Structure and electrical resistivity of mixed-valent $EuNi_2P_2$ at high pressure

Structure and electrical resistivity of mixed-valent EuNi$_2$P$_2$ at high pressure

S A Medvedev[1]**, P Naumov**[1]**, O Barkalov**[1]**, C Shekhar**[1]**,T Palasyuk**[2]**,
V Ksenofontov**[3] **and C Felser**[1,3]

[1] Max-Planck-Institute for Chemical Physics of Solids, D-01187 Dresden, Germany
[2] Institute of Physical Chemistry, Polish Academy of Sciences, PL-01224 Warsaw, Poland
[3] Institut für Anorganische und Analytische Chemie, Johannes Gutenberg-Universität, D-55099 Mainz, Germany
[4] Department Physik, Universität Paderborn, D-33095 Paderborn, Germany

E-mail: medvedie@cpfs.mpg.de

Abstract
The structural properties and electrical resistivity of homogeneous mixed-valent EuNi$_2$P$_2$ are studied at pressures up to 45 GPa. No structural phase transition is observed in the whole pressure range and the overall pressure behavior of the structural parameters is similar to that of related compounds in the collapsed tetragonal ThCr$_2$Si$_2$-type structure. Electrical resistivity measured up to 31 GPa at temperatures between 4 and 300 K exhibits continuous changes from the behavior typical for a mixed-valent Eu system to that of a normal metallic system at pressures above 20 GPa, indicating a transition of the strongly mixed-valent Eu atoms with a valence ~2.5 towards a pure trivalent state. No superconductivity was observed in the whole studied pressure-temperature range.

Keywords: mixed valence, high pressure, EuNi$_2$P$_2$

(Some figures may appear in colour only in the online journal)

1. Introduction

The peculiar physical properties of compounds based on rare-earth elements with unstable valence such as Ce, Eu and Yb, resulting in different phenomena such as valence fluctuations, spin fluctuations, the Kondo effect, heavy-fermion behavior and superconductivity, have attracted sustained interest in condensed matter physics in recent decades [1, 2]. The phenomenological description of these properties has been distinguished for Ce- and Yb-compounds between integer-valent Kondo- or intermediate-valent systems with properties resulting from a quantum mixing of two valence states induced by the hybridization between localized 4f electrons and conduction electrons [3, 4]. For mixed-valent Eu systems the properties were described as due to thermal fluctuations between two integer-valent Eu^{2+} and Eu^{3+} states with drastically different properties resulting from their 4f-configurations: 4f^7 with a $J = S = 7/2$ magnetic state for Eu^{2+}, providing a model system for pure spin magnetism, and the formally non-magnetic Eu^{3+} with a 4f^6 configuration, resulting in a non-magnetic $J = 0$ ground state, modified by the higher multiplett states with $J = 1, 2, 3\ldots$ populated by temperature and the Boltzmann factors according to their energy position above $J = 0$ [5].

Recent studies, however, also evidenced similarities between the properties of Ce-/Yb-systems and mixed-valent Eu systems. Optical conductivity [6], angle resolved photoemission [7] and x-ray magnetic circular dichroism studies [8] of EuNi$_2$P$_2$, a well-known and often investigated homogenously mixed-valent system, suggest that the hybridization between 4f and conduction electrons, which is responsible for the properties of Ce and Yb-systems, also plays an important role in mixed-valent Eu-systems. Similar conclusions were drawn in a recent study of Eu(Rh$_{1-x}$Ir$_x$)$_2$Si$_2$ [9]. Very recent studies of electronic and magnetic properties of EuNi$_2$P$_2$ revealed a heavy-fermion state based on the Kondo effect similarly to the prototypical heavy-fermion compound CeRu$_2$Si$_2$ [10].

