First-principles study of CaFe₂As₂ under pressure

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We perform first-principles calculations on CaFe₂As₂ under hydrostatic pressure. Our total-energy calculations show that though the striped antiferromagnetic (AFM) orthorhombic (OR) phase is favored at P = 0, a nonmagnetic collapsed tetragonal (cT) phase with diminished *c* parameter is favored for P > 0.36 GPa, in agreement with experiments. Rather than a mechanical instability, this is an enthalpically driven transition from the higher volume OR phase to the lower volume cT phase. A simple thermodynamic model provides an interpretation of the finite-temperature phase boundaries of the cT phase. Calculations of electronic density of states reveal pseudogaps in both OR and cT phases. Band-structure analysis provides insight into the origin of the pseudogaps while revealing the location and nature of hybridized Fe-*d* and As-*p* bonding orbitals.

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I. INTRODUCTION

Recent discoveries¹ of iron-based pnictides provide a rich arena to explore the interplay between structural, magnetic, and superconducting properties, and the consequent emergence of new physics. These materials provide insight into the competing roles of magnetism and pairing correlations, such as in the high-temperature cuprate superconductors. Among the pnictides, the 122 ternary compounds AFe_2As_2 (A = alkalineearth metal Ca, Ba, Sr), belonging to the ThCr₂Si₂ structure family, draw particular interest owing to the rich behavior observed upon chemical substitution or applying pressure,^{2–5} such as different structural phases and superconductivity. Applied pressure has the advantage of introducing less disorder compared to chemical substitution.

CaFe₂As₂, the smallest-volume member of this family, is of great current interest as it serves as a readily accessible system that exemplifies the key features of the AFe₂As₂ compounds.^{6,7} At ambient pressure, at $T_{c1} = 170$ K, CaFe₂As₂ undergoes a first-order transition from a high-temperature tetragonal (T) phase to a low-temperature orthorhombic (OR) phase, that is, striped along the *a* axis and antiferromagnetically ordered along the c axis. This may be viewed as a magnetostructural transition from a high-T phase with fluctuating magnetic moments⁸ to one with long-range antiferromagnetic (AFM) order. An intermediate orthorhombic nematic phase⁹ does not occur for A = Ca. The striped magnetic order drives the orthorhombic symmetry breaking with the antiferromagnetic bonds in the *a* direction being slightly longer than the ferromagnetic bonds in the b direction. The T-OR transition temperature T_{c1} decreases with applied pressure.

At low *T*, under hydrostatic pressure $P \sim 0.35$ GPa,⁷ the system undergoes a transition from the AFM-OR phase to a nonmagnetic tetragonal phase, but with a compressed *c*-axis value; this has been termed the "collapsed" tetragonal phase (cT). At high *T*, and P > 0.35 GPa, another first-order transition occurs at T_{c2} , from the tetragonal T to the collapsed cT phase. T_{c2} increases with pressure. Several features are sensitive to pressure conditions; in particular, lack of superconductivity up to $P \sim 0.65$ GPa for the case of hydrostatic pressure,⁶ compared to observation of superconductivity under condi-

tions creating uniaxial pressure.^{4,10} Some experiments¹¹ indicate the presence of a low-*T* tetragonal phase sandwiched between the OR and the cT phase, suggesting that superconductivity in a narrow region may be facilitated by the fluctuating moments present in the T phase. The transition from the OR to the cT phase occurs at lower pressures in the uniaxial case.^{4,10}

Prior electronic density functional theory (DFT) work¹² has considered the pressure and doping dependence of BaFe₂As₂. More recently, DFT studies compared nonhydrostatic (i.e., anisotropic) and hydrostatic pressure dependencies of BaFe₂As₂ and CaFe₂As₂,^{13,14} and proposed¹⁵ a Hund's-rule coupling model of the phase transitions in these compounds. Our DFT work provides a different understanding of CaFe₂As₂ under hydrostatic pressure, and goes beyond previous DFT work in a number of important ways.

The key results of our work are as follows: Total-energy considerations, as a function of pressure, lead to findings that agree well with experimental determination of electronic structure and magnetic ordering. Though the higher volume AFM-OR phase is favored at P = 0, the lower volume nonmagnetic cT phase is favored for $P \ge 0.36$ GPa. Hence we assert that the OR-cT transition is first order and enthalpy driven. We also incorporate a thermodynamic analysis of the cT phase boundary at nonzero temperature and pressure, based on vibrational entropy. Our density of states (DOS) calculations show pseudogaps in both OR and the cT phases around the Fermi level (E_F) , with the pseudogap being narrower and deeper in the OR phase. Band structure provides insight into the nature and origin of the pseudogaps in both phases, and also allows us to explore the possibility of orbital order in these systems. A notable outcome is the location and character of bonding orbitals consisting of hybridized As-p and Fe-d states, thereby providing an understanding of striped magnetic order in the OR phase, and of hopping mechanisms.

