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Emergence of Superconductivity in "32522" Structure of $(Ca_3Al_2O_{5-y})(Fe_2Pn_2)$ (Pn = As and P)

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ABSTRACT: Using a high-pressure technique, we have successfully synthesized $(Ca_3Al_2O_{5-y})(Fe_2Pn_2)$ (Pn = As and P), the first iron-based superconductors with the perovskite-based "32522" structure to be reported. The transition temperature (T_c) is 30.2 K for Pn = As and 16.6 K for Pn = P. The emergence of superconductivity is ascribed to the small tetragonal *a*-axis lattice constant of the materials. From these results, an empirical relationship is established between the *a*-axis lattice constant and T_c in iron-based superconductors, which offers a practical guideline for exploring new superconductors with higher T_c.

The seminal discovery of high-transition-temperature (high-T_c) superconductivity in $LaFeAsO_{1-x}F_x$[1] has led the development of various new iron (Fe)-based superconductors. These new superconductors share a common structural feature: they consist of antifluorite iron pnictogen (Fe_2Pn_2) layers sandwiched between so-called blocking layers, such as LnO (Ln = rare earth),[1−7] Ae (Ae = Ba, Sr, Ca, Eu),[8−13] and A (A = Li, Na).[14,15] Even iron-chalcogenide compounds FeSe[16] and KFe_2Se_2[17] with layered structure become superconducting. Among such materials, those possessing perovskite-type block layers (perovskite-based materials) have attracted considerable attention, owing to their rich material and structural variations and their high T_c.[18−25]

The chemical formula of perovskite-based materials is expressed either as $(Ae_{n+1}TM_nO_{3n-1-y})(Fe_2Pn_2)$ (abbreviated as TM-$(n+1)n(3n-1)22$(Pn)) or as $(Ae_{n+2}TM_nO_{3n-y})(Fe_2Pn_2)$ (TM-$(n+2)n(3n)22$(Pn)), and structures with Ae = Ca, Sr, Ba and TM = Mg, Al, Sc, Ti, V, Cr, Co, etc. are known. $Ca_4(Ti,Mg)_3O_8Fe_2As_2$ has a remarkably high T_c of 47 K,[18] and this class of materials has the second-highest T_c values among all Fe-based superconductors. Further, $(Sr_4Sc_2O_6)(Fe_2P_2)$ (Sc-42622(P))[19] and $(Ca_4Al_2O_6)(Fe_2P_2)$ (Al-42622(P))[20] have T_c = 17 K, which is the highest value among superconductors composed of FeP layers.

Some materials with a "42622" structure, such as $(Sr_4V_2O_6)(Fe_2As_2)$[23] and $(Sr_4(Mg,Ti)_2O_6)(Fe_2As_2)$,[24] exhibit superconductivity, while $(Sr_4Sc_2O_6)(Fe_2As_2)$[21] and $(Sr_4Cr_2O_6)(Fe_2As_2)$[22] do not. On the other hand, it is interesting to note that for "32522" structures, only non-superconducting materials, namely $(Sr_3Sc_2O_5)(Fe_2As_2)$[22] and $(Ba_3Sc_2O_5)(Fe_2As_2)$,[25] have been reported, even though the crystal structure is similar to that of the 42622 structure, where one AeO layer is incorporated into the 32522 structure.

The T_c variation among these materials indicates the existence of structural and chemical parameters that closely correlate with and possibly control T_c. Clarifying these parameters is particularly important since it should improve our understanding of the high-T_c mechanism and provide effective guiding principles for enhancing T_c.

Accordingly, we investigated these parameters while exploring new perovskite-based superconductors. In this paper we report the discovery of $(Ca_3Al_2O_{5-y})(Fe_2Pn_2)$ (Al-32522(Pn)) with T_c = 30.2 K (Pn = As) and 16.6 K (Pn = P), which are the first superconductors belonging to the 32522 family, the crystal structure of which is shown in Figure 1a. The emergence of superconductivity in these materials is ascribed to their *a*-axis lattice constants, which are smaller than those in their non-superconducting counterparts. Furthermore, by combining the present results and those obtained in previous studies, we demonstrate that there is a universal correlation between the *a*-axis lattice constant and T_c in FeAs superconductors. This relationship should prove useful as a practical guideline for optimizing T_c of various Fe-based superconductors.