Valence fluctuations might be of relevance for pressure-induced superconductivity, since T_c values as high as 30 K were recently observed in EuFe$_2$As$_2$ at pressures in the

vicinity of the onset of the Eu valence transition [11, 12]. This is an important aspect, since valence fluctuations appear in classical heavy-fermion systems [13], and Ce-valence fluctuations are considered to be responsible for high-pressure superconductivity in the classical heavy-fermion system $CeCu_2Si_2$ and related compounds with $ThCr_2Si_2$ structure. In this structure, superconductivity has also been observed in the closely related phosphide $LaRu_2P_2$ [14] and theoretically predicted in $SrRh_2P_2$ and related compounds by appropriate doping [15]. Therefore the investigated system, $EuNi_2P_2$, is of actual interest, because by application of pressure the Eu valence, and therefore modifications of the conduction band by $4f$ electron transfer and $4f$-hybridization, may induce electronic variations resulting in superconductivity.

Here we present the results of pressure dependent structural and electrical resistivity studies of the homogeneously mixed-valent $EuNi_2P_2$, which is unique among the mixed-valent Eu-compounds since the Eu valence is only weakly temperature dependent and remains close to 2.5, even at low temperatures instead of approaching 3. Therefore valence fluctuations in $EuNi_2P_2$ are significant even at cryogenic temperatures [16] as well as at elevated pressures [17].

2. Experimental methods

The polycrystalline sample of $EuNi_2P_2$ was prepared by solid-state reaction at ambient pressure by using high purity Eu (99.99%), Ni (99.999%) and P (99.99%) powders. The powders were thoroughly mixed in stoichiometric amounts and cold pressed into pellets. Then the pellets were sealed in an evacuated quartz tube and heated at a temperature of 900 °C for 24 h. This heat treatment was repeated at 1050 °C with intermediate grinding for better homogeneity. The synthesized sample was characterized by a laboratory x-ray diffraction technique. All diffraction peaks perfectly match the tetragonal $ThCr_2Si_2$ crystal structure of space group $I4/mmm$, the resulting lattice parameters $a = 3.941$ Å and $c = 9.477$ Å are very close to previous results [18, 19].

For the high pressure studies diamond anvil cells (DAC) equipped with diamonds with a 500 μm culet were used. The angle-dispersive x-ray diffraction studies were performed at room temperature at the beamline 01C2 of the National Synchrotron Radiation Research Centre (NSRRC, Taiwan, wavelength 0.564 Å) and at the beamline ID09 of the European Synchrotron Radiation Facility (ESRF, France, wavelength 0.4145 Å). For these studies, tungsten gaskets preindented to ~35 μm thickness were used. The powdered sample was loaded in a sample chamber of ~180 μm diameter with silicone oil as a pressure transmitting medium.

The pressure dependence of the electrical resistance between 4 and 300 K and up to 31 GPa was measured by the dc current van der Pauw technique (with a current of 32 μA) in a DAC equipped with a spring to ensure pressure stability against the temperature-driven contraction of the cell upon cooling [20, 21]. For insulating against the metallic gasket, a mixture of cubic BN with epoxy was used. The electrical leads were cut from a 5 μm thick Pt foil. The sample chamber had
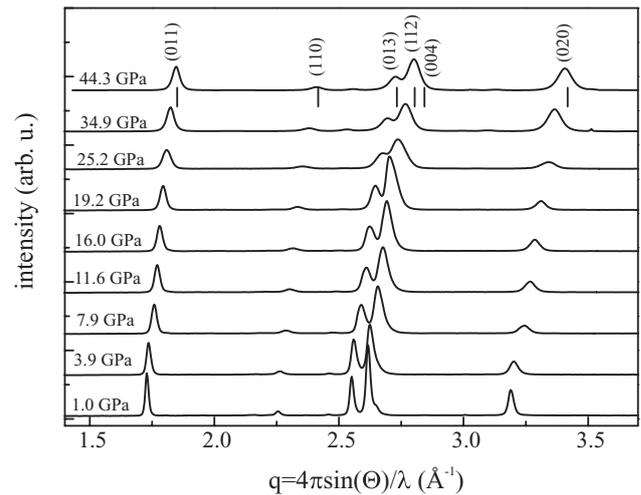
Figure 1. X-ray diffraction patterns of $EuNi_2P_2$ at different pressures. The pattern collected at 44.3 GPa is indexed with tetragonal $ThCr_2Si_2$-type structure, as indicated by the indexes above the calculated reflection positions.

a diameter of 150 μm and an initial thickness of 50 μm. The sample was loaded without a pressure transmitting medium. In both sets of experiments, the pressure was determined by the ruby luminescence method.