II. CRYSTAL STRUCTURE AND METHOD

The structures of interest are tetragonal, with Pearson symbol tI10 denoting body-centered tetragonal with ten atomic sites per unit cell, and orthorhombic, with Pearson symbol oF20 denoting face-centered orthorhombic with 20 atomic



FIG. 1. (Color online) Structures used in calculations; chemical species are indicated by color, vertical heights are indicated by atomic size. (a) Left panel shows the *c*-axis view [$z \in (0, c/2)$], with *ab*-plane stripe ordering denoted by +/-; (b) right panel shows the *b*-axis view [$y \in (0,b)$], with the *a*-axis stripe and the *c*-axis AFM ordering denoted by +/-. Atomic size indicates vertical height, smaller on top.

sites per unit cell. The oF20 crystal structure is a based on a $\sqrt{2} \times \sqrt{2}$ R45 tetragonal supercell of the tI10 structure, followed by a weak orthorhombic distortion. To improve consistency of our calculated property differences, we employ this tetragonal supercell for studies of the tetragonal structure, so we include 20 atoms in all our reported calculations. Calculations of the orthorhombic structure utilize spin polarization, with initial moments in the striped antiferromagnetic arrangement. Specifically, spins are ordered antiferromagnetically in the a direction, ferromagnetically in the b direction (i.e., "striped" in the *ab* plane), and antiferromagnetically in the c direction; see Fig. 1. The symmetry group of the atomic positions is I4/mmm (no. 139) for tI10, and Fmmm (no. 69) for oF20. This differs from a previous work, 14 where the ambient pressure OR calculations have been done for a nonmagnetic structure. This enables us to better contrast the band structures of the OR (striped AFM) and cT (nonmagnetic) phases, trace their origin and content, and discuss the resulting DOS and pseudogaps.

We utilize VASP^{16,17} to carry out first-principles totalenergy calculations, adopting projector augmented wave potentials.^{18,19} For a density functional we choose the PBE²⁰ generalized gradient approximation (GGA), as calculations utilizing LDA²¹ fail to stabilize the striped antiferromagnetic orthorhombic phase, and the PW91 GGA²² predicts the orthorhombic phase to be energetically unfavorable at low temperature and pressure. We relax all atomic positions and lattice parameters, and increase our k-point densities and plane-wave energy cutoff (to 340 eV) until energy differences have converged to 0.1 meV/atom. Unusual care in selection of density functional and convergence is required because of the extremely small energy differences of order 1 meV/atom that must be resolved. As in other DFT calculations, our values of the Fe moment are large ($m_{Fe} \approx 1.78 \mu_B$ at P = 0) compared to the experimental results $(0.8\mu_B)$.

III. "COLLAPSE" UNDER PRESSURE

A. T = 0 Total-energy considerations

Figure 2 shows the results of our calculation of total energy vs volume for the nonmagnetic cT and the AFM-OR phases, as



FIG. 2. (Color online) Calculated total energies (E) of the collapsed tetragonal (cT) and orthorhombic (OR) structures plotted against volume (V). The solid lines are cubic polynomial fits (see text; Table I); the dashed line of double tangency gives the critical pressure beyond which cT is stable despite its higher energy.

described above. For each structure α we fit $E_{\alpha}(V)$ to a cubic polynomial of the form $E_{\alpha} = E_{\alpha}^{0} + (1/2V_{\alpha})B_{\alpha}(V - V_{\alpha})^{2} + (1/6V_{\alpha}^{2})C_{\alpha}(V - V_{\alpha})^{3}$, where V_{α} and E_{α}^{0} are the volume and energy at P = -dE/dV = 0, B_{α} is the bulk modulus, and C_{α} is the nonlinear bulk modulus. Fitted values of these quantities are listed in Table I. The line of double tangency is $E_{t} = E^{0} - P_{c}^{0}V$, where $P_{c}^{0} = 0.022 \text{ eV/Å}^{3}$ (0.36 GPa) is the critical pressure.

