

Structural, electronic, and magnetic properties of MnO

J. E. Pask, D. J. Singh, I. I. Mazin, C. S. Hellberg, and J. Kortus

Center for Computational Materials Science, Naval Research Laboratory, Washington, DC 20375

(Received 13 December 2000; published 11 June 2001)

We calculate the structural, electronic, and magnetic properties of MnO from first principles, using the full-potential linearized augmented plane-wave method, with both local-density and generalized-gradient approximations to exchange and correlation. We find the ground state to be of rhombohedrally distorted $B1$ structure with compression along the $[111]$ direction, antiferromagnetic with type-II ordering, and insulating, consistent with experiment. We show that the distortion can be understood in terms of a Heisenberg model with distance dependent nearest-neighbor and next-nearest-neighbor interactions determined from first principles. Finally, we show that magnetic ordering can induce significant charge anisotropy, and give predictions for electric-field gradients in the observed rhombohedrally distorted structure.

DOI: 10.1103/PhysRevB.64.024403

PACS number(s): 75.30.Et, 75.10.Lp, 75.50.Ee, 76.60.Gv

I. INTRODUCTION

Since the recognition of their unusual insulating and magnetic properties over a half century ago, the first-row transition-metal monoxides have been the subject of much experimental and theoretical interest. Because they are highly correlated Mott or charge-transfer insulators,^{1,2} first-principles theoretical approaches based on density-functional theory (DFT) in the local-density approximation (LDA) (Refs. 3 and 4) have proven inadequate for understanding certain properties such as electrical conductivity and magnetic moments, and new or extended approaches such as self-interaction corrected,^{5,6} orbital polarization corrected,⁷ on-site Coulomb corrected (LDA+U),^{8,9} optimized effective potential,¹⁰ and model GW (Ref. 11) methods have been developed in order to address these deficiencies. Nevertheless, DFT-LDA-based approaches have proven successful in understanding a number of ground-state properties, most notably in the cases of MnO and NiO, which are correctly predicted to be insulating and antiferromagnetic with type-II ordering (though the gaps are underestimated).^{12–15} Moreover, the use of the generalized-gradient approximation (GGA) (Ref. 16) has been shown to yield further improvements.¹⁷ Here, we focus on the larger-moment compound MnO, from the standpoint of DFT in both LDA and GGA approximations.

Above the Néel temperature $T_N = 118$ K, MnO is a paramagnetic insulator with the rocksalt ($B1$) structure. Below T_N , it is a type-II antiferromagnetic (AFII) (Fig. 1) insulator with rhombohedrally distorted $B1$ structure. The rhombohedral distortion takes the form of a compression along the $[111]$ direction, taking cubic angles from 90° to 90.62° .¹⁸ Based upon augmented spherical wave (ASW) LDA calculations, Oguchi *et al.*^{13,14} showed that the electronic structure is very sensitive to the magnetic ordering, and that the LDA can predict MnO to be an insulator, but only when the magnetic ordering is AFII, as it is experimentally. Based again upon ASW-LDA calculations, Terakura *et al.*¹⁵ subsequently explained the stability of the AFII ordering relative to non-magnetic (NM), ferromagnetic (FM), and type-I antiferromagnetic (AFI) orderings in terms of the strong $dd\sigma$ coupling through the oxygens of opposite-spin cation sublattices

in the AFI ordering vs same-spin sublattices in the AFI. Using a linear combination of atomic orbitals (LCAO) LDA approach, Belkhir and Hugel¹⁹ examined the splitting of d subbands, concluding that pd hybridization in the AFII structure enhances the splitting relative to that predicted by classical ligand field theory. Using a linearized augmented plane-wave (LAPW) approach, Dufek *et al.*¹⁷ showed that

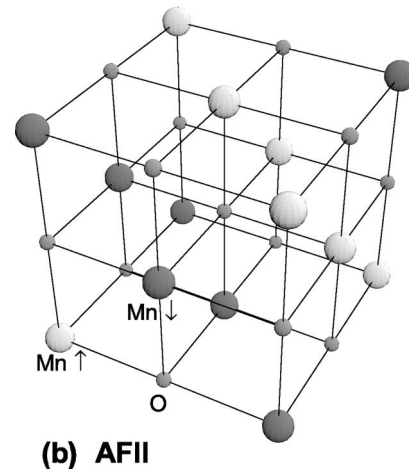
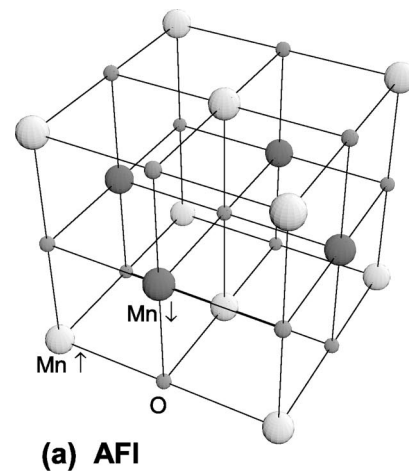


FIG. 1. (a) AFI ($[001]$) and (b) AFII ($[111]$) magnetic orderings.

