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Brief Reports

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Ab initio calculations of magnetic states of a Mo monolayer

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Using a scalar-relativistic norm-conserving pseudopotential and a Gaussian-orbital expansion, we have calculated the cohesive energy of a Mo monolayer film at seven different lattice constants a. For $a \geq 5.545$ bohrs a ferromagnetic state lies below the paramagnetic, but for $a \geq 5.147$ bohrs the antiferromagnetic state lies lowest.

Heine and Samson[1] (HS) have shown, within the tight-binding approximation, that the beginning and end of a transition-metal series have a propensity toward ferromagnetism while the middle of the series tends toward antiferromagnetism. This is the case for the bulk $3d$ series where Cr and Mn are antiferromagnetic and Fe, Co, and Ni are ferromagnetic. A glaring exception is Gd which is ferromagnetic although in the middle of the $4f$ series. This, however, is a consequence of an indirect-exchange interaction[2] which was not considered by HS. Because of their narrower energy bands, monolayer films are more likely to be magnetic than bulk crystals and thus allow the HS theory to be tested for elements that are not normally magnetic. For example Blügel, Weinert, and Dederichs[3] have performed *ab initio* calculations of V, Cr, Mn, Fe, Co, and Ni monolayers on Pd and Ag substrates and found V belongs in the antiferromagnetic group. The weight of experimental evidence is on the side of V on Ag being antiferromagnetic or nonmagnetic[4-6] although Rau *et al.*[7] find it ferromagnetic.

As far as we know there are no *ab initio* calculations of the magnetic properties of $4d$ transition-metal films in the published literature. We here report the results of such a calculation for a free-standing Mo(001) monolayer film as a function of its lattice constant a. We use the same relativistic norm-conserving pseudopotential that we[8] used for bulk Mo except that we do not include the spin-orbit term. We use an expansion of 56 Gaussian Bloch basis functions in the paramagnetic and ferromagnetic cases and twice as many in the antiferromagnetic. These consist of the four atomic s, p, and d Gaussians used by Chan, Vanderbilt, and Louie[9] in their bulk Mo calculation, one additional set of long-range atomic s and p Gaussians and two sets of s and p Gaussians in the hollow sites above and below the plane of the monolayer. These three new Gaussian exponents (the same Gaussians are used for all spherical harmonics as in Ref. 9) as well as the distance of the floating Gaussians from the plane were adjusted for each lattice constant to minimize the sum of the occupied one-electron eigenvalues in a zeroth-order potential constructed from a superposition of spherical unpolarized atomic charge densities. In Fig. 1 we show the two-dimensional Brillouin zone (BZ) and the 21 points which we sample in the $\frac{1}{8}$ irreducible wedge which represent 144 points in the full BZ. Also shown is how this BZ folds back into the smaller antiferromagnetic BZ leaving 12 points in the wedge. Sampling equivalent **k**'s eliminates one source of relative error in comparing the ferromagnetic and antiferromagnetic cohesive energies.

We used Kohn-Sham[10] exchange and Wigner[11] correla-

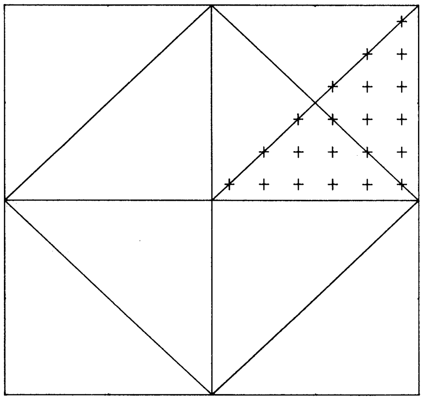

FIG. 1. Brillouin zones for monolayer Mo(001) film. The large square is the paramagnetic and ferromagnetic BZ and the small square is the $c(2\times2)$ BZ of the antiferromagnetic film. The 21 **k** points in the $\frac{1}{8}$ irreducible wedge at $\mathbf{k}=(1+2n,1+2m,1+2p)\pi/12a$ are displayed. Of these, 12 are in the $c(2\times2)$ BZ.