In the present study, polycrystalline samples of $(Ca_3Al_2O_{5-y})$-(Fe_2Pn_2) (Pn = P, As) were synthesized by a high-pressure method using a cubic-anvil-type apparatus, a versatile technique to obtain materials with extremely small volume beyond the limits of synthesis under ambient-pressure conditions.[26] The starting materials CaO, Al, As, P, Fe, and Fe_2O_3 were weighed with a nominal composition of $(Ca_3Al_2O_{5-y})(Fe_2Pn_2)$ and ground using an agate mortar and pestle in a glovebox filled with dry N_2 gas. The purity of the obtained samples was sensitive to the oxygen content $(5-y)$ in the starting mixture. The most suitable nominal oxygen content was determined to be $5-y = 4.4-4.6$, which was tuned by adjusting the ratio of Fe and Fe_2O_3. The mixed powder was loaded into a high-pressure cell and then heated at 1150 °C (Pn = As) or 1300 °C (Pn = P) for 1 h under a pressure of 4.5 GPa. To compensate for possible oxygen deficiency, some of the synthesized samples were post-annealed in a quartz tube at 360 °C for 120 h, together with a AgO pellet, which provided an oxygen partial pressure of ∼2 atm during the annealing process. Powder X-ray diffraction (XRD) patterns were measured on a Rigaku Ultima IV with Cu Kα radiation, and dc magnetic susceptibility was measured with a SQUID magnetometer (Quantum Design MPMS) in a magnetic field of 5 Oe. The resistivity was measured by the four-probe method.

Figure 1b,c shows the XRD patterns of as-synthesized Al-32522(As) and Al-32522(P). All the appreciable peaks can be indexed on the basis of the tetragonal crystal structure (*I*4/*mmm*) as shown in Figure 1a, with *a* = 3.742 Å and

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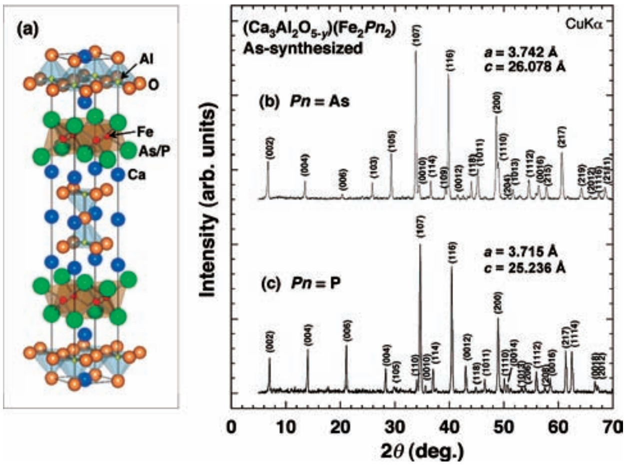

Figure 1. (a) Schematic crystal structure of Al-32522(Pn) and XRD patterns of as-synthesized (b) Al-32522(As) and (c) Al-32522(P).

c = 26.078 Å (Pn = As) and with a = 3.715 Å and c = 25.236 Å (Pn = P). We note that Al-32522(P) is the first reported material consisting of FeP layers to have the 32522 crystal structure. The lattice constant of Al-32522(As) is much smaller than that of known 32522 compounds, such as $(Sr_3Sc_2O_5)(Fe_2As_2)$ (a = 4.069 Å and c = 26.876 Å)[22] and $(Ba_3Sc_2O_5)(Fe_2As_2)$ (a = 4.133 Å and c = 28.355 Å), which are non-superconducting.[25] The smaller lattice constant is due to the ionic radii of Ca^{2+} (1.06 Å) and Al^{3+} (0.57 Å) being considerably smaller than those of Ba^{2+} (1.36 Å), Sr^{2+} (1.27 Å), and Sc^{3+} (0.83 Å). After post-annealing, the c-axis lattice constant of Al-32522(As) increased slightly to 26.329 Å, while the a-axis lattice constant was almost unchanged (a = 3.738 Å).

