Predicted Pressure-Induced *s*-Band Ferromagnetism in Alkali Metals

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First-principles density-functional-theory calculations show that compression of alkali metals stabilizes open structures with localized interstitial electrons which may exhibit a Stoner-type instability towards ferromagnetism. We find ferromagnetic phases of the lithium-IV-type, simple cubic, and simple hexagonal structures in the heavier alkali metals, which may be described as *s*-band ferromagnets. We predict that the most stable phases of potassium at low temperatures and pressures around 20 GPa are ferromagnets.

Among the elements, bulk ferromagnetism is found only in the first row of the transition metals and in the lanthanides, where partially filled $3d$ and $4f$ electronic shells of strongly localized orbitals are present. Magnetic order is normally reduced and eventually destroyed by the application of pressure because it tends to delocalize electronic states. The alkali metals are archetypal nearly free electron materials in which each atom contributes a single valence electron to a gas whose effective interaction with the ionic cores is weak. They might therefore be thought of as the least likely elements in which to find bulk ferromagnetism. The alkali metals, lithium (Li), sodium (Na), potassium (K), rubidium (Rb), cesium (Cs), and probably francium (Fr) (the most unstable naturally occurring element) adopt body-centered-cubic (bcc) phases under ambient conditions which, on compression, transform to face-centered-cubic (fcc) phases [1]. Diamond-anvil-cell experiments have shown, however, that they adopt more open structures at higher pressures [1]. Density-functional theory (DFT) calculations have reproduced the stability of the experimentally observed phases and have given insights into their electronic structures [2–6]. The most surprising result is that a large amount of valence charge in the open structures resides within the interstitial regions rather than in close proximity to the ions. This corresponds to the formation of "electrides" in which the interstitial electrons form the anions [5–8]. The open structures correspond to well-packed ionic solids when both the alkali metal ions and the centers of the interstitial electronic charges are designated as ionic positions [9].

The band structures of alkali metals deviate substantially from nearly free electron behavior under applied pressure [2–6]. The occupied valence bands become flatter than the corresponding nearly free electron ones and the occupied valence bandwidths are narrowed. Ashcroft and co-workers [2,3,8] have attributed this phenomenon to the interaction of the valence electrons with the relatively incompressible ionic cores that occupy an increasingly

large fraction of the total volume as pressure is increased. Under ambient conditions the effective interaction between the valence electrons and ionic cores is weak, but it becomes strongly repulsive under pressure and forces valence electrons to occupy interstitial positions [2,3]. The interstitial regions in close-packed structures are numerous, but small, and "cutting up" the valence charge into small regions increases the kinetic energy. The kinetic energy can, however, be reduced by adopting more open structures which have less numerous but larger interstitial regions in which to accommodate the valence electrons. This effect evidently overcomes the concomitant increase in core-core repulsion energy.

Structures may be stabilized by a mechanism involving an interaction between the Fermi surface and the Bragg planes (the FS-BP mechanism), which involves the action of the Fourier components of the lattice potential on the degenerate electron orbitals on the Bragg planes in reciprocal space [10]. The total energy may be lowered if a structure is adopted in which Bragg planes graze the Fermi surface, because the occupied orbitals just inside the Bragg plane are lowered in energy while those of the unoccupied orbitals just outside are raised. The FS-BP mechanism is likely to be involved in determining the details of the high-pressure structures of many of the alkalis [11,12]. The FS-BP mechanism normally operates when the density of electronic states $g(E)$ is large in the region around the Fermi energy E_F, but an alternative instability comes into play when $g(E)$ is also strongly peaked around E_F. In this case the energy may be lowered by transferring electrons from one spin channel to the other, resulting in ferromagnetism (FM). This is the Stoner instability [13]. The key quantities in Stoner's theory are $g(E_F)$ and the effective exchange interaction parameter I, with the instability to FM occurring when $g(E_F)I > 1$.

Motivated by the above analysis, we have investigated magnetic ordering in the alkalis under high pressures. We searched for low-enthalpy structures using *ab initio*

random structure searching (AIRSS) [14,15], which has been successfully applied to systems as diverse as metals under high pressures [5,9] and molecular solids [16,17]. We used the CASTEP plane-wave DFT code [18] and the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation density functional [19], and we also present results obtained with a Thomas-Fermi screened exchange functional (SX) [20] and the local spin density approximation (LSDA). We used ultrasoft pseudopotentials [21], treating all three electrons explicitly for Li, and nine electrons for the other alkalis. We used a Brillouin zone integration grid of spacing $2\pi \times 0.05$ Å^{-1} for the searches and a finer spacing of $2\pi \times 0.03$ Å^{-1} for the final results. For K we used basis set cutoff energies of 245 and 454 eV for the searching and final results, respectively, while cutoffs of similar high quality were used for the other elements. The phonon calculations were performed using a finite-displacement method and 64-atom supercells.