tion, spin polarized in the manner of von Barth and Hedin.[12] We used a supercell configuration with $3a_0$ between atomic planes where $a_0=5.943$ bohrs is the bulk lattice constant. This allowed us to calculate the cohesive energy exactly as we did for the bulk crystal[8] rather than using the somewhat more complicated thin-film method.[13] We fit the charge density and exchange-correlation potential at 4500 random points in the unit cell. Of these, 208 are on a radial mesh at random angles within a sphere of radius $a/4$ around the atom. Of the remaining points, three-fourths are taken to lie within $3a_0/4$ of the atomic plane. The fitting functions consisted of 306 symmetrized combinations of plane waves and 72 Gaussian lattice harmonics, up to $l=8$, for the largest a. For smaller a's the fit became numerically unstable so we cast out the longest-range Gaussians as needed, ending up with 54 at the smallest a. For the antiferromagnetic unit cell, both the number of fitting points and fitting functions are doubled. In the antiferromagnetic case we take the $(n+1)$st input potential to be

$$V_{\text{in}}^{n+1}(\mathbf{r},\sigma)=V_{\text{in}}^{n}(\mathbf{r},\sigma)+\alpha_n\Delta_{\text{sym}}^{n}(\mathbf{r},\sigma)+\beta_n\Delta_{\text{anti}}^{n}(\mathbf{r},\sigma)\ , \tag{1}$$

where

$$\Delta^n(\mathbf{r},\sigma)=V_{\text{out}}^{n}(\mathbf{r},\sigma)-V_{\text{in}}^{n}(\mathbf{r},\sigma)\ . \tag{2}$$

The difference between the nth iteration's spin-dependent[14] input and output potentials is separated into parts symmetric and antisymmetric under inversion through a point midway between the two atoms in the unit cell. Since only the spin density but not the charge density is different on the two atoms, $\Delta_{\text{anti}}^{n}(\mathbf{r},\sigma)$ arises only from V_{xc}, the exchange-correlation potential. Unlike the Coulomb potential, this is an antiscreening potential in the sense that if $V_{\text{xc out}}^{n}$ is more negative in some region than $V_{\text{xc in}}^{n}$ and therefore $V_{\text{xc in}}^{n+1}$ is made more negative in that region, charge will flow into that region making $V_{\text{xc out}}^{n+1}$ still more negative. If α_n in Eq. (1) is taken much larger than 0.3, succeeding Δ_{sym}'s will alternate in sign and grow whereas $\beta_n=2$ is typically used and it can occasionally be taken to be even larger. If we did not separate Δ^n into symmetric and antisymmetric parts, we would have to use a common $\alpha_n=0.3$ and the convergence of the antisymmetric part of the potential to self-consistency would be interminable.[15]

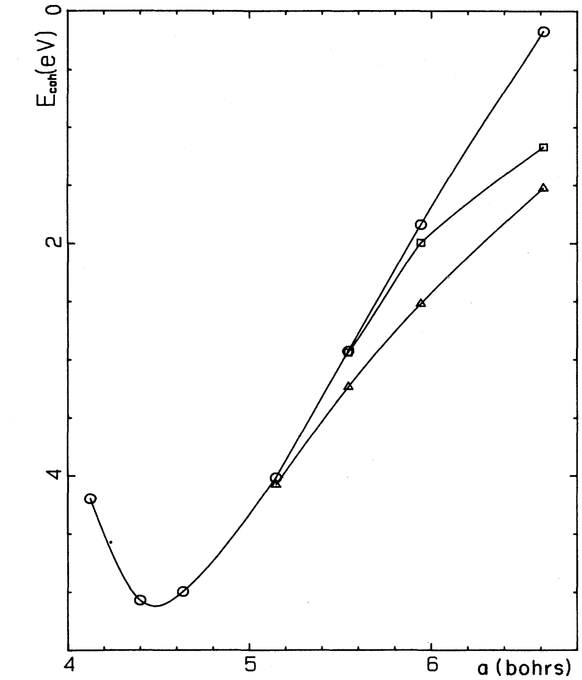

FIG. 2. The cohesive energy for the paramagnetic (○), antiferromagnetic (△), and ferromagnetic (□) Mo(001) films at the lattice constants listed in Table I.

In Table I are listed the cohesive energies for the paramagnetic, antiferromagnetic, and ferromagnetic states at seven different lattice constants. These are also plotted in Fig. 2. The cohesive energy is defined to be $E_{\text{coh}}=E_{\text{bind}}^{\text{crystal}}-E_{\text{bind}}^{\text{atom}}$ where $E_{\text{bind}}^{\text{atom}}=16.177\,04$ Ry is the calculated binding energy of the spin-polarized atom without the spin-orbit term. Thus as $a\to\infty$ in Fig. 2 the ferromagnetic and antiferromagnetic curves approach zero but $E_{\text{coh}}^{\text{para}}\to 4.193$ eV, the difference between the spin-polarized and unpolarized atomic energies. Note that only the paramagnetic state exists at the equilibrium value, $a=4.5$ bohrs and that this equilibrium nearest-neighbor distance lies between that of the bulk crystal, $a=\sqrt{3}a_0/2=5.147$ bohrs and the experimental value[16] of the Mo_2 bond length $R_0=3.65$ bohrs. Note also that local density calculations[17] for Mo_2 find that the dimer,

