

This is the accepted manuscript made available via CHORUS. The article has been published as:

Effect of pressure on superconductivity in NaAlSi

Leslie Schoop, Lukas Mchler, Jennifer Schmitt, Vadim Ksenofontov, Sergey Medvedev, Jrgen Nuss, Frederick Casper, Martin Jansen, R. J. Cava, and Claudia Felser

Phys. Rev. B **86**, 174522 — Published 30 November 2012

DOI: [10.1103/PhysRevB.86.174522](https://doi.org/10.1103/PhysRevB.86.174522)

The effect of pressure on superconductivity in NaAlSi

Leslie Schoop^{1,2,*}, Lukas MÜchler³, Jennifer Schmitt⁴, Vadim Ksenofontov⁴, Sergey Medvedev³, Jürgen Nuss⁵, Frederick Casper⁴, Martin Jansen⁵, R. J. Cava², and Claudia Felser^{3,4}

¹*Graduate School Material Science in Mainz, 55099 Mainz, Germany.*

²*Department of Chemistry, Princeton University, Princeton New Jersey 08544, USA.*

³*Max-Planck-Institut für Chemische Physik fester Stoffe, 01187 Dresden, Germany.*

⁴*Institut für Anorganische und Analytische Chemie,*

Johannes Gutenberg - Universität, 55099 Mainz, Germany. and

⁵*Max-Planck-Institut für Festkörperforschung Heisenbergstr. 1 70569 Stuttgart, Germany.*

(Dated: November 19, 2012)

The ternary superconductor NaAlSi, isostructural with LiFeAs, the '111' iron pnictide superconductor, is investigated under pressure. The structure remains stable up to 15 GPa. Resistivity and susceptibility measurements show an increase of T_c up to 2 GPa, followed by a decrease until superconductivity disappears at 4.8 GPa. Band structure calculations show that pressure should have a negligible effect on the electronic structure and the Fermi surface and thus the disappearance of superconductivity under pressure must have a different origin. We compare the electronic structure of NaAlSi under pressure with that of non superconducting isostructural NaAlGe.

PACS numbers: 71.20.-b 74.25.-q 74.62.Fj

I. INTRODUCTION

The ternary compound NaAlSi has been reported to be a conventional type II superconductor with a transition temperature of 7 K¹. This material crystallizes in the same structure as the '111' Fe-based superconductor LiFeAs (PbFCl-type, space group $P4/nmm$, $Z=2$)². The sp^3 hybridized Al and Si atoms form layers of edge-sharing tetrahedra, with Na layers sandwiched between them. There are also other known silicide superconductors i.e. CaAlSi and SrAlSi, which crystallize in a ternary version of the AlB_2 -type crystal structure, where Al and Si form hexagonal graphite-like layers³. In terms of the crystal structure, therefore, NaAlSi is comparable to LiFeAs while CaAlSi is comparable to MgB_2 . NaAlSi can therefore be seen as the non magnetic counterpart of LiFeAs, similar to how superconducting SnO is a nonmagnetic counterpart to isostructural superconducting FeSe⁴. The analysis of SnO showed that the Fermi surface topology and the degree of nesting are important for the superconductivity, but that spin fluctuations are not essential for the appearance of superconductivity in the '11' structure type; rather, the spin fluctuations increase the coupling and thereby the T_c . Similarly, the Fermi surfaces of NaAlSi and LiFeAs have been shown to have similarities⁵.

Density functional calculations have suggested that NaAlSi is a self doped low carrier density semi metal⁵. The density of states (DOS) shows a sharp peak within a pseudogap; the Fermi level lies at the upper slope. This peak has been associated with the transport and superconducting properties of NaAlSi⁵. NaAlGe, which crystallizes in the same structure and has a similar electronic structure, is not superconducting above 1.8 K¹. It was suggested that the high frequency phonons present in NaAlSi due to the lighter mass of Si play an important role for the superconductivity and therefore that NaAlSi is a BCS type superconductor¹. Due to the large energy scale available in pressure experiments, the effect of pressure on the superconducting transition temperature is of special interest. Pressure has been shown to influence T_c in various ways. In Fe-based superconductors, for example, pressure can increase T_c ⁶⁻¹², decrease T_c ^{13,14} or induce superconductivity¹⁵⁻¹⁷. In LiFeAs, however, T_c decreases with applied pressure¹⁴. In CaAlSi, pressures up to 2 GPa increase T_c , but in isostructural SrAlSi it is decreased¹⁸. Pressure can also induce structural phase transitions which can affect the superconducting properties dramatically, as in FeSe where a structural phase transition destroys the superconductivity⁶.

