# Local-density description of antiferromagnetic Cr

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Self-consistent local-spin-density-approximation (LSDA) –based calculations of magnetic and structural properties of bcc Cr are reported. Relatively poor agreement with experimental data is obtained. Either the calculated structural properties are significantly different from experiment or the magnetic moments are incorrect. Calculations using the von Barth–Hedin and Vosko exchange-correlation potentials yield magnetic moments in reasonable agreement with experiment but with poor structural properties. On the other hand, calculations performed using an $X\alpha$ potential yield better agreement with experimental structural data but with very poor magnetic moments. It is concluded that the LSDA provides an inadequate description of Cr.

## I. INTRODUCTION

Chromium metal, surfaces, and overlayers are known to display a number of interesting physical properties. Bulk Cr displays a long-wavelength spin-density wave with a short-range antiferromagnetic ordering and local moments of about $0.59\mu_B$. The Cr(001) surface which unlike its $4d$ and $5d$ analogues, Mo(001) and W(001), is not known to reconstruct,[1] is believed to order ferromagnetically with strongly enhanced magnetic moments.[2-6] Since it seems plausible that the strongly enhanced magnetism on the Cr(001) surface may be related to the instability against reconstruction of the Mo(001) and W(001) surfaces, we felt that it would be desirable to perform a total-energy study of the relationship between bonding and magnetism on this surface. This would necessarily involve calculating the dependence of the magnetic moments and total energies on the atomic positions. In order to assess the reliability of local-spin-density-approximation (LSDA) based calculations in this context we have used the general-potential linear-augmented-plane-wave LAPW method to perform calculations of the equilibrium structural and magnetic properties of bulk bcc Cr using three different exchange-correlation potentials, specifically, the von Barth–Hedin,[7] Vosko,[8] and the $X\alpha$ ($\alpha=2/3$) froms. It was found that as in the case of ferromagnetic bcc Fe,[9] relatively poor agreement with experiment is obtained indicating that LSDA-based calculations for Cr surfaces may be unreliable.

## II. METHODS

Since the general-potential LAPW method[10,11] has been described in detail elsewhere the computational technique is only discussed briefly. In the calculations reported here both the core and valence states were calculated self-consistently, the core states fully relativistically in an atomiclike approximation and the valence states in a scalar-relativistic approximation. Antiferromagnetic Cr was represented using a CsCl structure unit cell containing two Cr atoms. While this unit cell does not allow

calculations to be performed for the experimentally observed[12] spin-density-wave magnetic structure, it does permit calculations for a commensu. ate antiferromagnetically ordered state. In view of the large differences between the results of our calculations reported below and experiment it seems extremely unlikely that our conclusions would be altered if calculations were performed for a spin-density-wave structure. The calculations reported here were performed using a Cr muffin-tin sphere radius of 2.0 a.u. (these spheres are used to partition space only—no shape approximations to the potentials or charge densities are made in the general potential LAPW method). Well-converged results were obtained using basis sets consisting of about 200 LAPW's with a set of 56 special k points[13] being used for the Brillouin-zone averages.

In order to verify that the antiferromagnetic state is the true LSDA ground state, calculations were also carried out for the paramagnetic state and searched for a ferromagnetic state. It was found that the commensurate antiferromagnetic state is about 0.01 eV per atom lower in energy than the paramagnetic state using von Barth–Hedin potential. No stable ferromagnetic solution was found.

## III. RESULTS AND DISCUSSION

Our principle results for antiferromagnetic Cr are shown in Figs. 1 and 2, where the calculated total energies and magnetic moments as a function of the volume of the unit cell are shown for the three exchange-correlation potentials. The solid curves in Fig. 1 are fits of the Murnaghan equation of state[14] to the calculated total energies. The rms errors in the fits were less than 150 $\mu$Ry in all cases. The fitted bulk moduli and lattice parameters as well as the calculated magnetic moments *at the experimental lattice parameter* are given in Table I along with the experimental values[15-17] and the results of previous calculations.[6,18-23] Our results are in good agreement with most of the earlier calculations. It may be noted that the results obtained using the von
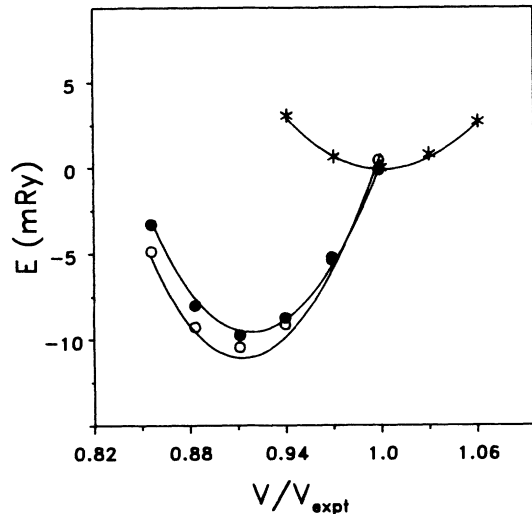
FIG. 1. Calculated total energies as a function of the volume $V$ of the unit cell. The experimental cell volume is denoted $V_{expt}$. The solid circles, open circles, and asterisks denote calculations performed using the von Barth–Hedin, Vosko, and $X\alpha$ potentials, respectively. The curves have been shifted so that the total energy at the experimental equilibrium volume is zero. The solid lines are fits to Murnaghan's equation of state.