Figure 2 implies that though the high volume OR phase is energetically favorable at low pressure, the enthalpies $(H = \vec{E} + P\vec{V})$ of the phases cross at P_c^0 , beyond which the high-energy cT phase, with diminished c parameter, has lower enthalpy relative to that of the OR phase. This is more clearly seen in Fig. 3 where we plot, for the OR and cT phases, the enthalpy difference $(\Delta H = H_{cT} - H_{OR})$, and the lattice parameters (a,b,c), versus pressure: While both the OR and the cT structures are stable across the pressure range studied, ΔH vanishes at $P_c^0 = 0.36$ GPa, causing the *c*-axis lattice parameter to switch from the higher value of 11.45 Åof the OR phase to a lower value of 10.45 Å, the defining feature of the collapsed cT phase. Thus, the OR-cT transition at T = 0 and finite P is a transition in thermodynamic stability, rather than a soft mode or irreversible mechanical instability as implied by the term "collapse." In particular, the OR phase continues to exist at high pressure (contrary to Ref. 13, and the cT phase is present at low pressure; they simply become metastable rather than thermodynamically stable.

Our calculated lattice parameters, shown in Fig. 3, across the pressure range ($0 \le P \le 1$ GPa) are within 2% of experiments. At P_c^0 the discontinuities in lattice parameters are $\Delta a = +0.04$ Å, $\Delta b = +0.14$ Å, and $\Delta c = -1.00$ Å, in good agreement with experiments.¹⁰ Within each phase, the lattice parameters vary smoothly with no singularity on

TABLE I. Properties of structures at $V = V_{\alpha}$. Length and volume units are in Å, energy in eV/atom, bulk moduli in GPa, and magnetic moments in Bohr magneton.

Structure	b/a	c/a	V_{lpha}	E^0_{lpha}	B_{lpha}	C_{lpha}	m_{Fe}
сТ	1	1.84	16.55	-6.1296	85.6	-654	0
OR	0.98	2.02	17.57	-6.1318	63.3	-152	1.78



FIG. 3. (Color online) The top two panels show the behavior of the calculated lattice parameters, a,b,c of OR and cT structures with pressure. The bottom panel shows the change in enthalpy, ΔH vs pressure *P*. Note the "jumps" in the lattice parameters at $P_c^0 = 0.36$ GPa (dashed lines), where $\Delta H = 0$.

crossing P_c^0 . On extending our calculations to higher pressures, P = 1.5 GPa, we do not find signatures for any other low-*T* transition.

B. Finite-temperature considerations

Although the first-principles results are derived at T =0 K, we can estimate the temperature-dependent variation of critical pressure $P_c(T)$ at low pressure to predict the finite-T phase boundary between the orthorhombic and collapsed tetragonal phases using a simple thermodynamic model. The Clausius-Clapeyron equation relates the slope of the phase boundary to the discontinuities in entropy (S) and volume (V)as $dP/dT = d\Delta S/d\Delta V$. We calculated $\Delta V \equiv V_{\rm cT} - V_{\rm OR} \approx$ 1 Å^3 /atom. Temperature-dependent entropy can be calculated by integrating C/T, where C is the heat capacity. We neglect the distinction between constant volume and constant pressure for low compressibility solids and assume that the dominant entropy contribution comes from the lattice phonons. Note that at low T the Debye approximation $C = (12\pi^4/5)k_B(T/\theta)^3$ becomes exact, where θ is the Debye temperature. Neglecting any temperature variation of θ , the entropy also varies as $(T/\theta)^3$. A value of $\theta_{OR} = 292$ K has been reported experimentally.²³ As we have not located an experimental value for θ_{cT} we estimate

$$\theta_{\rm cT} \sim \left(\frac{B_{\rm cT}}{B_{\rm OR}}\right)^{1/2} \left(\frac{V_{\rm cT}}{V_{\rm OR}}\right)^{1/6} \theta_{\rm OR} = 336 \,\mathrm{K} \tag{1}$$

according to the approximation of Madelung²⁴ and Einstein.²⁵ Note that $\Delta(\theta^{-3}) \approx (-3\Delta\theta)/\theta^4$.