TABLE I. Cohesive energy at several lattice constants for paramagnetic, antiferromagnetic, and ferromagnetic states of Mo monolayer. The magnetization is given in Bohr magnetrons for the ferromagnetic case.

a (bohrs)	$E_{\text{coh}}^{\text{para}}$ (eV)	$E_{\text{coh}}^{\text{AFM}}$ (eV)	$E_{\text{coh}}^{\text{FM}}$ (eV)	M^{FM}/μ_B
4.125	4.200			
4.400	5.070			
4.636	4.995			
5.147	4.017	4.079		
5.545	2.927	3.235	2.941	0.423
5.943	1.838	2.520	1.994	2.769
6.615	0.172	1.527	1.172	4.843

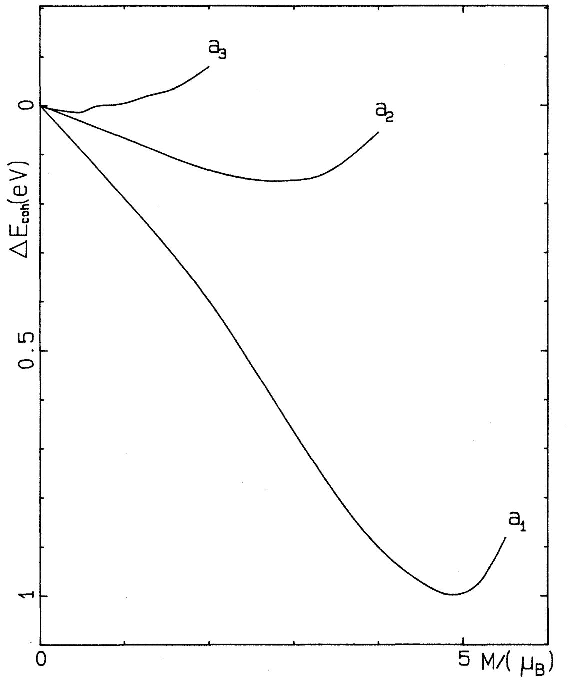

FIG. 3. Difference between ferromagnetic and paramagnetic cohesive energies as a function of magnetization for Mo(001) monolayer films at $a_3=5.545$, $a_2=5.943$, and $a_1=6.615$ bohrs.

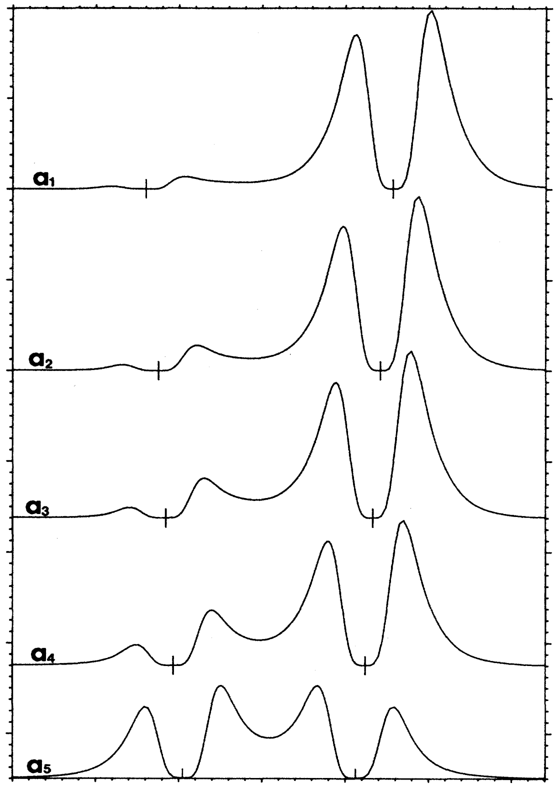

FIG. 4. The up-spin charge density in the antiferromagnetic Mo(001) film in arbitrary but consistent units for lattice constants $a_5=4.636$, $a_4=5.147$, $a_3=5.545$, $a_2=5.943$, and $a_1=6.615$ bohrs. The vertical lines represent the two atoms in the unit cell, and the charge is plotted along the line between the atoms and in the [001] direction along the film normal away from both atoms.

just like the monolayer, is nonmagnetic at equilibrium but becomes antiferromagnetic at larger bond lengths. Although, as far as we know they have not been performed, we predict that similar calculations for the bulk crystal will find the antiferromagnetic state lies lowest for lattice constants sufficiently larger than equilibrium.