In this paper we report susceptibility and resistivity measurements performed on NaAlSi under pressure, showing an increase of T_c up to 2 GPa followed by a decrease until superconductivity disappears rather abruptly at around 4.8 GPa. X-ray diffraction experiments under pressure show that the crystal structure remains stable up to 14.77 GPa, thus the disappearance of superconductivity is occurring within the '111' structure type regime. The effect of pressure on the electronic structure and the Fermi surface topology is investigated with density functional theory.

II. EXPERIMENTAL

NaAlSi was prepared by reacting the elements with a considerable excess of sodium, in the ratio of Na:Al:Si = 3:1:1. Since elemental sodium is very sensitive to air and moisture, all operations were performed under dried argon (Schlenktechnique or glove box with H_2O , $O_2 < 0.1$ ppm; MB 150B-G-II, M. Braun GmbH, Munich, Germany).

The starting materials (1-2 g) were placed in a tantalum tube, which was sealed under argon with an arc-welder. In order to prevent oxidation, the tantalum tube was encapsulated in a glass jacket under argon. The reaction mixture was heated with a rate of 50 K/h up to 970 K, annealed at this temperature for three days, and then cooled to room temperature at a rate of 50 K/h. In a second step, the excess sodium was distilled off the sample under a dynamic vacuum (10^{-4} mbar) at 500 K. Blue-metallic crystalline NaAlSi was obtained as a single phase product. The phase purity and crystal structure of the sample was verified by powder and single crystal X-ray diffraction using a D8 Focus diffractometer with $CuK_{\alpha 1}$ radiation and a graphite diffracted beam monochromator, and a SMART-APEX-I CCD X-ray diffractometer with graphite-monochromated MoK_{α} radiation, respectively (both Bruker AXS, Karlsruhe, Germany). The structure was refined from the single crystal data with a particular focus on the site occupation factors (SOF) of Na, Al, and Si. We found NaAlSi to crystallize in space group $P4/nmm$ (129), with $a=4.1247(4)$ Å, $c=7.368(1)$ Å; Na on position 2c ($z=0.6346(2)$), Al on 2a and Si on 2c ($z=0.2076(2)$). The structure of the sample was found to be fully ordered, and no deficiency on the sodium site was observed¹⁹.

High pressure angle dispersive X-ray diffraction studies were performed at room temperature at beam line 01C2 of the NSRRC (Taiwan). For these studies, the samples were loaded in a diamond anvil cell (DAC) with mineral oil as the pressure transmitting medium. Susceptibility measurements were performed in a CuBe cell, allowing hydrostatic pressure up to 1 GPa to be obtained, as well as in a SiC-anvil high-pressure cell made from a non magnetic hardened Cu-Ti alloy equipped with SiC-anvils. The diameter of the flat working surface of the SiC-anvil was 0.8 mm and the diameter of the hole in the gasket was 0.3 mm. The cell allows for obtaining quasi hydrostatic pressures up to 12 GPa²⁰. The hole was filled with the NaAlSi sample and Daphne oil as a pressure transmitting medium. Pressure was measured by the Ruby scale from small scattered chips; the pressure inhomogeneity was estimated as ≤ 0.5 GPa

across the sample. In the hydrostatic CuBe cell, the pressure was determined by the T_c of a small amount of included Sn. Both cells were mounted in a SQUID-magnetometer (MPMS-XL-5, Quantum Design). T_c was determined from the onset of the superconducting transition curve, i.e. from the intersection of two extrapolated straight lines, one drawn through the curve in the normal state and one drawn through the steepest part of the curve in the superconducting state. A DAC was used for electrical resistance measurements under high pressures. For insulating the gasket, a cubic BN/epoxy mixture was used, and, with platinum foil for the electrical leads. The diameter of the flat working surface of the diamond anvil was 0.5 mm and the diameter of the hole in the gasket was 0.07 mm. The hole was filled with the polycrystalline sample. The resistance was measured with a DC current source and voltmeter with the electrodes in the van der Pauw geometry. The pressure was measured at room temperature and below via the Ruby scale from small scattered chips; the pressure inhomogeneity was estimated as about 0.05 GPa across the sample. The temperature was measured with a calibrated Si diode with an accuracy of 0.1 K attached to the DAC.