Figure 2 shows the temperature dependence of the zero-field-cooled (ZFC) and field-cooled (FC) magnetic susceptibility (χ) for as-synthesized Al-32522(As), post-annealed Al-32522(As), and as-synthesized Al-32522(P) samples. T_c of as-synthesized Al-32522(As), determined from the onset of the diamagnetic signal, is 18.5 K. Upon post-annealing, T_c increased to 30.1 K, most likely because the carrier concentration was improved by the elimination of oxygen deficiency. Al-32522(P) exhibited a superconducting transition at 16.0 K, which was close to the highest T_c value (17 K) among the FeP-based superconductors.[19,20] For Al-32522(P), post-annealing does not yield any change in T_c (not shown). The superconducting volume fractions estimated from the magnitude of χ (ZFC) at 5 K were 108%, 151%, and 73% for as-synthesized Al-32522(As), post-annealed Al-32522(As), and as-synthesized Al-32522(P), respectively, thus indicating bulk superconductivity.

The temperature-dependent resistivity (ρ) is also shown in Figure 2 for as-synthesized Al-32522(As), annealed Al-32522(As), and as-synthesized Al-32522(P). The T_c values determined from the onset of the resistivity transition were 19.4 K (Pn = As, as-synthesized), 30.2 K (Pn = As, post-annealed), and 16.6 K (Pn = P, as-synthesized), in good agreement with T_c determined from χ. Metallic behavior ($d\rho/dT > 0$) was observed in the samples at all temperatures. There was no kink in the resistivity corresponding to an antiferromagnetic/orthorhombic transition,[1−13] indicating that these materials are different from the parent phase, which exhibits long-range structural and magnetic orders at low temperatures.

The present results suggest that the emergence of superconductivity in Al-32522(As) comes from, or at least is related to, the smaller a-axis lattice constant. To investigate whether this trend is general, in Figure 3 the T_c values of the perovskite-based superconductors[18−22,25] reported so far are plotted against their a-axis lattice constants, together with those of LnFeAsO-based superconductors (Ln-1111(As), Ln = lanthanide).[27−29] In Ln-1111(As), a universal relationship between T_c and the a-axis lattice constant is already established, in which the highest T_c is attained when the a-axis lattice constant is ∼3.91.[27−29] Figure 3 clearly indicates that the same trend also holds in perovskite-based materials. It is particularly remarkable that all the experimental

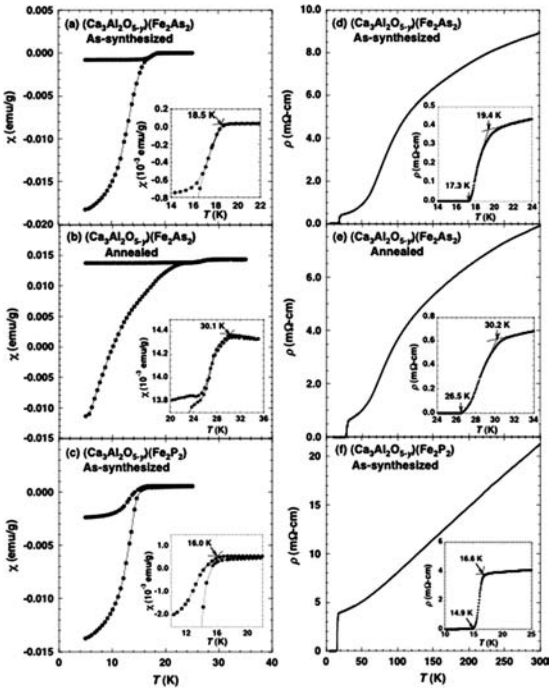

Figure 2. Temperature dependence of ZFC and FC magnetic susceptibility (χ) for (a) as-synthesized Al-32522(As), (b) postannealed Al-32522(As), and (c) as-synthesized Al-32522(P). Temperature dependence of the resistivity is shown for (d) as-synthesized Al-32522(As), (e) postannealed Al-32522(As), and (f) as-synthesized Al-32522(P).

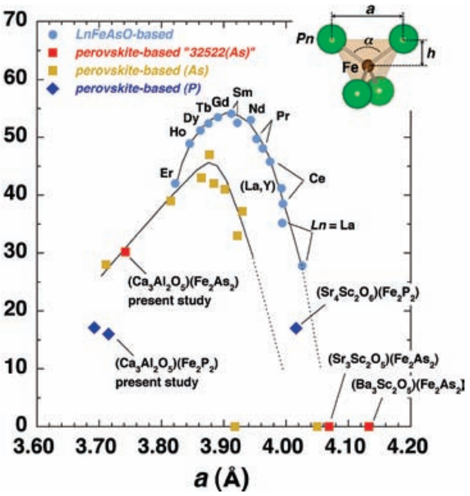

Figure 3. Plot of T_c versus a-axis lattice constant for perovskite- and LnFeAsO-based materials reported to date. Inset: relationship among the a-axis lattice constant, α, and h in a Pn-Fe-Pn tetrahedron.