3. Results and discussion

3.1. XRD studies of $EuNi_2P_2$

X-ray diffraction (XRD) patterns of $EuNi_2P_2$ recorded at different pressures at room temperature are shown in figure 1. Up to the highest pressure the sample can be indexed with the $ThCr_2Si_2$-type structure. Lattice parameters at the lowest pressures are in agreement with the values at ambient pressure [18, 19]. As can be seen in figure 2, the lattice parameters and unit cell volume are reduced smoothly with increasing pressure, with no evidence of a structural phase transition as observed in the several Eu-transition metal pnictides with $ThCr_2Si_2$-type structure [22–25]. The reason is that $EuNi_2P_2$ is already in the so-called collapsed tetragonal (CT) phase, which is obtained in other isostructural EuT_2X_2 compounds (with T = Co, Fe and X = P, As [18]) under application of high pressure with first or second-order phase transitions as exemplified for $EuFe_2As_2$ and $EuCo_2As_2$ [24, 25]. These phase transitions are approached by quite an unusual variation of the a- and c-axes, here an increase of the a-axis under pressure, reflected also in a strong decrease of the c/a ratio with pressure. This c/a ratio is around 3.0 for the normal tetragonal phase at ambient pressure, e.g. for $EuFe_2As_2$, $EuCo_2P_2$ and $EuFe_2P_2$ at 3.10, 3.01, and 2.94, respectively [22, 23]). In the CT phase, the c/a ratios are markedly smaller, below 2.5 for the above compounds at high pressure. $EuNi_2P_2$ has with $c/a = 2.408$ an even smaller ratio, which corresponds to a P-P distance along the c-axis of 2.37 Å. This is in the range of a P-P single bond [18, 19, 26], whereas much longer P-P distances in other Eu-T-pnictides (e. g. 3.27 Å in $EuCo_2P_2$ [19]) imply essentially no P-P bonding along the c-axis.
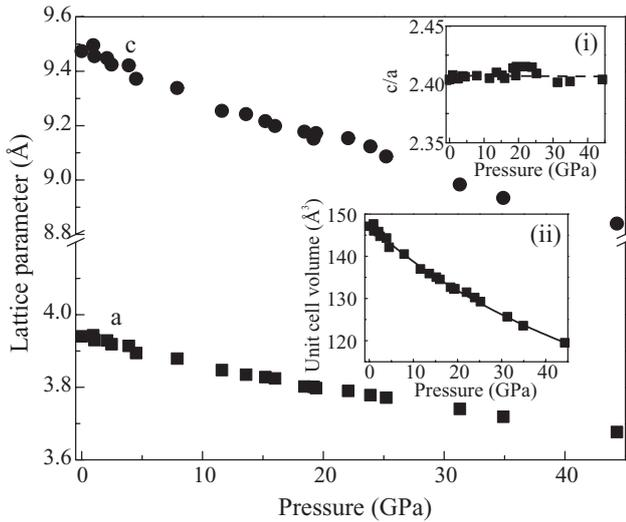
Figure 2. Pressure dependence of lattice parameters of the tetragonal unit cell of $EuNi_2P_2$. Inset (i) shows the c/a ratio, remaining near unchanged around the value 2.408(0.003) over the studied pressure range. Inset (ii) shows the fit of the Birch-Murnaghan equation of state to the experimental pressure-volume data with $B = 147.9$ GPa and $B_0' = 3.4$. The error bars of the lattice parameters are smaller than the symbols size.

