. Rev. Lett.* **85** 626
[2] Gegenwart P, Custers J, Geibel C, Neumaier K, Tayama T, Tenya K, Trovarelli O and Steglich F 2002 *Phys. Rev. Lett.* **89** 056402
[3] Plessel J, Abd-Elmeguid M M, Sanchez J P, Knebel G, Geibel C, Trovarelli O and Steglich F 2003 *Phys. Rev.* B **67** 180403(R)
[4] Custers J, Gegenwart P, Wilhelm H, Neumaier K, Tokiwa Y, Trovarelli O, Geibel C, Steglich F, Pépin C and Coleman P 2003 *Nature* **424** 524
[5] Felner I and Nowik I 1983 *Solid State Commun.* **47** 831
[6] Tung L D, Franse J J M, Buschow K H J, Brommer P E and Thuy N P 1997 *J. Alloys Compounds* **260** 35
[7] Szytula A, Ślaski M, Ptasiewicz-Bak H, Leciejewicz J and Zygmunt A 1984 *Solid State Commun.* **52** 395
[8] Ślaski M, Leciejewicz J and Szytula A 1983 *J. Magn. Magn. Mater.* **39** 268
[9] Melamud M, Pinto H, Felner I and Shaked H 1984 *J. Appl. Phys.* **55** 2034
[10] Quezel S, Rossat-Mignod J, Chevalier B, Lejay P and Etourneau J 1984 *Solid State Commun.* **49** 685
[11] Hossain Z, Trovarelli O, Geibel C and Steglich F 2001 *J. Alloys Compounds* **323/324** 396
[12] Graf T, Hundley M F, Modler R, Movshovich R, Thompson J D, Mandrus D, Fisher R A and Phillips N E 1998 *Phys. Rev.* B **57** 7442
[13] Kawarazaki S, Sato M, Miyako Y, Chigusa N, Watanabe K, Metoki N, Koike Y and Nishi M 2000 *Phys. Rev.* B **61** 4167
[14] Gómez Berisso M, Pedrazzini P, Sereni J G, Trovarelli O, Geibel C and Steglich F 2002 *Eur. Phys. J.* B **30** 343
[15] Araki S, Settai R, Kobayashi T C, Harima H and Ōnuki Y 2001 *Phys. Rev.* B **64** 224417
[16] Movshovich R, Graf T, Mandrus D, Thompson J D, Smith J L and Fisk Z 1996 *Phys. Rev.* B **53** 8241
[17] Araki S, Nakashima M, Settai R, Kobayashi T C and Ōnuki Y 2002 *J. Phys.: Condens. Matter* **14** L377
[18] Gegenwart P, Langhammer C, Geibel C, Helfrich R, Lang M, Sparn G, Steglich F, Horn R, Donnevert L, Link A and Assmus W 1998 *Phys. Rev. Lett.* **81** 1501
[19] Stockert O, Faulhaber E, Zwicknagl G, Stüßer N, Jeevan H S, Deppe M, Borth R, Küchler R, Loewenhaupt M, Geibel C and Steglich F 2004 *Phys. Rev. Lett.* **92** 136401
[20] Bauer E D, Frederick N A, Ho P-C, Zapf V S and Maple M B 2002 *Phys. Rev.* B **65** 100506(R)
[21] Goremychkin E A, Osborn R, Bauer E D, Maple M B, Frederick N A, Yuhasz W M, Woodward F M and Lynn J W 2004 *Phys. Rev. Lett.* **93** 157003
[22] Thalmeier P 2006 *Physica* B **378–380** 261
[23] See e.g. Buschow K H J and de Boer F R 2003 *Physics of Magnetism and Magnetic Materials* (Dordrecht: Kluwer Academic/Plenum) p 56
[24] Shigeoka T, Fujii H, Yonenobu K, Sugiyama K and Date M 1989 *J. Phys. Soc. Japan* **58** 394
[25] Santini P, Amoretti G, Blaise A and Caciuffo R 1993 *J. Appl. Phys.* **73** 6560
[26] Jobiliong E, Brooks J S, Choi E S, Lee H and Fisk Z 2005 *Phys. Rev.* B **72** 104428
[27] Kawano S, Onodera A, Achiwa N, Nakai Y, Shigeoka T and Iwata N 1995 *Physica* B **213/214** 321