

# Density functional study of BaNi<sub>2</sub>As<sub>2</sub>: Electronic structure, phonons, and electron-phonon superconductivity

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We investigate the properties of BaNi<sub>2</sub>As<sub>2</sub> using first-principles calculations. The band structure has a similar shape to that of BaFe<sub>2</sub>As<sub>2</sub>, and in particular shows a pseudogap between a manifold of six heavy *d* electron bands and four lighter *d* bands, i.e., at an electron count of six *d* electrons per Ni. However, unlike BaFe<sub>2</sub>As<sub>2</sub>, where the Fermi energy occurs at the bottom of the pseudogap, the two additional electrons per Ni in the Ni compound place the Fermi energy in the upper manifold. Thus BaNi<sub>2</sub>As<sub>2</sub> has large Fermi surfaces very distinct from BaFe<sub>2</sub>As<sub>2</sub>. Results for the phonon spectrum and electron-phonon coupling are consistent with a classification of this material as a conventional phonon-mediated superconductor although spin fluctuations and nearness to magnetism may be anticipated based on the value of  $N(E_F)$ .

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## I. INTRODUCTION

The finding of superconductivity in F-doped LaFeAsO by Kamihara and co-workers<sup>1</sup> has led to considerable interest as this provides an alternative noncuprate route to high critical temperature ( $T_c$ ) superconductivity. Since this finding, high  $T_c$  superconductivity has been found in many related phases that can be generally characterized into four different groups according to their parent compounds: (i) LaFeAsO,<sup>1-3</sup> (ii) BaFe<sub>2</sub>As<sub>2</sub>,<sup>4,5</sup> (iii) LiFeAs,<sup>6</sup> and (iv)  $\alpha$ -FeSe.<sup>7</sup> The precise mechanism of superconductivity in these compounds is yet to be established, but is strongly thought to be unconventional. This is based in part on calculations of the electron-phonon coupling,<sup>8,9</sup> which is too small to account for any appreciable superconductivity and on the proximity to magnetism.<sup>10-14</sup> These compounds show considerable variation in doping levels (i.e., hole or electron doped), chemical pressure, and chemistry of the non-Fe layers, while remaining superconducting. However, there are three main threads joining these compounds together. The parent compounds have spin-density wave (SDW) order with the possible exception of the LiFeAs phase, exist in a tetragonal structure, and possess iron in a two-dimensional (2D) square lattice sheet. There is a clear association between suppression of the SDW order and appearance of superconductivity in the phase diagrams, although recent work does show some range of coexistence of magnetism and superconductivity.<sup>15,16</sup> Importantly, the SDW phase is accompanied by an orthorhombic distortion. Depending on the specific material, this distortion occurs at a temperature higher than the SDW ordering temperature or coincident with it.<sup>4,10,17</sup>

In addition, Ronning *et al.*<sup>18</sup> recently reported both the occurrence of a first-order phase transition at  $T_0=130$  K with characteristics similar to the structural transition seen in the Fe-As based superconductors, and a superconducting transition with  $T_c=0.7$  K in BaNi<sub>2</sub>As<sub>2</sub>. Since Fe and Ni are ambient temperature ferromagnets and many Fe and Ni com-

pounds show magnetism, it is plausible to expect that Ni can fill in the role of Fe in these compounds. Indeed, superconductivity is also observed in LaNiPO,<sup>19</sup> LaNiAsO,<sup>20,21</sup> and LaNiBiO.<sup>22</sup> However, these compounds do not display the structural or magnetic transitions characteristic of the Fe-As-based parent compounds. Moreover, it was recently shown that LaNiPO can be explained as a conventional electron-phonon superconductor.<sup>23</sup>