The $ThCr_2Si_2$-type structure of $EuNi_2P_2$ appears to be stable over the whole studied pressure range similarly to the stability of the CT phase in related compounds up to very high pressures [24, 25]. The c/a ratio remains essentially unchanged throughout the studied pressure range up to 45 GPa, see inset (i) in figure 2. Thus, the crystalline lattice of $EuNi_2P_2$ shrinks quite uniformly, similar to the behavior observed in the high pressure CT phases of the other related compounds [22–25]. A fit of the Birch-Murnaghan equation-of-state to the experimental pressure-volume data, see inset (ii) of figure 2, reveals for $EuNi_2P_2$ a bulk modulus and its pressure derivative values $B_0 = 147.9(3.1)$.GPa and $B_0' = 3.4(0.5)$. These values compare well with available data for a collapsed tetragonal phase of Eu-transition metal pnictides, e.g. $B_0 = 134.0(1.6)$.GPa and $B_0' = 3.3(0.2)$ for $EuFe_2As_2$ [24], and $B_0 = 111.0(2.0)$.GPa and $B_0' = 3.06$ for $EuCo_2As_2$ [25].

3.2. High pressure resistivity studies of $EuNi_2P_2$

The temperature dependence $(4 K < T < 300 K)$ of the electrical resistivity $\rho(T)$ of $EuNi_2P_2$ for different pressures up to 31 GPa is shown in figure 3(*a*). There is no evidence of a superconducting transition above 4 K in the whole studied pressure range.

Our data at the lowest pressure are in good qualitative agreement with published resistivity data at ambient pressure [6, 27]. Upon cooling at 0.4 GPa the resistivity first increases slightly, then passes through a broad maximum around 150 K followed by a rapid decrease towards low temperatures. At low temperatures a Fermi-liquid behavior with a T^2-dependence of resistivity is observed over a significant temperature range up to 30 K (figure 3(*b*)), also in agreement with the recent data on $EuNi_2P_2$ single crystals at ambient

pressure, exhibiting characteristic differences for different crystal orientations [6, 10].

Such S-shaped $\rho(T)$ curves observed in $EuNi_2P_2$ at low pressures are typical for Eu-based valence fluctuating systems [27, 28]. Qualitatively this resistivity anomaly can be described by a dynamic alloy model [29]. The mixed-valent Eu-system can be considered as an alloy containing Eu^{2+} and Eu^{3+} ions with corresponding occupation probabilities p_2 and p_3. At each temperature the minority Eu-ions are described as 'impurities' producing an elastic Coulomb scattering potential for the conduction electrons. This scattering potential is not static but fluctuates due to the fact that the Eu-ions are fluctuating between two valence states. The scattering potential does not explicitly depend on temperature but indirectly by the temperature variation of mean valence (occupation probabilities p_2 and p_3). Thus, the largest scattering of the conduction electrons arises at a temperature where the system shows the steepest valence change, which gives rise to a resistivity maximum [29, 30]**.**

With increasing pressure, the maximum in the resistivity curve shifts towards higher temperatures and tends to be smeared out, so above 7.5 GPa the resistivity increases monotonically with temperature up to 300 K, although an anomalous curvature of the $\rho(T)$ dependence with indication of saturation at higher temperatures is still observable at pressures up to 16 GPa. At pressures above 20 GPa, the $\rho(T)$ dependence of $EuNi_2P_2$ is characteristic of a normal metal. Note that there are only minor differences between $\rho(T)$ curves at 24 and 31 GPa, which can be attributed solely to the volume reduction under compression. Thus there is strong evidence that Eu is in the trivalent state at pressures above 24 GPa, also from comparison with the resistivity curve $EuNi_2Si_2$, where Eu is trivalent [27]. This pressure seems to be sufficient for a full transition into the trivalent state. These arguments are further supported by a high-pressure Mössbauer study of $EuNi_2P_2$, where at 4.2 K Eu valence changes from 2.55 at ambient pressure already to 2.8 at 9.5 GPa [17].

The low temperature resistivity of $EuNi_2P_2$ at all pressures exhibits a Fermi-liquid behavior according to $\rho(T) = \rho_0 + AT^2$ (figure 3(*b*)). The value of A decreases strongly with increasing pressures up to 7 GPa and then approaches small values at higher pressures (figure 3(*c*)). Similar high-pressure behavior was reported for heavy-fermion compounds when application of pressure increases the hybridization between f–states and conduction bands causing the strong increase of Kondo-temperature T_K and the change of $\rho(T)$ dependence indicating a crossover to an intermediate-valence state [31, 32].