III. COMPUTATIONAL DETAILS

The calculations were performed in the framework of density functional theory (DFT) using the WIEN2K²¹ code with a full-potential linearized augmented plane-wave and local orbitals [FP-LAPW + lo] basis^{22–24} together with the PBE parameterization²⁵ of the GGA as the exchange-correlation functional. The plane wave cut-off parameter $R_{MT}K_{MAX}$ was set to 8 and the irreducible Brillouin zone was sampled by 2772 k-points. For each pressure, we used the experimental lattice constants and performed a minimization of forces for all atoms. The experimental values of the atomic position parameters agree well with the values obtained from the Rietveld refinements of our data, which were performed up to 2.2 GPa. (For pressures above 2.2 GPa the quantitative refinements of the atomic positions was not reliable due to an unfavorable signal to noise ratio.)

IV. RESULTS

Fig 1 shows the results of the dc susceptibility measurements. The T_c of the sample at ambient pressure is with 7.4 K, slightly above the previously reported T_c . T_c increases up to a pressure of 2 GPa and then decreases until it is fully suppressed at 4.8 GPa. The maximum T_c obtained is 8.6 K in the hydrostatic pressure cell. Superconductivity is restored after releasing the pressure, but with a lower T_c . The reason for the decrease in T_c is not known but it may be due to the introduction of defects.

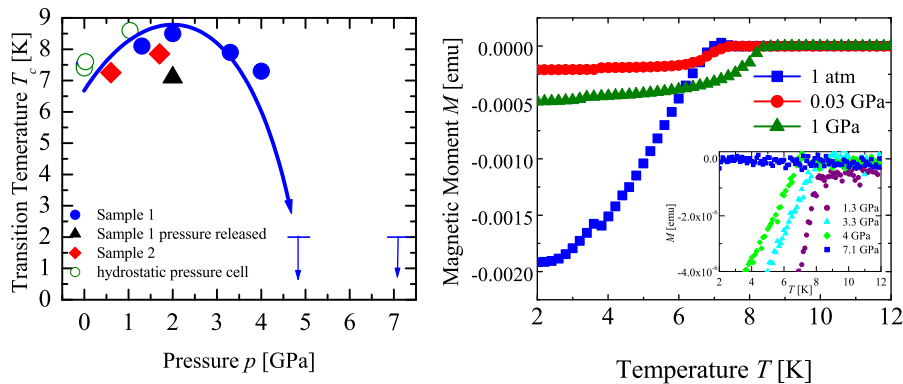


FIG. 1. left: T_c vs. pressure for NaAlSi as determined by dc susceptibility measurements. Two samples were measured in the SiC anvil cell, and one in the hydrostatic pressure cell. The blue line is a guide to the eye. right: data obtained in the hydrostatic pressure cell, and in the SiC anvil cell (insert) (color online).

The resistivity measurements show metallic behavior. There is already no sign of superconductivity at 3.5 GPa. At lower pressures the samples show a drop in resistivity at about 7.3 K (0.5 GPa) and 8.8 K (3.5 GPa). Fig 2 shows that the residual resistance ratio (RRR) decreases with increasing pressure. This is most straightforwardly interpreted as being due to an increasing number of scattering centers i.e. defects or dislocations induced at high pressures. In general, the trend in NaAlSi is that the resistance increases with pressure. This is unusual because in metals, the resistivity usually decreases with pressure²⁶. This can again be interpreted as implying that pressure

induces scattering defects into the sample. Alternatively, were the material near an electronic instability, it could indicate a significant change in the carrier concentration or type under pressure. We do not observe a metal to semiconductor transition in the resistivity up to 9 GPa, therefore a transition to a semiconducting state can be ruled out as a possibility for the reason for the disappearance of superconductivity.