We performed spin-polarized calculations, starting some relaxations in a high spin state with an average spin density of one electron per atom and others with zero average spin density. In each calculation the spin density was allowed to evolve freely as the structure was relaxed. We also performed calculations without spin polarization. The use of a wide variety of starting structures and spin states was important in allowing many different spin and atomic configurations to be accessed. We used the calculated spin density to distinguish between paramagnetic (PM), FM, and antiferromagnetic (AFM) states. The main searches were performed at pressures around those at which experiments show that the fcc structures transform to more open phases. We performed searches with unit cells containing up to eight atoms, relaxing a total of about 1500 structures. Calculations for other known structures of the alkalis which have more than eight atoms per cell were also performed, namely, a periodic structure of space group $I4/mcm$ with 56 atoms which is a good analogue of the K-III (Rb-IV) incommensurate host-guest structure, and the 84-atom Cs-III structure and the related 52-atom structure of Rb-III [1].

Our static-lattice coexistence pressures are in good agreement with the measured room-temperature phase transition pressures. Our coexistence pressure for K-fcc and K-III of 19.8 GPa is close to the experimental transition pressure of 23 GPa [1]. Marqués *et al.* [22] have reported finding the K-III phase in some high-pressure experiments and K-$hP4$ in others, which is consistent with our finding that K-$hP4$ is only slightly less stable than K-III. Our coexistence pressure for the Rb-fcc and Rb-IV phases of 14.2 GPa is in excellent agreement with the experimental transition pressure of 14 GPa [1]. We obtain a coexistence pressure for Cs-fcc and Cs-III of 4.8 GPa, compared with the experimental transition pressure of 4.2 GPa [1]. We find Cs-IV to be stable from 4.8–10 GPa, in excellent agreement with experiment [1]. We

find no region of stability for the observed Cs-III structure which in our calculations only becomes more stable than fcc at 4.9 GPa, although this is a small discrepancy. In general we find that our calculated coexistence pressures can be brought into agreement with the experimental data by rigidly shifting the enthalpy curves by less than 5 meV, which indicates the high level of accuracy of our calculations.

We found $cI16$ (Li-IV type), simple cubic (sc), and simple hexagonal (sh) phases of K, Rb, Cs, and Fr with strong FM ordering, and a weakly FM Cs-fcc phase, see Fig. 1. The enthalpy reductions due to the formation of FM moments in the sc phases are similar to those in the corresponding sh phases. The sh phases are more stable than the sc phases at lower pressures in K and Rb, and more stable at all pressures in Cs. We did not find any spin-polarized states of Li or Na in our fully converged calculations, but we can obtain them by reducing the number of k points. This shows that Li and Na are close to a FM instability and demonstrates the importance of carefully studying the convergence with respect to the k-point sampling, as we have done. We predict FM K-$cI16$ to be the most stable in the range 18.5–20 GPa and FM K-sc to be the most stable in the range 20–22 GPa. The FM ordering leads to an energy gain of a few tens of meV per atom. When the centers of the interstitial electronic charges are designated as ionic positions, sc becomes the CsCl structure, sh the MgB$_2$ structure, and $cI16$ the Th$_3$P$_4$ structure [23], with the Cs, Mg, and P sites being those of the cations and the Cl, B, and Th sites being those of the interstitial electrons.

To explore the sensitivity to the density functional we also performed calculations using a Thomas-Fermi SX functional [20] and the LSDA. For the SX calculations we used a screening wave vector of $k_s = 0.764$ a.u., which corresponds to a Wigner-Seitz radius of $r_s = 4.2$ a.u. This is larger than the value of $r_s = 3.4$ a.u. obtained from the average valence charge density of FM K-sc at 20 GPa, but the results are rather insensitive to reasonable variations in k_s as it is proportional to the one-sixth power of the average charge density. Using the SX functional instead of PBE stabilizes FM K-sc over K-fcc by about 15 meV per atom. We expect that the sc phases of each of the alkalis would be further stabilized with respect to the fcc phases when calculated with the SX functional. We did not find magnetic ordering in K when using the LSDA functional which predicts K-sc to be stable above about 20 GPa, in disagreement with experiment. Given that the pressures of the observed transitions calculated within PBE are in very good agreement with experiment, we are inclined to believe that it gives a better description of compressed alkalis than the LSDA or SX functionals.