data on perovskite-based materials fall along a single curve, in spite of the wide variation of their perovskite-based units. Along this curve, T_c peaks at $a = 3.88$ Å, which is slightly smaller than in the case of Ln-1111(As). By assuming a universal curve, the relatively low T_c of Al-32522(As) is naturally explained by the fact that its *a*-axis lattice constant is too small compared with the optimal value. We hypothesize that higher-T_c superconductivity is likely to be discovered in materials with an *a*-axis lattice constant close to 3.88 Å.

Figure 3 also suggests that there is an upper limit on the *a*-axis constant, around 4.0 Å, for the emergence of superconductivity. The absence of superconductivity in other 32522 materials, namely $(Sr_3Sc_2O_5)(Fe_2As_2)$ and $(Ba_3Sc_2O_5)(Fe_2As_2)$, can be ascribed to their extraordinarily long *a*-axis lattice constants.

To date, the relationship between T_c and structural parameters has been extensively researched. In particular, the close correlation between T_c and the shape of the $FeAs_4$ tetrahedron, which is characterized by the As−Fe−As bond angle (α)[30,31] and the height of As atoms relative to the Fe plane (h),[32] has been pointed out. Empirically, T_c takes a maximum value when $\alpha = 109.5°$ (corresponding to a regular tetrahedron)[30,31] or when $h = 1.38$ Å.[32] Various theoretical proposals have been put forward to account for this correlation.[33−36] We note that the correlation found in the present study is essentially consistent with the previous findings, because the shape of the $FeAs_4$ tetrahedron is primarily determined by the *a*-axis lattice constant in actual materials. Indeed, increasing (respectively decreasing) the *a*-axis lattice constant results in stretching (respectively squeezing) of the $FeAs_4$ tetrahedron along the *c*-axis, which in turn decreases (respectively increases) α and increases (respectively decreases) h. Note that the Fe−Pn bond length does not depend much on other material properties ($l_{Fe-As} = 2.40 \pm 0.02$ Å and $l_{Fe-P} = 2.26 \pm 0.02$ Å).[20,30,31,37,38] The relationship among the *a*-axis lattice constant, α, and h in $FePn_4$ tetrahedron is schematically shown in the inset of Figure 3. For reference, h and α of the post-annealed Al-32522(As) were calculated as 1.485 Å and 103.1°, respectively, which are too high and too narrow in comparison with the optimal values. Also, these values for non-superconducting $(Sr_3Sc_2O_5)(Fe_2As_2)$ ($a = 4.069$ Å)[22] are $h = 1.335$ Å and $\alpha = 113.3°$, which also deviate from the optimal values, but in the opposite direction.

Although the number of data points is limited, the T_c of FeP-based materials is different from that of the FeAs-based counterparts in that it does not exhibit any appreciable dependence on the *a*-axis lattice constant. These results suggest either that their electronic structure is completely insensitive to the details of the crystal structure (in contrast to FeAs-based materials) or that realizing high-T_c materials is hindered between $a = 3.7$ Å (Al-32522(P) and Al-42622(P)) and 4.0 Å (Sc-42622(P)). It is highly desirable to synthesize FeP-based materials possessing the intermediate lattice constants to investigate this point.

In summary, we used a high-pressure technique to synthesize $(Ca_3Al_2O_{5-y})(Fe_2Pn_2)$ (Pn = As and P), which exhibit superconductivity at 30.1 and 16.6 K for Pn = As and P, respectively. The emergence of superconductivity in these materials with the 32522 structure is ascribed to their small *a*-axis lattice constant. On the basis of the experimental results, an empirical relationship was established between the *a*-axis lattice constants and T_c in Fe-based superconductors. This relationship will potentially be useful as a guideline for exploring new superconductors with higher T_c.

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REFERENCES

(1) Kamihara, Y.; Watanabe, T.; Hirano, M.; Hosono, H. *J. Am. Chem. Soc.* **2008**, *130*, 3296.

(2) Chen, X. H.; Wu, T.; Wu, G.; Liu, R. H.; Chen, H.; Fang, D. F. *Nature* **2008**, *453*, 761.