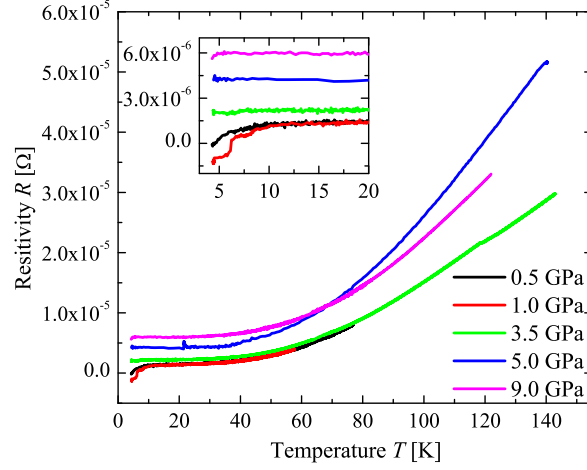


FIG. 2. Resistivity versus temperature for different pressures (color online).

X-ray diffraction experiments were performed up to 14.77 GPa. Up to this pressure, no structural phase transition was observed, the NaAlSi structure is maintained (Figure 4). All patterns were refined with the Rietveld method²⁷ in the program FULLPROF²⁸. Preferred orientation due to the plate-like habit of the material was included; consistent with expectations, the amount of preferred orientation in the DAC increased with pressure. The lattice constants and the cell volume decrease smoothly but not linearly with increasing pressures. No significant differences were observed in the diffraction patterns between pressures of 4 and 6 GPa where the superconductivity is suppressed. Refinements of internal coordinates were considered reliable up to pressures of 2.2 GPa (see section V).

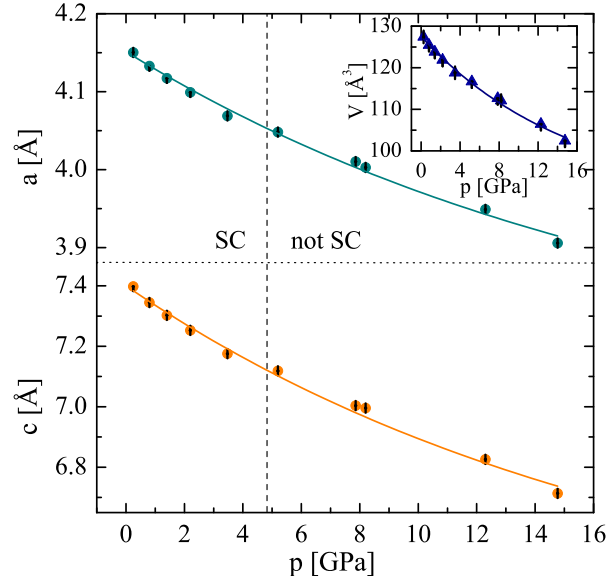


FIG. 3. Pressure dependence of the lattice constants a and c and the unit cell volume V of NaAlSi (color online).

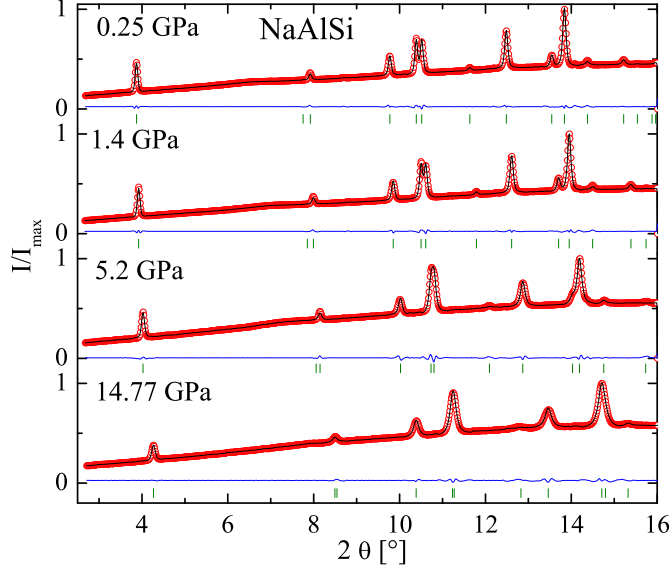


FIG. 4. Rietveld refinements of NaAlSi at 0.25 GPa, 1.4 GPa, 5.2 GPa and 14.77 GPa. The high background is a result of the Compton scattering from the diamond in the DAC (color online).

V. DISCUSSION

Band structure calculations were performed for three different pressures; 0.25 GPa, 2.2 GPa, the pressure closest to $T_{c,max}$, and 5.2 GPa, where superconductivity is no longer present. The lattice constants obtained by high pressure X-ray diffraction were employed, and the structure was relaxed through minimization of forces in order to obtain the internal atomic coordinates. The parameters employed are presented in Table 1. Until 2.2 GPa, which is the pressure up to which reliable refinements of the internal coordinates were possible, the experimental and calculated values agree well.