In this Brief Report we report the details of our calculations of the electronic structure, phonons, and electron-phonon coupling of BaNi<sub>2</sub>As<sub>2</sub>. The band structure of BaNi<sub>2</sub>As<sub>2</sub> is similar to that reported for BaFe<sub>2</sub>As<sub>2</sub>,<sup>24-26</sup> but the Fermi level is shifted up owing to the higher valence electron count in Ni<sup>2+</sup> than in Fe<sup>2+</sup>. Hence, with a larger Fermi surface and higher carrier density, BaNi<sub>2</sub>As<sub>2</sub> has remarkably different electronic properties from BaFe<sub>2</sub>As<sub>2</sub>. A similar increase in the Fermi surface area is also found in LaNiPO for essentially the same reason.<sup>23</sup> Also similar to the case of LaNiPO, we obtain a much larger value of electron-phonon coupling constant  $\lambda_{ep}=0.76$  in BaNi<sub>2</sub>As<sub>2</sub> compared to the Fe-based compounds [for example, in LaFeAsO  $\lambda_{ep}=0.21$  (Ref. 8)]. This suggests that the mechanism of superconductivity in BaNi<sub>2</sub>As<sub>2</sub> is similar to that of LaNiPO and is different from the Fe-based compounds.

## II. METHODS AND STRUCTURE

The electronic structure calculations were performed within the local-density approximation (LDA) with the general potential linearized augmented plane-wave (LAPW) method,<sup>27</sup> similar to the calculations reported for LaFeAsO.<sup>11</sup> We used LAPW spheres of radius 2.2  $a_0$  for Ba and 2.1  $a_0$  for Ni and As. BaNi<sub>2</sub>As<sub>2</sub> occurs in a body-centered-tetragonal structure ( $I4/mmm$ ) with Ba, Ni, and As at the positions  $2a(0,0,0)$ ,  $4d(0.5,0,0.25)$ , and  $4e(0,0,z_{As})$ , respectively. Here  $z_{As}$ , the As height above the Ni square planes, is a structural parameter governing the Ni-As dis-

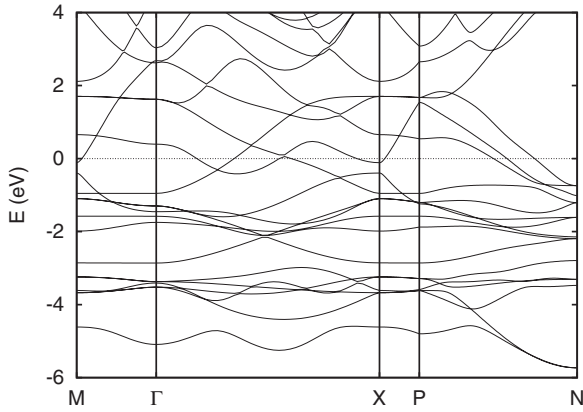


FIG. 1. Calculated LDA band structure of non-spin-polarized  $\text{BaNi}_2\text{As}_2$ .

tance and the distortion of the As tetrahedra that coordinate the Ni in this material. In our calculations, we used experimental lattice parameters ( $a=4.112 \text{ \AA}$  and  $c=11.54 \text{ \AA}$ ) (Ref. 18) but employed the computed  $z_{\text{As}}$  obtained via non-spin-polarized energy minimization.

The phonon dispersions and electron-phonon coupling were calculated using linear response as implemented in QUANTUM ESPRESSO code,<sup>28</sup> similar to the calculations reported for  $\text{LaFeAsO}$  and  $\text{LaNiPO}$ .<sup>8,9,23</sup> The linear-response calculations were also done with experimental lattice parameters, using ultrasoft pseudopotentials within the generalized gradient approximation (GGA) of Perdew *et al.*<sup>29</sup> An  $8 \times 8 \times 8$  grid was used for the zone integration in the phonon calculations, while a more dense  $32 \times 32 \times 8$  grid was used for the zone integration in the electron-phonon coupling calculations. The basis set cutoff for the wave functions was 40 Ry, while a 400 Ry cutoff was used for the charge density.