(3) Ren, R.-A.; Yang, J.; Lu, W.; Yi, W.; Shen, X.-L.; Li, Z.-C.; Che, G.-C.; Dong, X.-L.; Sun, L.-L.; Zhou, F.; Zhao, Z.-X. *Europhys. Lett.* **2008**, *82*, 57002.

(4) Ren, R.-A.; Yang, J.; Lu, W.; Yi, W.; Che, G.-C.; Dong, X.-L.; Sun, L.-L.; Zhou, F.; Zhao, Z.-X. *Mater. Res. Innovations* **2008**, *12*, 106.

(5) Ren, R.-A.; Che, G. C.; Dong, X. L.; Yang, J.; Lu, W.; Yi, W.; Shen, X. L.; Li, Z. C.; Sun, L. L.; Zhou, F..; Zhao, Z. X. *Europhys. Lett.* **2008**, *83*, 17002.

(6) Kito, H.; Eisaki, H.; Iyo, A. *J. Phys. Soc. Jpn.* **2008**, *77*, 063707.

(7) Wang, C.; Li, L.; Chi, S.; Zhu, Z.; Ren, Z.; Li, Y.; Wang, Y.; Lin, X.; Luo, Y.; Jiang, S.; Xu, X.; Cao, G.; Xu, Z. *Europhys. Lett.* **2008**, *83*, 67006.

(8) Rotter, M.; Tagel, M; Johrendt, D. *Phys. Rev. Lett.* **2008**, *101*, 107006.

(9) Chen, G. F.; Li, Z.; Li, G.; Hu, W. Z.; Dong, J.; Zhang, X. D.; Zheng, P.; Wang, N. L.; Luo, J. L. *Chin. Phys. Lett.* **2008**, *25*, 3403.

(10) Sasmal, K.; Lv, B.; Lorenz, B.; Guloy, A. M.; Chen, F.; Xu, Y. Y.; Chu, C. W. *Phys. Rev. Lett.* **2008**, *101*, 107007.

(11) Shirage, P. M.; Miyazawa, K.; Kito, H.; Eisaki, H.; Iyo, A. *Appl. Phys. Exp.* **2008**, *1*, 081702.

(12) Wu, G.; Chen, H.; Wu, T.; Xie, Y. L.; Yan, Y. J.; Liu, R. H.; Wang, X. F.; Ying, J. J.; Chen, X. H. *J. Phys.: Condens. Matter.* **2008**, *20*, 422201.

(13) Qi, Y.; Gao, Z.; Wang, L.; Wang, D.; Zhang, X.; Ma, Y. *New J. Phys.* **2008**, *10*, 123003.

(14) Tapp, J. H.; Tang, Z.; Lv, B.; Sasmal, K.; Lorenz, B.; Chu, P. C. W.; Guloy, A. M. *Phys. Rev. B* **2008**, *78*, 060505.

(15) Parker, D. R.; Pitcher, M. J.; Baker, P.; Franke, I.; Lancaster, T.; Blundell, S. J.; Clarke, S. *Chem. Commun.* **2009**, 2189–2191.

(16) Hsu, F.-C.; Luo, J.-Y.; Yeh, K.-W.; Chen, T.-K.; Huang, T.-W.; Wu, P. M.; Lee, Y. -C.; Huang, Y.-L.; Chu, Y.-Y.; Yan, D.-C.; Wu, M.-K. *Proc. Natl. Acad. Sci. U.S.A.* **2008**, *105*, 14262.

(17) Guo, J.; Jin, S.; Wang, G.; Wang, S.; Zhu, K.; Zhou, T.; He, M.; Chen, X. *Phys. Rev. B* **2010**, *82*, 180520.

(18) Ogino, H.; Shimizu, Y.; Ushiyama, K.; Kawaguchi, N.; Kishio, K.; Shimoyama, J. *Appl. Phys. Exp.* **2010**, *3*, 63103.

(19) Ogino, H.; Matsumura, Y.; Katsura, Y.; Ushiyama, K.; Horii, S.; Kishio, K.; Shimoyama, J. *Supercond. Sci. Technol.* **2009**, *22*, 075008.

(20) Shirage, P. M.; Kihou, K.; Lee, C. H.; Kito, H.; Eisaki, H.; Iyo, A. *Appl. Phys. Lett.* **2010**, *97*, 172506.