We used the fixed-moment method[18] to evaluate $E_{\rm coh}^{\rm FM}$ and the magnetization listed in the last column of Table I. In Fig. 3 we plot $E_{\rm coh}^{\rm FM}(M)$ for three different lattice constants. These curves were fit with parabolas about their minima to obtain the results listed in Table I. It would be interesting to compare a set of such curves for both the bulk and monolayer over an entire transition-metal series. We note that monolayer Mo has a second-order phase transition to the ferromagnetic state with decreasing lattice constant (assuming one ignores the antiferromagnetic state) and in that respect is similar to bulk Fe rather than to bulk Cr which is first order according to the calculations of Moruzzi, Marcus, and Pattnaik.[19]

In his thesis Blügel[20] has calculated the total energy of Mo(001) monolayer in the ferromagnetic and antiferromagnetic states at $a=a_0$. He finds $E_{\rm coh}^{\rm AFM}-E_{\rm coh}^{\rm FM}=0.503$ eV in good agreement with our 0.526 eV. He also obtains $M^{\rm FM}=2.04\mu_B$ within the inscribed sphere which seems consistent with our $2.77\mu_B$ for the entire unit cell. We have nothing to directly compare with his inscribed sphere $M^{\rm AFM}=2.96\mu_B$, however, in Fig. 4 we plot the up-spin density along the line connecting the two atoms in the antiferromagnetic unit cell as well as along the film normal away from the two atoms. It is interesting to note that even for $a=5.147$ bohrs where $E_{\rm coh}^{\rm AFM}$ is only 0.062 eV larger than $E_{\rm coh}^{\rm para}$ the spin density is strongly antiferromagnetic.

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[1] V. Heine and J. H. Samson, J. Phys. F **13**, 2155 (1983).

[2] B. R. Cooper, in *Solid State Physics*, edited by F. Seitz, D. Turnbull, and H. Ehrenreich (Academic, New York, 1968), Vol. 21, p. 393.

[3] S. Blügel, M. Weinert, and P. H. Dederichs, Phys. Rev. Lett. **60**, 1077 (1988).

[4] H. Seigmann, in *Solvay Conference on Surface Science*, Vol. 14 of *Springer Series in Surface Sciences*, edited by F. W. de Wette (Springer, Berlin, 1988), p. 466.

[5] J. L. Erskine (private communication).

[6] M. Stampanoni, A. Vaterlaus, D. Pescia, M. Aeschlimann, F. Meier, W. Dürr, and S. Blügel, Phys. Rev. B **37**, 10380 (1988).

[7] C. Rau, C. Liu, G. Xing, and C. Jin, J. Vac. Sci. Technol. **5**, 740 (1987).

[8] M. J. Zhu, D. M. Bylander, and L. Kleinman, Phys. Rev. B **36**, 3182 (1987).

[9] C. T. Chan, D. Vanderbilt, and S. G. Louie, Phys. Rev. B **33**, 7941 (1986).

[10] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965). Note that unlike Ref. 8, we do not use the relativistic form of the exchange functional here.

[11] E. Wigner, Phys. Rev. **46**, 1002 (1934).

[12] U. von Barth and L. Hedin, J. Phys. C **5**, 1629 (1972).

[13] L. Kleinman and K. Mednick, Phys. Rev. B **23**, 4960 (1981).

[14] The calculation is actually performed only for electrons of one spin. The spin density of opposite sign which is needed to calculate $V^{n}_{\text{out}}(\mathbf{r},\sigma)$ is obtained by a translation of a.

[15] In the ferromagnetic case we separated the potential into $\overline{V}=\frac{1}{2}[V(\uparrow)+V(\downarrow)]$ and $\delta V=\frac{1}{2}[V(\uparrow)-V(\downarrow)]$. Although δV is an exchange-correlation potential and is seen with opposite sign by the up and down spins, because of the spin imbalance it has a net effect on the charge density and hence on the Coulomb potential. Thus the Δ associated with it can be weighted only slightly more heavily than the Δ associated with $\overline{V}$.

[16] Y. M. Eframov, A. N. Samailova, V. B. Kozkukhowsky, and L. V. Gurvich, J. Mol. Spectrosc. **73**, 430 (1978).

[17] S. Lee, D. M. Bylander, and L. Kleinman, Phys. Rev. B **37**, 10035 (1988).

[18] K. Schwarz and P. Mohn, J. Phys. F **14**, L129 (1984).

[19] V. L. Moruzzi, P. M. Marcus, and P. C. Pattnaik, Phys. Rev. B **37**, 8003 (1988).

[20] S. Blügel, Ph.D. thesis, Jülich Report No. 2197, 1988.