The internal parameter  $z_{\text{As}}$  was again relaxed in the calculation of phonon properties. The values we obtained for  $z_{\text{As}}$  (LDA: 0.346 and GGA: 0.351) agree well with the experimental value of  $z_{\text{As}}=0.3476$ . This is in contrast to  $\text{BaFe}_2\text{As}_2$ ,<sup>26</sup> and other Fe-based superconductors where LDA and GGA calculations done in this way noticeably underestimate  $z_{\text{As}}$  but it is similar to the case of  $\text{LaNiPO}$ . It has been suggested that this underestimation of  $z_{\text{As}}$  in Fe-based superconductors is due to its coupling with magnetism.<sup>13,30,31</sup> This underestimation may be indicative of strong spin fluctuations in the paramagnetic superconducting parts of the phase diagrams of the Fe-based materials. The absence of this discrepancy between the experimental and calculated value of  $z_{\text{As}}$  in  $\text{BaNi}_2\text{As}_2$  then indicates that the magnetic character of  $\text{BaNi}_2\text{As}_2$  is different from that of  $\text{BaFe}_2\text{As}_2$  and other Fe-based superconductors.

### III. RESULTS

The calculated band structure and electronic density of states (DOS) are shown in Figs. 1 and 2, respectively. The Fermi surface is shown in Fig. 3. The pnictogen  $p$  states occur between  $-6$  and  $-3$  eV, with respect to the Fermi energy, consistent with an anionic  $\text{As}^{3-}$  species, and modest hybridization of the As  $p$  states with Ni  $d$  states similar to the

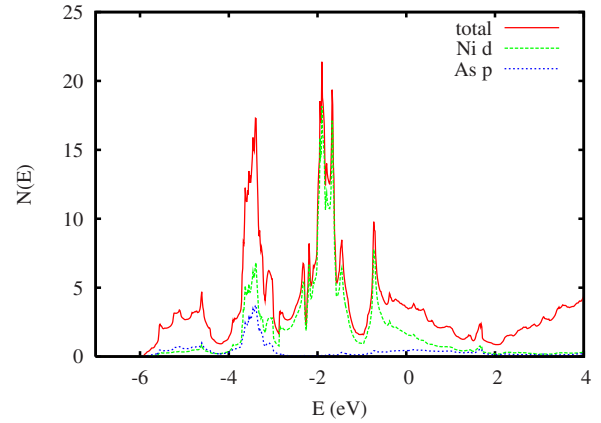


FIG. 2. (Color online) Calculated LDA electron density of states of non-spin-polarized  $\text{BaNi}_2\text{As}_2$  and projections onto the LAPW spheres on a per formula unit basis.

Fe-based materials. As expected, Ba occurs as  $\text{Ba}^{2+}$  with the Ba derived valence states well above the Fermi energy. As such, Ni has a nominal valence  $\text{Ni}^{2+}$  with eight  $d$  electrons per Ni. The manifold of six heavy bands between  $-3.0$  and  $-1.0$  eV has Ni  $d$  character and accounts for six electrons per Ni. There is a pseudogap at this point separating the heavy bands from a manifold of lighter bands that span between  $-1.0$  and  $2.0$  eV. The light bands accommodate the remaining  $d$  electrons and show Ni  $d$  character accompanied by some mixing with As  $p$  states. It may be seen that the band structure and DOS of  $\text{BaNi}_2\text{As}_2$  are qualitatively very similar to that of  $\text{BaFe}_2\text{As}_2$  (Refs. 24–26), with the exception that  $\text{Ni}^{2+}$  crucially contains two more valence electrons than  $\text{Fe}^{2+}$ . This causes the Fermi level to shift up away from the pseudogap into the upper manifold. As a result, compared to  $\text{BaFe}_2\text{As}_2$ ,  $\text{BaNi}_2\text{As}_2$  has a large multisheet Fermi surface very different from the Fe-based materials. Despite the fact that there are disconnected sheets of Fermi surface, two-gap superconductivity is unlikely. This is due to the low  $T_c$ , which would impose an extraordinary requirement on the interband scattering. The value of the DOS at  $E_F$  is  $N(E_F)=3.57 \text{ eV}^{-1}$ , on a per formula unit (two Ni atoms) both spins basis. This is lower than  $\text{LaFeAsO}$ , but is comparable to some of the other Fe-As-based materials.