(21) Ogino, H.; Katsura, Y.; Horii, S.; Kishio, K.; Shimoyama, J. *Supercond. Sci. Technol.* **2009**, *22*, 85001.

(22) Zhu, X.; Han, F.; Mu, G.; Zeng, B.; Cheng, P.; Shen, B.; Wen, H.-H. *Phys. Rev. B* **2009**, *79*, 24516.

(23) Zhu, X.; Han, F.; Mu., G.; Cheng, P.; Shen., B.; Zheng, B.; Wen, H. H. *Phys. Rev. B* **2009**, *79*, 220512(R).

(24) Sato, S.; Ogino, H.; Kawaguchi, N.; Katsura, Y.; Kishio, K.; Shimoyama, J. *Supercond. Sci. Technol.* **2010**, *23*, 045001.

(25) Kawaguchi, N.; Ogino, H.; Shimizu, Y.; Kishio, K.; Shimoyama, J. *Appl. Phys. Exp.* **2010**, *3*, 63102.
(26) Shirage, P. M.; Miyazawa, K.; Ishikado, M.; Kihou, K.; Lee, C. H.; Takeshita, N.; Matsuhata, H.; Kumai, R.; Tomioka, Y.; Ito, T.; Kito, H.; Eisaki, H.; Shamoto, S.; Iyo, A. *Physica C* **2009**, *469*, 355.
(27) Miyazawa, K.; Kihou, K.; Shirage, P. M.; Lee, C. H.; Kito, H.; Eisaki, H.; Iyo, A. *J. Phys. Soc. Jpn.* **2009**, *78*, 034712.
(28) Miyazawa, K.; Ishida, S.; Kihou, K.; Shirage, P. M.; Nakajima, M.; Lee, C. H.; Kito, H.; Tomioka, Y.; Ito, T.; Eisaki, H.; Yamashita, H.; Mukuda, H.; Tokiwa, K.; Uchida, S.; Iyo, A. *Appl. Phys. Lett.* **2010**, *96*, 72514.
(29) Shirage, P. M.; Miyazawa, K.; Kihou, K.; Lee, C. H.; Kito, H.; Tokiwa, K.; Tanaka, Y.; Eisaki, H.; Iyo, A. *Europhys. Lett.* **2010**, *92*, 57011.
(30) Lee, C. H.; Iyo, A.; Eisaki, H.; Kito, H.; Fernandez-Diaz, M. T.; Ito, T.; Kihou, K.; Matsuhata, H.; Braden, M.; Yamada, K. *J. Phys. Soc. Jpn.* **2008**, *77*, 083704.
(31) Zhao, J.; Huang, Q.; Cruz, C. d. l.; Li, S.; Lynn, J. W.; Chen, Y.; Green, M. A.; Chen, G. F.; Li, G.; Li, Z.; Luo, J. L.; Wang, N. L.; Dai, P. *Nat. Mater.* **2008**, *7*, 953.
(32) Mizuguchi, Y.; Hara, Y.; Deguchi, K.; Tsuda, S.; Yamaguchi, T.; Takeda, K.; Kotegawa, H.; Tou, H.; Takano, Y. *Supercond. Sci. Technol.* **2010**, *23*, 054013.
(33) Vildosola, V.; Pourovskii, L.; Arita, R.; Biermann, S. E.; Georges, A. *Phys. Rev. B* **2008**, *78*, 064518.
(34) Kuroki, K.; Usui, H.; Onari, S.; Arita, R.; Aoki, H. *Phys. Rev. B* **2009**, *79*, 224511.
(35) Sawatzky, G. A.; Elfimov, I. S.; Brink, J.; van den; Zaanen, J. *Europhys. Lett.* **2009**, *86*, 17006.
(36) Miyake, T.; Kosugi, T.; Ishibashi, S.; Terakura, K. *J. Phys. Soc. Jpn.* **2010**, *79*, 123713.
(37) Kimber, S. A. J.; Kreyssig, A.; Zhang, Y.-Z.; Jeschke, H. O.; Valenti, R.; Yokaichiya, F.; Colombier, E.; Yan, J.; Hansen, T. C.; Chatterji, T.; McQueeney, R. J.; Canfield, P. C.; Goldman, A. I.; Argyriou, D. N. *Nat. Mater.* **2009**, *8*, 471.
(38) Rotter, M.; Heike, C.; Johrendt, D. *Phys. Rev. B* **2010**, *82*, 014513.