Approximating ΔV and $\Delta \theta$ as constants allows us to integrate the Clausius-Clapeyron equation, yielding

$$P_c(T) = P_c^0 - \frac{3\pi^4}{5} \left(\frac{k_B \Delta \theta}{\Delta V}\right) \left(\frac{T}{\theta}\right)^4.$$
 (2)

Putting in our numerical values, $k_B \Delta \theta / \Delta V = 0.69$ GPa and $P_c^0 = 0.36$ GPa, we can invert Eq. (2) to find the $T_c(P)$ phase boundary:

$$T_c(P) = 124 \text{ K} \times (P - 0.36)^{1/4}$$
 (3)

in units of K. Equation (3) implies that the boundary of the collapsed tetragonal phase rises vertically from its low-temperature limit of 0.36 GPa, then bends sharply to the right towards higher pressures, in qualitative agreement with experiment.^{6,7} Note that the precise value of θ_{cT} only influences the prefactor of Eq. (3). The boundary curves to the right towards higher pressure (contrary to Ref. 15 because the higher bulk modulus of the cT phase reduces its entropy and hence raises its Gibbs free energy, G = E + PV - TS, relative to the OR phase. At high temperature, it thus requires a higher pressure to favor the lower volume, but lower entropy, collapsed tetragonal phase.

Experimentally the collapsed tetragonal cT phase borders the orthorhombic OR phase at low temperatures, but it borders the noncollapsed tetragonal T phase at high temperatures. In fact, the high-temperature T phase resembles the OR phase in terms of its lattice parameters and even exhibits magnetic moment fluctuations matching the striped antiferromagnetic structure with correlation lengths of order 6–8 Å.⁸ The T phase is essentially the OR phase with a loss of long-range order in magnetization leading to a loss of orthorhombicity (i.e., a = b), and hence the extrapolation of the cT-OR boundary to higher temperature and pressure should remain a good first approximation to the cT-T phase boundary.¹⁰

IV. ELECTRONIC STRUCTURE

A. Pseudogaps in the density of states

Our electronic structure calculations give band dispersions along different k directions, and the density of states (DOS). In our DOS calculations (Fig. 4), both OR and cT phases exhibit pseudogaps around E_F . Useful insight into the material may be gained by exploring the dispersion and pseudogap features in further detail. We present the pseudogap region of DOS alongside the selected dispersion relations for individual bands for both OR and cT phases. Aside from the total DOS, the figures also show the Fe, As, and Ca partial DOS; the total DOS is dominated by Fe-d orbitals. The pseudogap in the OR phase is narrow and centered on E_F , while it is broader and shifted up from E_F in the cT phase. This overall behavior persists for P > 0. For simplicity of discussion we label the reciprocal spaces using primitive orthorhombic notation [i.e., $X = (\pi/2a, 0, 0)$ and $R = (\pi/2a, \pi/2b, \pi/2c)$ where a, b, and c are the relaxed P = 0 lattice constants of the 20-atom cells]. The pseudogaps in both OR and cT cases arise from the paucity of states near the Fermi level in the Γ -R direction, this being so over a wider energy range in the cT case. We note that the width and location of our DFT-calculated pseudogaps compare well with LDA + DMFT calculations²⁶ at P = 0 (i.e., DMFT and PBE both incorporate important correlations that are missing from LDA).

On considering orbital decomposition of the DOS in the OR phase as shown in Fig. 4, we find that Fe- d_{xz} (green curves) and Fe- d_{yz} (blue curves) show strong pseudogap features near E_F , this being stronger for Fe- d_{yz} . To explore possible orbital ordering, we examined the band occupation on the first Fe atom ("Fe1," here at x = y = z = 1/4, with majority spin up). This atom contributes spin up d_{yz} primarily to the DOS peak at $E \approx -1.5$ eV and spin down d_{yz} to the peak at $E \approx 0.5$. The



FIG. 4. (Color online) Total densities of states (top panel, units states/eV/atom). Selected dispersion relations and partial DOS for cT (center) and OR (bottom) phases at P = 0. E_F is denoted by dashed lines. Dispersion relation and partial DOS *d* orbitals pertain to Fe. As and Ca partial densities of states are multiplied by 2 for clarity. All DOS calculations were performed with the tetrahedron method, but Gaussian smearing of 0.05 eV was applied in top panel for clarity.

 d_{xz} orbital is less strongly split, with spin up primarily at $E \approx -0.6$ and spin down at $E \approx -0.4$ eV with some spin down also above E_F . Integrating up to the Fermi level, we find the spin up occupancies are equal, $n_{xz,\uparrow} = n_{yz,\uparrow} = 0.82$, while the down occupancies differ, $n_{xz,\downarrow} = 0.56 > n_{yz,\downarrow} = 0.36$. Hence the occupation number difference $(n_{xz,\uparrow} + n_{xz,\downarrow}) - (n_{yz,\uparrow} + n_{yz,\downarrow}) = 0.20$ equals the moment difference $(n_{yz,\uparrow} - n_{yz,\downarrow}) - (n_{xz,\uparrow} - n_{xz,\downarrow}) = 0.20$. These findings are qualitatively similar to those obtained within a Hartree-Fock treatment²⁷ of an interacting Hamiltonian.