The calculated phonon dispersions of  $\text{BaNi}_2\text{As}_2$  are shown in Fig. 4. The corresponding phonon density of states and Eliashberg spectral function  $\alpha^2F(\omega)$  are shown in Fig. 5.

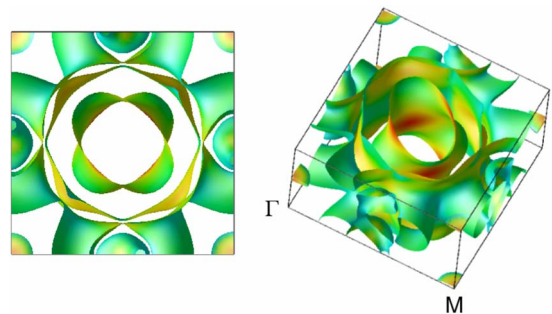


FIG. 3. (Color online) Calculated LDA Fermi surface of non-spin-polarized  $\text{BaNi}_2\text{As}_2$ . The shading is by velocity.

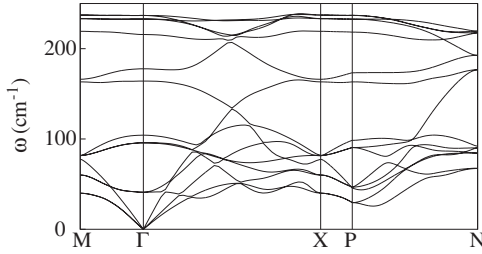


FIG. 4. Calculated GGA phonon dispersion curves of non-spin-polarized  $\text{BaNi}_2\text{As}_2$ .

There are 15 phonon bands extending up to  $\sim 230 \text{ cm}^{-1}$ . The bands below  $120 \text{ cm}^{-1}$  show Ba, Ni, and As characters while the region above it contains bands of mostly Ni and As character. From Fig. 5, we can see that the electron-phonon spectral function is enhanced relative to the phonon density of states in the low frequency modes. The projected phonon density of states plots (Fig. 5, middle and bottom) show that this enhancement occurs in the region where there is high Ni and As character, although the enhancement cannot be attributed to solely in-plane or out-of-plane character. This is in contrast to the case of  $\text{LaFeAsO}$  where the spectral function more closely follows in proportionality to the phonon density of states in this energy region.<sup>8</sup> It should be noted that doped  $\text{LaFeAsO}$  was shown to have a rather low overall electron-phonon coupling ( $\lambda_{\text{ep}} \sim 0.2$ ) which cannot explain the superconductivity,<sup>8</sup> while  $\text{LaNiPO}$  was shown to be readily

explained as conventional electron-phonon superconductor.<sup>23</sup> For  $\text{BaNi}_2\text{As}_2$ , we obtain a value of the electron-phonon coupling  $\lambda_{\text{ep}} = 0.76$  with logarithmically average frequency  $\omega_{\text{ln}} = 73 \text{ cm}^{-1}$ . Inserting these numbers into the simplified Allen-Dynes formula,

$$k_B T_c = \frac{\hbar \omega_{\text{ln}}}{1.2} \exp \left\{ - \frac{1.04(1 + \lambda_{\text{ep}})}{\lambda_{\text{ep}} - \mu^*(1 + 0.62\lambda_{\text{ep}})} \right\}, \quad (1)$$

with  $\mu^* = 0.12$ , we obtain  $T_c \sim 4 \text{ K}$ , which overestimates but is reasonably in accord with the experimental low value of  $T_c = 0.7 \text{ K}$ .<sup>18</sup> As mentioned, the total DOS per formula unit at the Fermi energy is  $N(E_F) = 3.57 \text{ eV}^{-1}$ . With a typical  $3d$  Stoner parameter  $I \sim 0.7 - 0.8 \text{ eV}$ , this yields a Stoner enhancement  $(1 - NI)^{-1} \sim 3$  (note that in this formula  $N$  is per atom per spin). This enhancement is sufficient to indicate the presence of spin fluctuations that would depress the electron-phonon  $T_c$  and may therefore explain why the experimental  $T_c$  is reduced compared with the calculated value based on  $\lambda_{\text{ep}}$ .