TABLE I. Lattice constants and internal coordinates employed for the band structure calculations, as well as experimental inter atomic distances.

P [GPa]	a [Å]	c [Å]	z_{Na} (calc)	z_{Na} (exp)	z_{Si} (calc)	z_{Si} (exp)	Al-Al [Å]	Al-Si [Å]	Si-Si [Å]
0.25	4.16	7.40	0.63456	0.63275	0.20738	0.20999	2.93473	2.5983	4.15043
2.2	4.10	7.25	0.63515	0.63094	0.21150	0.21234	2.89850	2.5635	4.09910
5.2	4.05	7.12	0.63478	0.62182	0.21538	0.19884	2.86247	2.4680	4.04815

Figure 4 shows the calculated DOS of NaAlSi at different pressures. No obvious change of the DOS at the Fermi level is observed, although bands away from E_F are shifted in a rigid-band model fashion. The calculations therefore suggest that changes in the DOS under pressure can neither explain the disappearance of the superconductivity near 5 GPa in NaAlSi, nor the increase of T_c up to 2 GPa; if the DOS were the dominant determinant of the T_c in NaAlSi then in the BCS picture the DOS and T_c would change in parallel, which is not the case here.

Figure 5 compares the band structures of NaAlSi and NaAlGe. For NaAlGe the experimental lattice constants and coordinates² were employed. The character of the bands was investigated for the ambient pressure calculations. The Al- s bands are shown in red and the Si- $p_{x,y}$ bands in blue. The Al- s band lies below the Si/Ge- $p_{x,y}$ band. Pressure moves the bands a bit closer together, but the effect is very small. Therefore, the calculations confirm the experimental results of the resistivity measurements, that the reason for the disappearance of superconductivity cannot be due to a metal insulator transition, because the system can only become semiconducting if the Al- s band is pushed above the Si- $p_{x,y}$ band with pressure, which appears very unlikely. Due to very small Al-Al distances in the structure (2.93 Å) the bandwidth of the Al- s band is very large. This strong bonding is probably the reason why the structure is stable over a wide range of pressure. The anti bonding band along the Γ -M line moves closer to E_F with pressure. In contrast to previous calculations⁵, the current calculations do not support the presence of an electron pocket on

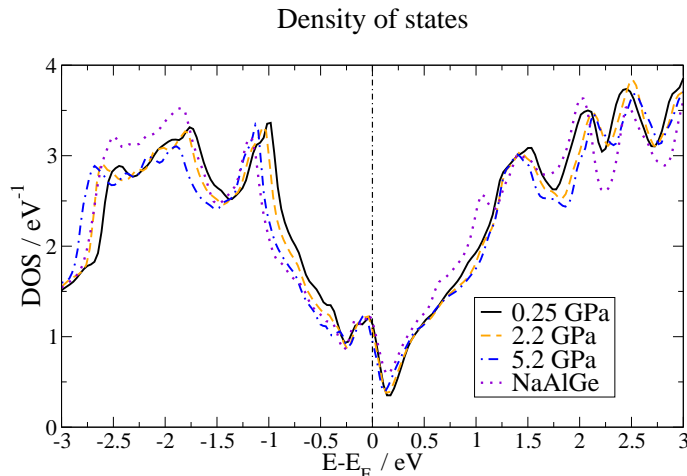


FIG. 5. Effect of pressure on the calculated density of states (color online).

the Γ -M line due to this antibonding band. Its position is strongly dependent on the z coordinate of the Si and the lattice constants. The lattice constants used in our calculations are based on our experimental results. In addition we optimized the lattice constants and positions with DFT and found the values to be in good agreement. The z coordinates used were determined with DFT and found to be in good agreement with the experimental values up to 2.2 GPa (Table 1). Only minor changes in the Fermi surface topology occur with pressure, and no significant changes in nesting properties are observed. Furthermore the band structures of NaAlSi and NaAlGe are very similar and the DOS at E_F is comparable in both compounds. This again implies that the DOS is not the primary determinant of T_c in these materials. The influence of pressure on the superconducting transition temperature may therefore be due to a change in phonon frequencies or electron-phonon coupling, consistent with the proposal for the reason why NaAlGe does not superconduct¹. The band character plots indicate that NaAlSi has a stronger sp -hybridization than NaAlGe. This indicates that the strength of hybridization might influence the superconducting properties. However we do not observe a change of hybridization strength in NaAlSi with pressure.