B. Hybridization of Fe and As orbitals

Prominent As-*p* orbitals hybridized with Fe-*d* lie above E_F (unoccupied) in the cT phase but are below E_F (occupied) in OR. Hybridization primarily involves d_{xz} and d_{yz} orbitals, consistent with two-band models^{28,29} for indirect electron hopping and striped magnetic order.

Figure 5 illustrates Γ point wave functions parallel to the *xy* plane at *z* = 0.30, between the lower Fe plane at *z* = 0.25 and the adjacent As atoms at *z* = 0.36 (actually 0.365 for cT and 0.363 for ortho). Projected positions of the Fe atoms at (x, y) = (1/4, 3/4) are shown as red circles. But since we are above the Fe plane, Fe orbitals of d_{xz} and d_{yz} type appear as



FIG. 5. (Color online) Wave functions at z = 0.30. (a),(b) OR spin up As-Fe hybrids; (c) cT Ca-Fe hybrid. Red circles locate Fe atoms at z = 1/4.

lobes of positive (green) and negative (magenta) values of the wave function on opposite sides of the atom. Two spin-up wave functions are shown for the OR structure. The first, Fig. 5(a), at E = -0.76 eV corresponds to d_{xz} orbitals on the majority spin-up Fe atoms (here at x = 1/4) hybridized with p_z orbitals on the adjacent As atoms [here at (x, y) = (0, 0) and (1/2, 1/2)].

The corresponding spin-down wave function (not shown) is similar but shifted to the majority spin-down Fe atoms (at x = 3/4). The second, Fig. 5(b), at E = -0.61 eV, has no notable spin dependence, and features Fe- d_{yz} orbitals, again hybridized with As- p_z . This pair of states thus reflects the formation of striped magnetic order within the xy plane.

A representative wave function is shown for the cT structure, Fig. 5(c), at E = -0.22 eV. This state consists of bonding interactions of Fe- d_{yz} orbitals weakly hybridized with Ca- d_{yz} . A second wave function degenerate with this involves d_{xz} orbitals instead of d_{yz} . In the band-structure plot, another pair of degenerate states appears at E = -0.09 eV. These states are similar to those just described except they reverse sign between the lower (z = 1/4) and the upper (z = 3/4) Fe atoms. As a result, they do not hybridize with the Ca-d orbitals. A set of Fe d_{xz} and d_{yz} states is also evident around E = -0.42 eV. However, these states properly belong at the collapsed tetragonal M point. They have been folded back to the Γ point owing to the orthorhombic supercell.

V. CONCLUSION

While existing literature discusses the transition from the orthorhombic to the tetragonal phase under pressure as a "collapse" into the so-called collapsed tetragonal phase, our total-energy calculations reveal that the transition is in fact a first-order enthalpic transition. In our calculations, both the magnetic orthorhombic and the nonmagnetic tetragonal phases remain mechanically stable to high hydrostatic pressures, at least 1.5 GPa; however the tetragonal phase is favored enthalpically for P > 0.36 GPa. Our results are in good agreement with experimental determination of electronic structure and magnetic ordering. Our thermodynamic analysis based on the Clausius-Clapeyron relation provides an understanding the finite-temperature phase boundary between OR and cT phases. Our detailed electronic structure calculations reveal interesting pseudogap features near the Fermi level in both OR and cT phases, shed light on ordering of Fe-d orbitals in OR phase, and identify the location and nature of bonding orbitals comprised of Fe-d and As-p electronic states in both OR and cT phases. The hybridization results provide an understanding of striped magnetic order in the OR phase, and also of hopping mechanisms in this material.