#### IV. CONCLUSIONS

In summary, we have presented electronic structure calculations that show  $\text{BaNi}_2\text{As}_2$  has very different electronic properties compared to the Fe-based high  $T_c$  superconductors. Even though it has a band structure similar to that of  $\text{BaFe}_2\text{As}_2$ , the Fermi level lies in the upper manifold away

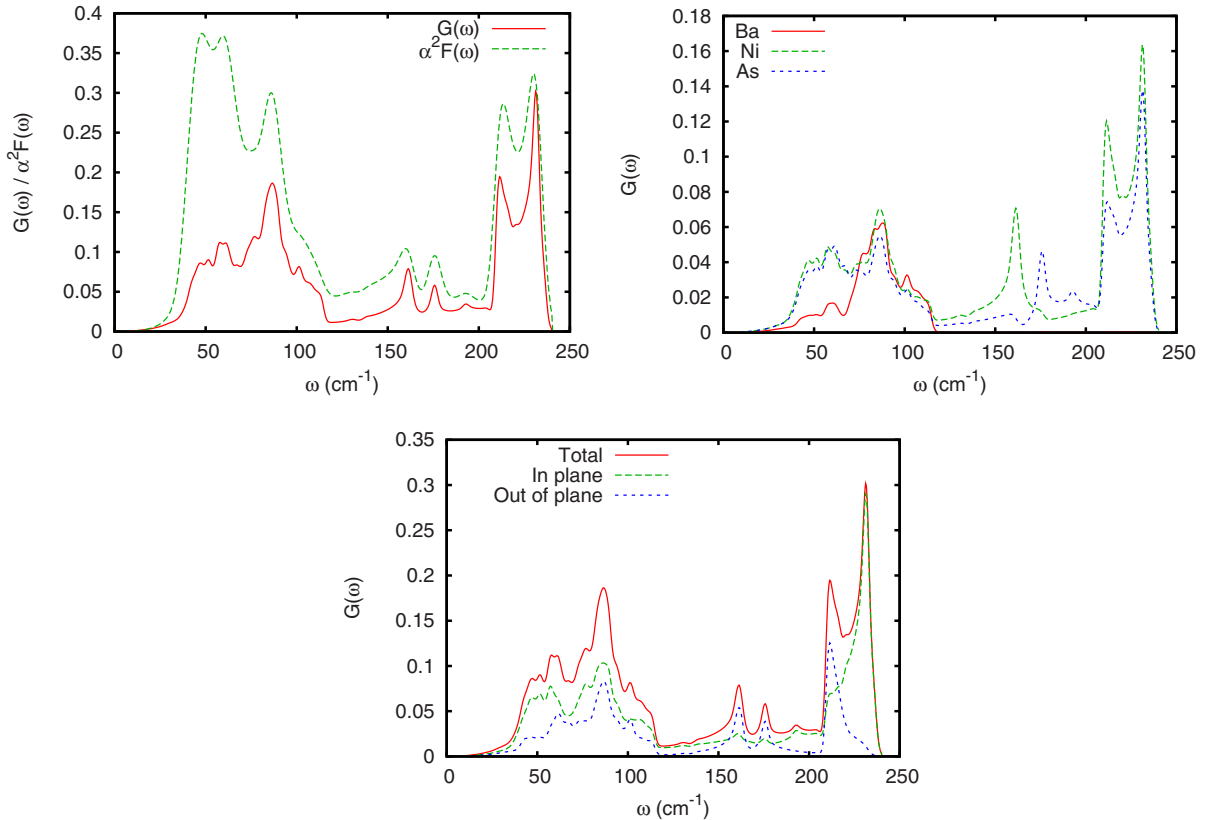


FIG. 5. (Color online) Top left: Calculated GGA phonon density of states  $G(\omega)$  and electron-phonon spectral function  $\alpha^2 F(\omega)$  for non-spin-polarized  $\text{BaNi}_2\text{As}_2$ . Top right: projected phonon density of states for each atom of  $\text{BaNi}_2\text{As}_2$ . Bottom: phonon density of states weighted by in-plane or out-of-plane character, i.e., atomwise projections of eigenvectors in the  $ab$  plane and along the  $c$  axis, respectively.

from the pseudogap due to higher number of valence electrons in  $\text{Ni}^{2+}$ . This gives  $\text{BaNi}_2\text{As}_2$  a large Fermi surface in contrast to the small surfaces in the Fe-based superconductors. We obtain a moderately high  $N(E_F)=3.57 \text{ eV}^{-1}$ , which would yield a Stoner renormalization of  $\sim 3$ , consistent with spin fluctuations that would reduce the electron-phonon  $T_c$ . Nonetheless, the calculated value for electron-phonon coupling constant is  $\lambda_{\text{ep}}=0.76$ , which is ample for a description

of  $\text{BaNi}_2\text{As}_2$  as an electron-phonon superconductor similar to  $\text{LaNiPO}$ .