Calculations of the harmonic vibrational modes of K-fcc, K-sc, and FM K-sc showed them to be dynamically stable. The phonon modes of K-sc are substantially softer than those of K-fcc, and including the zero-point enthalpy
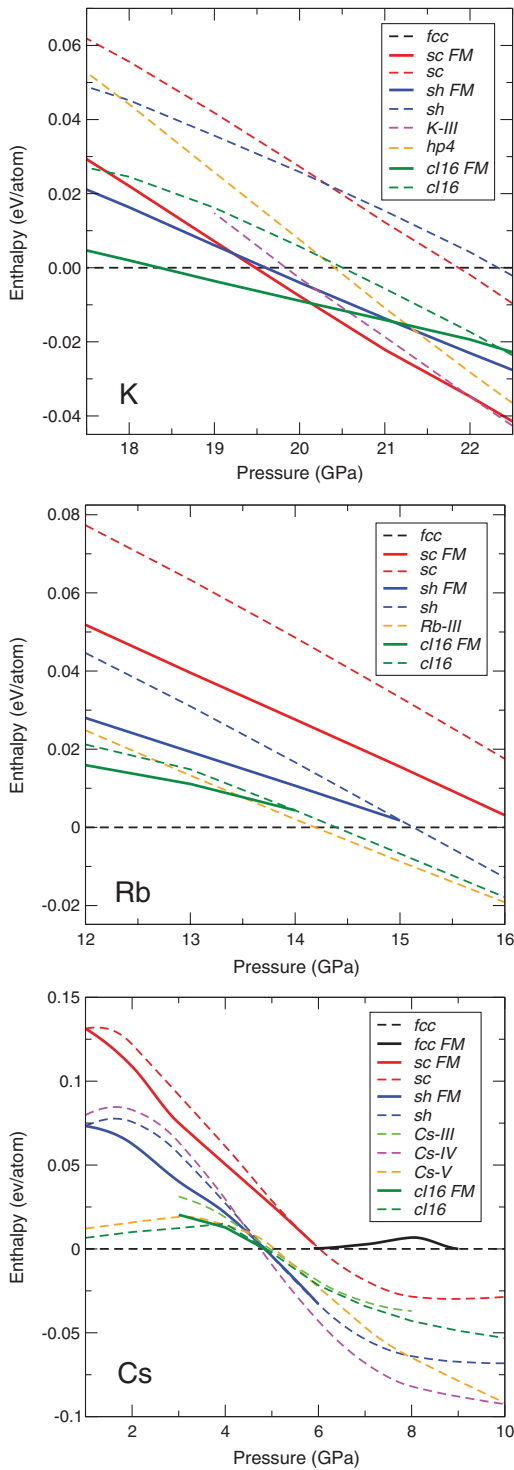
FIG. 1 (color).   Enthalpy-pressure curves for the FM and PM phases of K, Rb, and Cs. Differences in enthalpy from the fcc phase are plotted. FM phases are shown as solid lines and PM phases as dashed lines.
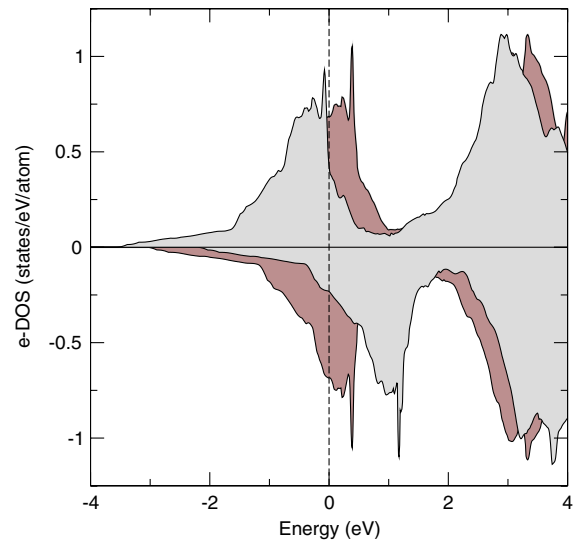

FIG. 2 (color online).   Electronic density of states, $g(E)$, of K-sc at 20 GPa. Data for the PM phase are shown in brown or dark gray and for the FM phase in light gray. The Fermi energy is shown as a vertical dotted line.

but heating will reduce the mean magnetic moment and eventually destroy the magnetism.