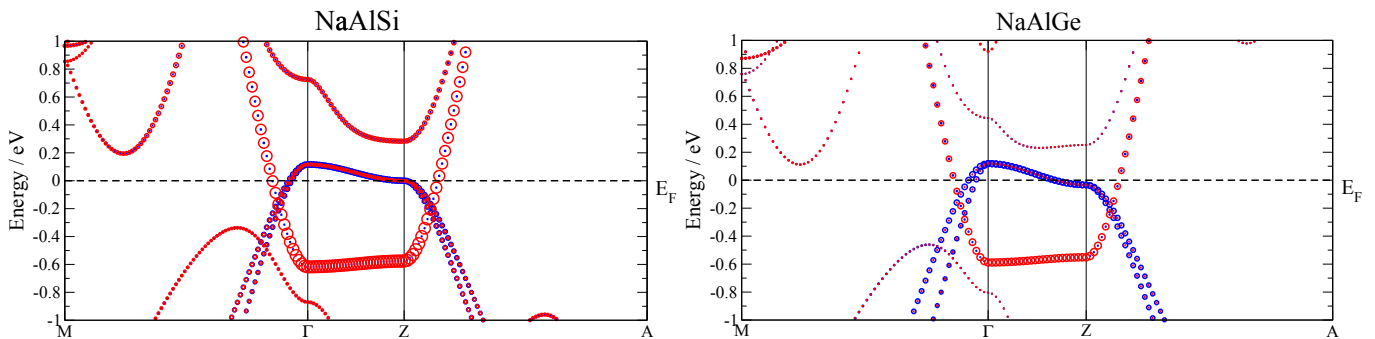


FIG. 6. Comparison of the electronic structures of NaAlSi at 0.25 GPa pressure and of NaAlGe at ambient pressure. Red dots indicate the character of the Al- s orbital, whereas the blue dots indicate the character of the Si/Ge- $p_{x,y}$ orbitals (color online).

VI. SUMMARY AND CONCLUSIONS

In summary we have shown that the T_c of NaAlSi increases first with pressure and is then suppressed rather quickly near 5 GPa. This behavior cannot be attributed to a structural phase transition, because none is observed, but the possibility that there may be a subtle structural distortion within the compound without a change in structure type cannot be excluded by the current data. Although pressure has a strong effect on the superconductivity, the calculations show that it should not have a significant effect on the electronic structure. Similarly, comparison of the calculated electronic structures of superconducting NaAlSi and non superconducting NaAlGe, showed that the

electronic structure cannot explain the different behavior regarding superconductivity. Further experimental and theoretical work will be required to determine what the dominant factors are in determining T_c in these main-group non-magnetic analogs of the 111 pnictide superconductors.

ACKNOWLEDGMENTS

The work at Princeton was supported by the Department of Energy grant DE-FG02-98-ER45706.