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- <sup>1</sup>Y. Kamihara, T. Watanabe, M. Hirano, and H. Hosono, *J. Am. Chem. Soc.* **130**, 3296 (2008).
- <sup>2</sup>G. F. Chen, Z. Li, G. Li, J. Zhou, D. Wu, J. Dong, W. Z. Hu, P. Zheng, Z. J. Chen, H. Q. Yuan, J. Singleton, J. L. Luo, and N. L. Wang, *Phys. Rev. Lett.* **101**, 057007 (2008).
- <sup>3</sup>X. Zhu, H. Yang, L. Fang, G. Mu, and H. H. Wen, *Supercond. Sci. Technol.* **21**, 105001 (2008).
- <sup>4</sup>M. Rotter, M. Tegel, D. Johrendt, I. Schellenberg, W. Hermes, and R. Pottgen, *Phys. Rev. B* **78**, 020503(R) (2008).
- <sup>5</sup>M. Rotter, M. Tegel, and D. Johrendt, *Phys. Rev. Lett.* **101**, 107006 (2008).
- <sup>6</sup>X. C. Wang, Q. Q. Liu, Y. X. Lv, W. B. Gao, L. X. Yang, R. C. Yu, F. Y. Li, and C. Q. Jin, arXiv:0806.4688 (unpublished).
- <sup>7</sup>F. C. Hsu, J. Y. Luo, K. W. Yeh, T. K. Chen, T. W. Huang, P. M. Wu, Y. C. Lee, Y. L. Huang, Y. Y. Chu, D. C. Yan, and M. K. Wu, arXiv:0807.2369 (unpublished).
- <sup>8</sup>L. Boeri, O. V. Dolgov, and A. A. Golubov, *Phys. Rev. Lett.* **101**, 026403 (2008).
- <sup>9</sup>I. I. Mazin, D. J. Singh, M. D. Johannes, and M. H. Du, *Phys. Rev. Lett.* **101**, 057003 (2008).
- <sup>10</sup>C. de la Cruz, Q. Huang, J. W. Lynn, J. Li, W. Ratcliff II, J. L. Zarestky, H. A. Mook, G. F. Chen, J. L. Luo, N. L. Wang, and P. Dai, *Nature (London)* **453**, 899 (2008).
- <sup>11</sup>D. J. Singh and M. H. Du, *Phys. Rev. Lett.* **100**, 237003 (2008).
- <sup>12</sup>Q. Huang, J. Zhao, J. W. Lynn, G. F. Chen, J. L. Luo, N. L. Wang, and P. Dai, *Phys. Rev. B* **78**, 054529 (2008).
- <sup>13</sup>I. I. Mazin and M. D. Johannes, arXiv:0807.3737 (unpublished).
- <sup>14</sup>G. F. Chen, Z. Li, D. Wu, G. Li, W. Z. Hu, J. Dong, P. Zheng, J. L. Luo, and N. L. Wang, *Phys. Rev. Lett.* **100**, 247002 (2008).
- <sup>15</sup>H. Chen, Y. Ren, Y. Qiu, W. Bao, R. H. Liu, G. Wu, T. Wu, Y. L. Xie, X. F. Wang, Q. Huang, and X. H. Chen, arXiv:0807.3950 (unpublished).