Barth–Hedin and Vosko potentials are similar, as might be expected from the similarity of the two potentials. The magnetic moments obtained using these exchange-correlation potentials are about 18% larger than the experimental value. We consider this level of agreement to be quite satisfactory, particularly in view of the fact that our calculations were performed for a commensurate antiferromagnetic structure. The calculated bulk moduli, however, are about 40% larger than experiment and the lattice parameters about 3% too small. These relatively
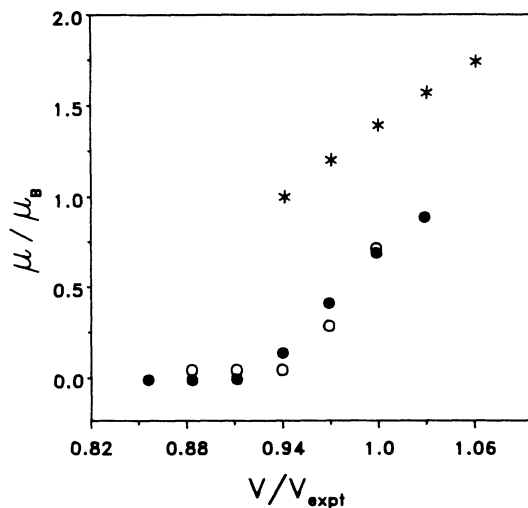


FIG. 2. Calculated magnetic moments as a function of the cell volume. The solid circles, open circles, and asterisks denote calculations performed using the von Barth–Hedin, Vosko, and $X\alpha$ potentials, respectively.

large discrepancies indicate that these exchange-correlation potentials do not provide an adequate description of Cr. The $X\alpha$ potential, on the other hand, was found to yield significantly better structural properties for Cr. The calculated bulk modulus using this potential is within 21% of experiment and the lattice parameter within 0.2%. Unfortunately, while the calculated structural properties are improved when the $X\alpha$ potential is used, the predicted magnetic moment of $1.5\mu_B$ is far too large, indicating that as in the case of the other two exchange-correlation potentials tested, the $X\alpha$ form does not properly describe Cr.

Wang et al.[9] have performed LSDA-based calculations of the structural and magnetic properties of ferromagnetic bcc Fe using the Vosko exchange-correlation potential, obtaining a result similar to that obtained in the present study for Cr, i.e., a significantly smaller lattice parameter and larger bulk modulus than experimentally observed and concluding that LSDA does not adequately describe the magnetic interaction in the 3d transition metals. We believe that the failure of the LSDA to adequately describe Cr may be related to the large errors in Fe and that the present results support the view of Wang et al. that the LSDA is unreliable for magnetic 3d transition metals. In any case, the present results suggest that in order to reliably treat Cr and quite likely Cr surfaces it may be necessary to go beyond the LSDA.

## IV. CONCLUSIONS

Structural and magnetic properties of antiferromagnetic Cr have been calculated within the LSDA using three

TABLE I. Lattice parameter $a$, bulk modulus $B$, and magnetic magnetic moment $M$ of Cr. The last two calculations are for the magnetic moments of central layer atoms in slab calculations. The exchange-correlation potentials are denoted as von Barth–Hedin (vBH) and Hedin-Lundqvist (HL).