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- ¹Y. Kamihara, W. Watanabe, M. Hirano, and H. Hosono, J. Am. Chem. Soc. **130**, 3296 (2008).
- ²P. Alireza, Y. T. Ko, J. Gillett, C. M. Petrone, J. M. Cole, G. G. Lonzarich, and S. E. Sebastian, J. Phys.: Condens. Matter **21**, 012208 (2009).
- ³A. Mani, S. Ghost, S. Paulraj, A. Bharathi, and C. S. Sundar, Europhys. Lett. **87**, 17004 (2009).
- ⁴M. S. Torikachvili, S. L. Bud'ko, N. Ni, P. C. Canfield, and S. T. Hannahs, Phys. Rev. B **80**, 014521 (2009).
- ⁵ S. R. Saha, N. P. Butch, T. Drye, J. Magill, S. Ziemak, K. Kirshenbaum, P. Y. Zavalij, J. W. Lynn, and J. Paglione, Phys. Rev. B **85**, 024525 (2012).
- ⁶W. Yu, A. A. Aczel, T. J. Williams, S. L. Bud'ko, N. Ni, P. C. Canfield, and G. M. Luke, Phys. Rev. B **79**, 020511 (2009).
- ⁷P. C. Canfield, S. L. Bud'ko, N. Ni, A. Kreyssig, A. I. Goldman, R. J. McQueeney, M. S. Torikachvili, D. N. Argyriou, G. Luke, and W. Yu, Physica C **469**, 404 (2009).
- ⁸S. O. Diallo, D. K. Pratt, R. M. Fernandes, W. Tian, J. L. Zarestky, M. Lumsden, T. G. Perring, C. L. Broholm, N. Ni, S. L. Bud'ko, P. C. Canfield, H.-F. Li, D. Vaknin, A. Kreyssig, A. I. Goldman, and R. J. McQueeney, Phys. Rev. B **81**, 214407 (2010).
- ⁹R. M. Fernandes, L. H. VanBebber, S. Bhattacharya, P. Chandra, V. Keppens, D. Mandrus, M. A. McGuire, B. C. Sales, A. S. Sefat, and J. Schmalian, Phys. Rev. Lett. **105**, 157003 (2010).
- ¹⁰A. Kreyssig, M. A. Green, Y. Lee, G. D. Samolyuk, P. Zajdel, J. W. Lynn, S. L. Budko, M. S. Torikachvili, N. Ni, S. Nandi, J. B. Leao, S. J. Poulton, D. N. Argyriou, B. N. Harmon, R. J. McQueeney, P. C. Canfield, and A. I. Goldman, Phys. Rev. B 78, 184517 (2008).
- ¹¹K. Prokes, A. Kreyssig, B. Ouladdiaf, D. K. Pratt, N. Ni, S. L. Bud'ko, P. C. Canfield, R. J. McQueeney, D. N. Argyriou, and A. I. Goldman, Phys. Rev. B **81**, 180506 (2010).

- ¹²M. D. Johannes, I. I. Mazin, and D. S. Parker, Phys. Rev. B 82, 024527 (2010).
- ¹³N. Colonna, G. Profeta, A. Continenza, and S. Massidda, Phys. Rev. B 83, 094529 (2011).
- ¹⁴M. Tomic, R. Valenti, and H. O. Jeschke, Phys. Rev. B 85, 094105 (2012).
- ¹⁵W. Ji, X.-W. Yan, and Z.-Y. Lu, Phys. Rev. B **83**, 132504 (2011).
- ¹⁶G. Kresse and J. Hafner, Phys. Rev. B **47**, RC558 (1993).
- ¹⁷G. Kresse and J. Furthmuller, Phys. Rev. B **54**, 11169 (1996).
- ¹⁸P. E. Blochl, Phys. Rev. B **50**, 17953 (1994).
- ¹⁹G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1999).
- ²⁰J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
- ²¹J. P. Perdew and A. Zunger, Phys. Rev. B 23, 5048 (1981).
- ²²J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, Phys. Rev. B 46, 6671 (1992).
- ²³F. Ronning, T. Klimczuk, E. D. Bauer, H. Volz, and J. D. Thompson, J. Phys.: Condens. Matter **20**, 342203 (2008).
- ²⁴E. Madelung, Phys. Z. **11**, 898 (1910).
- ²⁵A. Einstein, Ann. Phys. **34**, 170 (1911).
- ²⁶Z. Yin, K. Haule, and G. Kotliar, Nat. Phys. 7, 294 (2011).
- ²⁷M. Daghofer, Q.-L. Luo, R. Yu, D. X. Yao, A. Moreo, and E. Dagotto, Phys. Rev. B **81**, 180514 (2010).
- ²⁸Y. Ran, F. Wang, H. Zhai, A. Vishwanath, and D.-H. Lee, Phys. Rev. B **79**, 014505 (2009).
- ²⁹S. Raghu, X.-L. Qi, C.-X. Liu, D. J. Scalapino, and S.-C. Zhang, Phys. Rev. B **77**, 220503 (2008).