- <sup>16</sup>A. J. Drew, C. Niedermayer, P. J. Baker, F. L. Pratt, S. J. Blundell, R. H. Lancaster, R. H. Liu, G. Wu, X. H. Chen, I. Watanabe, V. K. Malik, A. Dubroka, M. Roessle, K. W. Kim, C. Baines, and C. Bernhard, arXiv:0807.4876 (unpublished).
- <sup>17</sup>J. Q. Yan, A. Kreyssig, S. Nandi, N. Ni, S. L. Budko, A. Kracher, R. J. McQueeney, R. W. McCallum, T. A. Lograsso, A. I. Goldman, and P. C. Canfield, *Phys. Rev. B* **78**, 024516 (2008).
- <sup>18</sup>F. Ronning, N. Kurita, E. D. Bauer, B. L. Scott, T. Park, T. Klimczuk, R. Movshovich, and J. D. Thompson, *J. Phys.: Condens. Matter* **20**, 342203 (2008).
- <sup>19</sup>T. Watanabe, H. Yanagi, T. Kamiya, Y. Kamihara, H. Hiramatsu, M. Hirano, and H. Hosono, *Inorg. Chem.* **46**, 7719 (2007).
- <sup>20</sup>Z. Li, G. F. Chen, J. Dong, G. Li, W. Z. Hu, D. Wu, S. K. Su, P. Zheng, T. Xiang, N. L. Wang, and J. L. Luo, *Phys. Rev. B* **78**, 060504(R) (2008).
- <sup>21</sup>T. Watanabe, H. Yanagi, Y. Kamihara, T. Kamiya, M. Hirano, and H. Hosono, *J. Solid State Chem.* **181**, 2117 (2008).
- <sup>22</sup>V. L. Kozhevnikov, O. N. Leonidova, A. L. Ivanovskii, I. R. Shein, B. N. Goshchitskii, and A. E. Karkin, arXiv:0804.4546 (unpublished).
- <sup>23</sup>A. Subedi, D. J. Singh, and M. H. Du, *Phys. Rev. B* **78**, 060506(R) (2008).
- <sup>24</sup>I. A. Nekrasov, Z. V. Pchelkina, and M. V. Sadovskii, *JETP Lett.* **88**, 144 (2008).
- <sup>25</sup>F. Ma, Z. Y. Lu, and T. Xiang, arXiv:0806.3526 (unpublished).
- <sup>26</sup>D. J. Singh, *Phys. Rev. B* **78**, 094511 (2008).
- <sup>27</sup>D. J. Singh and L. Nordstrom, *Planewaves, Pseudopotentials and the LAPW Method*, 2nd ed. (Springer, Berlin, 2006).
- <sup>28</sup>S. Baroni *et al.* (<http://www.quantum-espresso.org>).
- <sup>29</sup>J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
- <sup>30</sup>Z. P. Yin, S. Lebègue, M. J. Han, B. P. Neal, S. Y. Savrasov, and W. E. Pickett, *Phys. Rev. Lett.* **101**, 047001 (2008).
- <sup>31</sup>I. I. Mazin, M. D. Johannes, L. Boeri, K. Koepernik, and D. J. Singh, *Phys. Rev. B* **78**, 085104 (2008).