-
- * schoop@uni-mainz.de
- ¹ S. Kuroiwa, H. Kawashima, H. Kinoshita, H. Okabe, and J. Akimitsu, *Physica C: Superconductivity* **466**, 11 (2007).
 - ² W. Westerhaus and H. Schuster, *Z Naturforsch B* **34**, 352 (1979).
 - ³ B. Lorenz, J. Lenzi, J. Cmaidalka, R. Meng, Y. Sun, Y. Xue, and C. Chu, *Physica C: Superconductivity* **383**, 191 (2002).
 - ⁴ M. Forthaus, K. Sengupta, O. Heyer, N. Christensen, A. Svane, K. Syassen, D. Khomskii, T. Lorenz, and M. Abd-Elmeguid, *Physical review letters* **105**, 157001 (2010).
 - ⁵ H. Rhee, S. Banerjee, E. Ylvisaker, and W. Pickett, *Physical Review B* **81**, 245114 (2010).
 - ⁶ S. Medvedev, T. McQueen, I. Troyan, T. Palasyuk, M. Eremets, R. Cava, S. Naghavi, F. Casper, V. Ksenofontov, G. Wortmann, *et al.*, *Nature Materials* **8**, 630 (2009).
 - ⁷ S. Margadonna, Y. Takabayashi, Y. Ohishi, Y. Mizuguchi, Y. Takano, T. Kagayama, T. Nakagawa, M. Takata, and K. Prassides, *Physical Review B* **80**, 064506 (2009).
 - ⁸ S. Masaki, H. Kotegawa, Y. Hara, H. Tou, K. Murata, Y. Mizuguchi, and Y. Takano, *Journal of the Physical Society of Japan* **78**, 3704 (2009).
 - ⁹ G. Garbarino, A. Sow, P. Lejay, A. Sulpice, P. Toulemonde, M. Mezouar, and M. Núñez-Regueiro, *EPL (Europhysics Letters)* **86**, 27001 (2009).
 - ¹⁰ D. Braithwaite, B. Salce, G. Lapertot, F. Bourdarot, C. Marin, D. Aoki, and M. Hanfland, *Journal of Physics: Condensed Matter* **21**, 232202 (2009).
 - ¹¹ Y. Mizuguchi, F. Tomioka, S. Tsuda, T. Yamaguchi, and Y. Takano, *Applied Physics Letters* **93**, 152505 (2008).
 - ¹² D. Zocco, J. Hamlin, R. Baumbach, M. Maple, M. McGuire, A. Sefat, B. Sales, R. Jin, D. Mandrus, J. Jeffries, *et al.*, *Physica C: Superconductivity* **468**, 2229 (2008).
 - ¹³ N. Takeshita, A. Iyo, H. Eisaki, H. Kito, and T. Ito, *Journal of the Physical Society of Japan* **77**, 075003 (2008).
 - ¹⁴ S. Zhang, X. Wang, R. Sammynaiken, J. Tse, L. Yang, Z. Li, Q. Liu, S. Desgreniers, Y. Yao, H. Liu, *et al.*, *Physical Review B* **80**, 014506 (2009).
 - ¹⁵ P. Alireza, Y. Ko, J. Gillett, C. Petrone, J. Cole, G. Lonzarich, and S. Sebastian, *Journal of Physics: Condensed Matter* **21**, 012208 (2009).
 - ¹⁶ M. Torikachvili, S. Budko, N. Ni, and P. Canfield, *Physical review letters* **101**, 57006 (2008).
 - ¹⁷ L. Schoop, S. Medvedev, V. Ksenofontov, A. Williams, T. Palasyuk, I. Troyan, J. Schmitt, F. Casper, C. Wang, M. Eremets, *et al.*, *Physical Review B* **84**, 174505 (2011).
 - ¹⁸ B. Lorenz, J. Cmaidalka, R. Meng, and C. Chu, *Physical Review B* **68**, 014512 (2003).
 - ¹⁹ Further details may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (Fax: +49-7247-808-666; E-mail: [crysdata\(at\)fiz-karlsruhe.de](mailto:crysdata(at)fiz-karlsruhe.de), [http://www.fiz-karlsruhe.de/request for deposited data.html](http://www.fiz-karlsruhe.de/request%20for%20deposited%20data.html)) on quoting the CSD number 424543.
 - ²⁰ P. Alireza and G. Lonzarich, *Review of Scientific Instruments* **80**, 023906 (2009).
 - ²¹ P. Blaha, K. Schwarz, G. Madsen, D. Kvasnicka, and J. Luitz, *WIEN2k, An Augmented Plane Wave+ Local Orbitals Program for calculating Crystal Properties*, Technische Universität Wien, Austria (2001).
 - ²² D. J. Singh and L. Nordström, *Planewaves, Pseudopotentials, and the LAPW Method*, Springer, New York, 2nd ed. (2006).
 - ²³ G. K. H. Madsen, P. Blaha, K. Schwarz, E. Sjöstedt, and L. Nordström, *Phys. Rev. B* **64**, 195134 (2001).
 - ²⁴ E. Sjöstedt, L. Nordström, and D. J. Singh, *Solid State Communications* **114**, 15 (2000).
 - ²⁵ J. P. Perdew, K. Burke, and M. Ernzerhof, *Physical Review Letters* **77**, 3865 (1996).
 - ²⁶ P. Bridgman, *Proceedings of the National Academy of Sciences of the United States of America* **3**, 10 (1917).
 - ²⁷ H. Rietveld, *Journal of Applied Crystallography* **2**, 65 (1969).
 - ²⁸ Juan and Rodriguez-Carvajal, *Physica B: Condensed Matter* **192**, 55 (1993).