|  | $a$ (Å) | $B$ (Mbar) | $M$ ($\mu_B$) |
|---|---|---|---|
| This study:    vBH | 2.798 | 2.65 | 0.70 |
| Vosko | 2.792 | 2.86 | 0.67 |
| $X\alpha$ ($\alpha=\frac{2}{3}$) | 2.875 | 1.50 | 1.39 |
| Wigner (paramagnetic)[a] | 2.806 | 2.77 | |
| HL (paramagnetic)[b] | 2.805 | 2.70 | |
| vBH (LASW method)[c] | 2.855 | 2.13 | 0.59 |
| vBH (LMTO method)[d] | | 2.36 | 0.29 |
| vBH (LMTO method)[e] | | | 0.60 |
| $X\alpha$, $\alpha=0.7$ (LCAO DVM)[f] | | | 0.64 |
| vBH (slab LAPW method)[g] | | | 0.89 |
| Experiment (Refs. 15–17) | 2.879 | 1.90 | 0.59 |

[a]Reference 18.
[b]Reference 19.
[c]Reference 20, with the linear-augmented-spherical-wave method.
[d]Reference 21, with the linear-muffin-tin-orbital method.
[e]Reference 22.
[f]Reference 23, with the linear combination of atomic orbitals–discrete variational method.
[g]Reference 6.

different exchange-correlation potentials, none of which adequately describes this material. Either the calculated structural properties are significantly different from experiment or the magnetic moments are in error. We interpret this failure as an indication that the LSDA does not adequately describe Cr and that it may be necessary to go beyond the local approximation to perform reliable calculations of structural and magnetic properties of bulk Cr and its surfaces and interfaces.

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[1]J. S. Foord and R. M. Lambert, Surf. Sci. **115**, 141 (1982).

[2]G. Allan, Surf. Sci. **74**, 79 (1978).

[3]H. Hasegawa, J. Phys. F **16**, 1555 (1986).

[4]C. Rau and S. Eichner, Phys. Rev. Lett. **47**, 939 (1981).

[5]L. E. Klebanoff, S. W. Robey, G. Liu, and D. A. Shirley, Phys. Rev. B **30**, 1048 (1984).

[6]C. L. Fu and A. J. Freeman, Phys. Rev. B **33**, 1755 (1986); J. Magn. Magn. Mater. **54-57**, 777 (1986).

[7]U. von Barth and L. Hedin, J. Phys. C **5**, 1692 (1972).

[8]S. H. Vosko, L. Wilk, and M. Nusair, Can. J. Phys. **58**, 1200 (1980); S. H. Vosko and L. Wilk, Phys. Rev. B **22**, 3812 (1980).

[9]C. S. Wang, B. M. Klein, and H. Krakauer, Phys. Rev. Lett. **54**, 1852 (1985).

[10]O. K. Andersen, Phys. Rev. B **12**, 3060 (1975); E. Wimmer, H. Krakauer, M. Weinert, and A. J. Freeman, *ibid.* **24**, 864 (1981); D. R. Hamann, Phys. Rev. Lett. **42**, 662 (1979).

[11]S. H. Wei and H. Krakauer, Phys. Rev. Lett. **55**, 1200 (1985); S. H. Wei, H. Krakauer, and M. Weinert, Phys. Rev. B **32**,

7792 (1985).

[12]For a review see E. Fawcett, Rev. Mod. Phys. **60**, 209 (1988).

[13]A. Baldereschi, Phys. Rev. B **7**, 5212 (1973); D. J. Chadi and M. L. Cohen, *ibid.* **8**, 5747 (1973); H. J. Monkhorst and J. D. Pack, *ibid.* **13**, 5188 (1976); **16**, 1748 (1977).

[14]F. D. Murnaghan, Proc. Natl. Acad. Sci. U.S.A. **30**, 244 (1944).

[15]G. Shirane and W. J. Takei, J. Phys. Soc. Jpn. **17**, Suppl. B-III, 35 (1962).

[16]D. I. Bolef and J. de Klerk, Phys. Rev. **129**, 1063 (1963).

[17]W. B. Pearson, *Handbook of Lattice Spacings and Structures of Metals* (Pergamon, New York, 1958), Vol. 4.

[18]L. F. Mattheiss and D. R. Hamann, Phys. Rev. B **33**, 823 (1986).

[19]V. L. Moruzzi, A. R. Williams, and J. K. Janak, Phys. Rev. B **15**, 2854 (1977).

[20]J. Kubler, J. Magn. Magn. Mater. **20**, 277 (1980).

[21]H. L. Skriver, J. Phys. F **11**, 97 (1981).

[22]F. Herman and P. Lambin, Phys. Rev. B **31**, 4394 (1985).

[23]N. Hirashita, G. Yokoyama, T. Kambara, and K. I. Gondaira, J. Phys. F **11**, 2371 (1981).