The overall pressure behavior of the $\rho(T)$ dependence in $EuNi_2P_2$ remarkably closely resembles the resistivity behavior in $CeCu_2Si_2$ at pressures above 8 GPa, here *above* the second superconducting dome [32]. The pressure phase diagram of this archetypical heavy-fermion compound (and its structural relatives $CeCu_2Ge_2$ and $CeCu_2(Si_{1-x}Ge_x)_2$ [32–34]) reveals the existence of two distinct domes of different superconducting phases. The one low pressure is close to an antiferromagnetic quantum critical point and superconductivity is induced by magnetically mediated electron pairing. The second dome at higher pressures coincides with a first-order
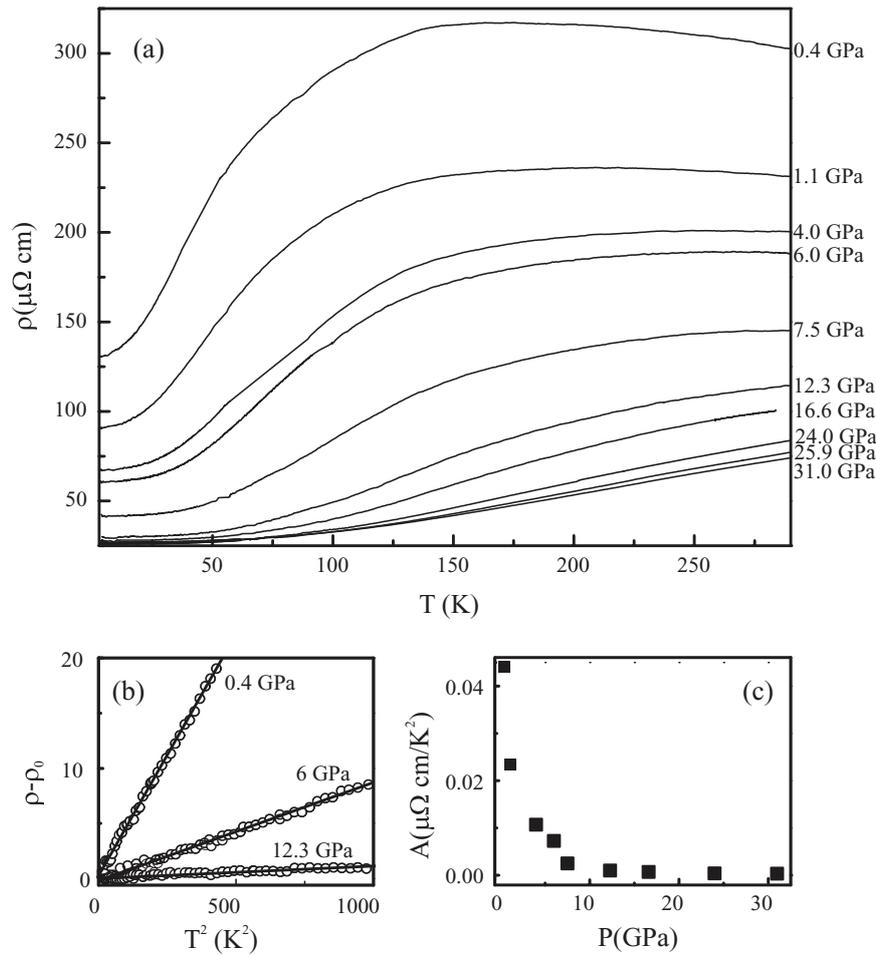
Figure 3. (*a*) The $\rho(T)$ isobars of $EuNi_2P_2$ at different pressures denoted on the right. (*b*) Plot of the low-temperature resistivity versus T^2 at selected pressures, exemplifying the Fermi-liquid behavior. The straight lines represent fits of $\rho(T) = \rho_0 + AT^2$ to the data. (*c*) Plot of the pressure variation of the A coefficient derived from these fits.