The valence electron density of states of the PM and FM states of K-sc at 20 GPa are shown in Fig. 2. In the PM system, E_F is close to the top of a large peak in $g(E)$ and the system is ripe for a Stoner instability. E_F falls just above the peak for the majority-spin band in FM K-sc and well below the peak for the minority spin band. FM K-sc is about 35 meV per atom more stable than PM K-sc, which is sufficient to make FM K-sc the most stable phase in the pressure range 20–22 GPa. K-sc achieves its maximum spin moment of about 0.72 electrons per atom at 22 GPa, while the maximum spin moment in FM K-sh of about 0.62 electrons per atom occurs at 20 GPa, and the maximum spin moment of $cI16$ is about 0.4 electrons per atom. We can estimate the Stoner parameter as $I \simeq \Delta \epsilon / M$, where $\Delta \epsilon$ is the energy shift between the up- and down-spin bands and M is the magnetization. For FM K-sc this gives $I = 1.7$ eV, which is larger than the values deduced for FM in transition metals [24].

The spin densities of FM K-sc and FM K-sh at 20 GPa are shown in Fig. 3. A large blob of spin-polarized charge density resides on the interstitial site at the center of the cube of K-sc, while the spin polarization on the atomic sites is small. The spin polarization on the atoms is also small in FM K-sh, and the interstitial spin density is more diffuse. The FM phases might be described by a Hubbard-like model [25] using tight-binding s orbitals centered on the interstitial regions. The magnetic state would then be described as s-band FM.

We are not aware of any experimental evidence for magnetic ordering in bulk alkali metals, although there is evidence of it in low-dimensional systems. Theoretical
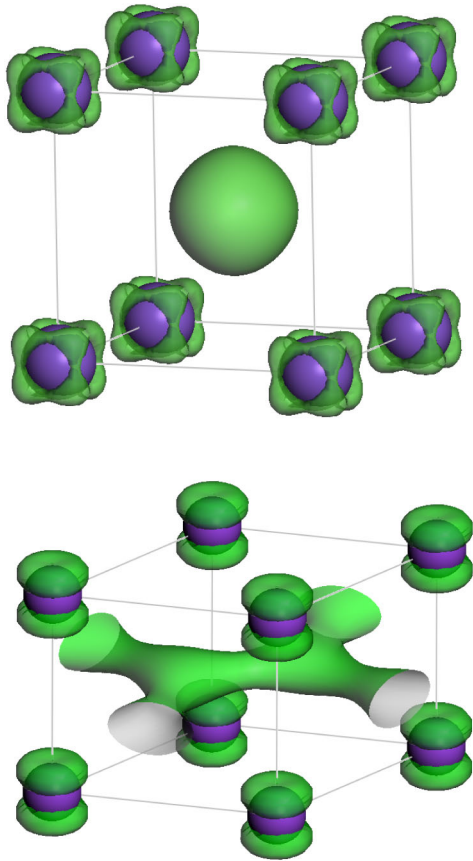
stabilizes K-sc and FM K-sc over K-fcc by about 25 meV per atom at 20 GPa. The stability of K-sc and FM K-sc over K-fcc is slightly increased by including the vibrational contribution to the free energy at a temperature of 300 K,

FIG. 3 (color online). Spin density of FM K-sc (top) and FM K-sh (bottom) at 20 GPa. The isosurfaces are at 0.05 and 0.045 electrons per atom per Å^3, respectively. The small spheres (purple) represent atoms.

Low-temperature experiments are needed to test our predictions.

In summary, we predict mechanically stable FM phases of the heavier alkali metals to have low enthalpies at pressures just above the stability ranges of the fcc phases. The FM $cI16$, sc, and sh structures can be described as s-band electride ferromagnets. FM K-$cI16$ and K-sc are predicted to be the most stable phases at low temperatures and pressures around 20 GPa.

work by Overhauser [26] suggested that charge-density and spin-density-wave instabilities might occur in alkali metals at low pressures, but these ideas have not been widely accepted. A DFT study found spontaneous magnetization in "Na wires" modeled by jellium [27], and Bergara *et al.* [28] found instabilities to FM in atomically thin Li and Na wires. FM ground states are, however, forbidden in strictly one-dimensional systems by the Lieb-Mattis theorem [29] and, in quasi-one-dimensional systems, quantum fluctuations tend to suppress FM. Experimental observations of FM in K clusters incorporated within a zeolite [30] and AFM in K clusters in a nanographite-based host [31] have also been reported. We have used AIRSS to search for structures of small unsupported K clusters, finding that some weakly AFM states are energetically favorable and that quite strongly FM phases with moments up to about 0.5 electrons per atom occur at higher energies. Electride formation in alkali metal clusters at ambient pressure is highly unlikely because the bonds are too long, and the magnetic ordering must be produced by some other mechanism. It might be possible to further stabilize FM phases of bulk alkali metals by alloying them with other alkalis or other species.

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