isostructural phase transition with a weak volume collapse [33, 35] indicating a transition into the intermediate-valence state. Superconductivity in this phase is supposed to be driven by critical Ce-valence fluctuations [33, 36–38]. $EuNi_2P_2$ as a strongly mixed-valent and non-magnetic system with CT structure is obviously beyond the region of a critical valence transition and therefore superconductivity is not observed. It is worth noting that in the intensively studied family of iso-structural iron pnictides, AFe_2As_2 (A = Ba, Sr, Ca), the pressure induced non-magnetic CT structure is believed to be non-superconducting [39]. Thus the similarity between the high-pressure behavior of resistivity in $EuNi_2P_2$ and the archetypical heavy-fermion compound $CeCu_2Si_2$ implies that heavy-fermion or Kondo behavior might be expected in related Eu compounds. So, the heavy-fermion state based on the Kondo effect in $EuNi_2P_2$ reported very recently [10] also shows similarities with the prototypical heavy-fermion compound $CeRu_2Si_2$. Our present results on the high-pressure behavior of $EuNi_2P_2$ provide further similarities between the properties of Ce-based systems and mixed-valent Eu-systems. Further insight can be achieved by the substitution of Ni by earlier transition elements (Fe, Co) or of P by more electronegative atoms as supposed in recent optical and photoemission studies of $EuNi_2P_2$ [6, 7]. Indeed, evidence for dense Kondo behavior

in $EuFe_2P_2$ has been recently reported [40] and therewith one might expect the observation of superconductivity under pressure to be analogous to the closely related $BaNi_2(Ge_{1-x}P_x)_2$ system [41], where the transition to the collapsed phase above $x = 0.5$ obviously induced superconductivity with $T_c = 2.9$ K at $x = 0.8$ and $T_c = 2.5$ K for $BaNi_2P_2$ [41]. We will proceed with our investigations in these directions.

4. Conclusions

Structural properties and electrical resistivity of homogeneous mixed-valent $EuNi_2P_2$ have been studied at pressures up to 45 GPa. The tetragonal structure of $EuNi_2P_2$ is stable in the whole pressure range and the overall pressure behavior of the structural parameters is similar to that of related compounds in the collapsed tetragonal $ThCr_2Si_2$-type structure. Electrical resistivity measured up to 31 GPa at temperatures between 4 and 300 K exhibits continuous changes from the behavior typical for a mixed-valent Eu system to that of a normal metallic system at pressures above 20 GPa indicating a transition of the strongly mixed-valent Eu atoms with an initial valence of ~2.5 towards a pure trivalent state. No superconductivity was observed in the whole studied pressure-temperature range.

Acknowledgment

References

[1] Falicov L M, Hanke W and Maple M B (eds) 1981 *Valence Fluctuations in Solids. Int. Conf. on Valence Fluctuations in Solids* (Amsterdam: North-Holland)

[2] Müller-Hartmann E, Roden B and Wohlleben D (eds) 1985 *Proc. Int. Conf. on Valence Fluctuations (Colgne, Germany, 27–30 August 1984) J. Magn. Magn. Mater.* **47–48**

[3] Gegenwart P, Si Q and Steglich F 2008 *Nat. Phys.* **4** 186

[4] Si Q, and Steglich F 2010 *Science* **329** 1161

[5] Franz W, Steglich F, Zell W, Wohlleben D and Pobell F 1980 *Phys. Rev. Lett.* **45** 64

[6] Guritanu V, Seiro S, Sichelschmidt J, Caroca-Canales N, Iizuka T, Kimura S, Geibel C and Steglich F 2012 *Phys. Rev. Lett.* **109** 247207

[7] Danzenbächer S *et al* 2009 *Phys. Rev. Lett.* **102** 026403

[8] Matsuda Y H, Ouyang Z W, Nojiri H, Inami T, Ohwada K, Suzuki M, Kawamura N, Mitsuda A and Wada H 2009 *Phys. Rev. Lett.* **103** 046402

[9] Seiro S and Geibel C 2011 *J. Phys.: Condens. Matter* **23** 375601

[10] Hiranaka Y *et al* 2013 *J. Phys. Soc. Japan* **82** 083708

[11] Miclea C F, Nicklas M, Jeevan H S, Kasinathan D, Hossain Z, Rosner H, Gegenwart P, Geibel C and Steglich F 2009 *Phys. Rev.* B **79** 212509

[12] Matsubayashi K *et al* 2011 *Phys. Rev.* B **84** 024502

[13] Watanabe S and Miyake K 2012 *J. Phys.: Condens. Matter* **24** 294208

[14] Jeitschko W, Glaum R and Boonk L 1987 *J. Solid State Chem.* **69** 93

[15] Johrendt D, Felser C, Jepsen O, Andersen O K, Mewis A and Rouxel J 1997 *J. Solid State Chem.* **130** 254

[16] Nagarajan R, Shenoy G K, Gupta L C and Sampathkumaran E V 1985 *J. Magn. Magn. Mater.* **47** 413

[17] Perscheid B, Sampathkumaran E V and Kaindl G 1985 *J. Magn. Magn. Mater.* **47** 410

[18] Jeitschko W and Jaberg B 1980 *J. Solid State Chem.* **35** 312

[19] Marchand R and Jeitschko W J 1978 *Solid State Chem.* **24** 351

[20] Gavriliuk A G, Mironovich A A and Struzhkin V V 2009 *Rev. Sci. Instrum.* **80** 043906

[21] Eremets M I 1996 *High Pressure Experimental Methods* (Oxford: Oxford University Press)

[22] Huhnt C, Schlabitz W, Wurth A, Mewis A and Reehuis M 1997 *Phys. Rev.* B **56** 13796

[23] Huhnt C, Schlabitz W, Wurth A, Mewis A and Reehuis M 1998 *Physica* B **252** 44

[24] Uhoya W, Tsoi G, Vohra Y K, McGuire M A, Sefat A S, Sales B C, Mandrus D and Weir S T 2010 *J. Phys.: Condens. Matter* **22** 292202

[25] Bishop M, Uhoya W, Tsoi G, Vohra Y K, Sefat A S and Sales B C 2010 *J. Phys.: Condens. Matter* **22** 425701

[26] Hoffmann R and Zheng C 1985 *J. Phys. Chem.* **89** 4175

[27] Patil S, Nagarajan R, Gupta L C, Padalia B D and Vijayaraghavan R 1990 *Solid State Commun.* **76** 1173

[28] Patil S, Nagarajan R, Gupta L C, Padalia B D and Vijayaraghavan R 1990 *Physica* B **163** 340

[29] Wohlleben D and Wittershagen B 1985 *Adv. Phys.* **34** 403

[30] Wada H, Hundley M F, Movshovich R and Thompson J D 1999 *Phys. Rev.* B **59** 1141

[31] Kagayama T, Oomi G, Takahashi H, Mori N, Onuki Y and Komatsubara T 1992 *J. Alloys Compounds* **181** 185

[32] Bellarbi B, Benoit A, Jaccard D, Mignot J M and Braun H F 1984 *Phys. Rev.* B **30** 1182

[33] Yuan H Q, Grosche F M, Deppe M, Geibel C, Sparn G and Steglich F 2003 *Science* **302** 2104

[34] Kobayashi T C, Miyazu T, Takeshita N, Shimizu K, Amaya K, Kitaoka Y and Onuki Y 1998 *J. Phys. Soc. Japan* **67** 996

[35] Onodera A, Tsuduki S, Ohishi Y, Watanuki T, Ishida K, Kitaoka Y and Onuki Y 2002 *Solid State Commun.* **123** 113

[36] Onishi Y and Miyake K 2000 *J. Phys. Soc. Japan* **69** 3955

[37] Holmes A T, Jaccard D and Miyake K 2004 *Phys. Rev.* B **69** 024508

[38] Miyake K 2007 *J. Phys.: Condens. Matter* **19** 125201

[39] Soh J H *et al* 2013 *Phys. Rev. Lett.* **111** 227002

[40] Feng C M, Ren Z, Xu S G, Jiang S A, Xu Z A, Cao G H, Nowik I, Felner I, Matsubayashi K and Uwatoko Y 2010 *Phys. Rev.* B **82** 094426

[41] Hirai D, von Rohr F and Cava R J 2012 *Phys. Rev.* B **86** 100505