the GGA can yield further improvements to LDA results, finding a minor improvement of the gap from 1.0 eV to 1.4 eV and of the Mn spin magnetic moments from $3.72\mu_B$ to $4.15\mu_B$, relative to experimental values of 3.6–3.8 eV and 4.58 – $4.79\mu_B$, respectively. Using an LCAO Hartree-Fock (HF) approach, Towler *et al.*²⁰ calculated structural, magnetic, elastic, and vibrational properties. They determined the correct AFII ground state and a rhombohedral distortion angle of 90.47° , very close to the experimental value. Mackrodt *et al.*²¹ subsequently applied the same methodology to the calculation of phase transitions under pressure. Using a linear muffin-tin orbital atomic sphere approximation (LMTO-ASA) approach, Cohen *et al.*²² calculated low- and high-pressure properties of MnO in the context of an investigation of magnetic-moment collapse, and found that the GGA yielded an improved lattice constant, bulk modulus, and magnetic moment relative to LDA results. More recently, using a plane-wave pseudopotential (PWPP) GGA approach, supplemented by LDA+U calculations, Fang *et al.*²³ investigated low- and high-pressure properties. They determined the correct AFII ground state, a rhombohedral distortion angle of $\approx 92^\circ$, somewhat larger than the experimental value, magnetic moments, and a phase transition to a metallic NiAs structure at high pressure. Massidda *et al.*²⁴ have investigated magnetic-order-induced anisotropies in linear-response properties using a combination of *ab initio* and model calculations. In the course of their study, they determined a ground-state distortion angle of 90.66° , very close to the experimental value, and showed that the zone-center optic phonon frequencies and Born effective charge tensor exhibit significant magnetic-order-induced anisotropies, even when assuming the perfect rocksalt structure, contrary to the assumption of cubic symmetry commonly made in interpreting experimental data.

The mechanism underlying the rhombohedral distortion below T_N was examined by Kanamori²⁵ in the late 1950s. Based upon paramagnetic susceptibility data, it was concluded that there are significant exchange interactions between nearest-neighbor (NN) cations and, based upon Curie-Weiss and Néel temperature data, that these interactions are predominantly direct in nature. It was further concluded, consistent with earlier suggestions of Greenwald and Smart,²⁶ that the rhombohedral distortion below T_N is due to these NN interactions. Assuming distance dependent NN and next-nearest-neighbor (NNN) interactions, Rodbell and Owen²⁷ subsequently used a molecular-field approach to derive an expression for the distortion which supported the above conclusions, having explicit dependence only upon the NN interactions. Lines and Jones²⁸ subsequently deduced the same expression from a Heisenberg model containing only NN and NNN interactions, and used a Green's-function approach²⁹ in the random-phase approximation to evaluate the exchange constants based upon susceptibility data. More recently, Oguchi *et al.*^{13,14} calculated exchange constants based on *ab initio* ASW-LDA calculations, employing the Korringa-Kohn-Rostoker coherent potential approximation (KKR-CPA). In this work they showed that interactions beyond NNN were in fact negligible, justifying the assumption made almost universally in previous work. The constants ob-

tained, however, were about three times larger than those determined from experimental data. Among the reasons suggested for the discrepancy were the assumption that total-energy differences were well represented by eigenvalue-sum differences, and spherical approximations in the ASW and KKR-CPA calculations. Subsequently, Solovyev and Terakura³⁰ calculated exchange constants based on LMTO-ASA-LDA calculations in the context of a discussion of single-particle theoretical approaches to MnO. In this work, they employed an expression³¹ for the exchange constants based on infinitesimal displacements from the ground-state configuration rather than finite rotations in a random medium as in Refs. 13 and 14, and employed spherical approximations as before. The constants obtained were, however, again significantly larger than those determined from experimental data. The main reason suggested for the discrepancy was the underestimation of intra-atomic exchange and charge-transfer energies in the LDA.

Here, we calculate the structural, electronic, and magnetic properties of MnO by the full-potential linearized augmented plane-wave method, using both LDA and GGA approximations to exchange and correlation, thus improving upon spherical, pseudopotential, and/or strictly LDA approximations in earlier work. We show that the observed rhombohedral distortion can be understood in terms of a Heisenberg model with distance dependent NN and NNN interactions determined from *ab initio* calculations, without the CPA or spherical approximations. And lastly, we consider the charge anisotropy induced by magnetic ordering through *ab initio* calculations of electric-field gradients.

II. CRYSTAL, ELECTRONIC, AND MAGNETIC STRUCTURE

General potential LAPW (Ref. 32) calculations were carried out for NM, FM, AFI, and AFII magnetic orderings. Well-converged basis sets were employed with a plane-wave cutoff of 18.9 Ry, corresponding to an average of ≈ 109 basis functions per atom (the exact number being \mathbf{k} dependent).³³ Local orbital extensions³⁴ were used for Mn $l = 1, 2, 3$ and O $l = 1, 2$ channels to include higher-lying semi-core states and relax linearization errors. Core states were treated fully relativistically in a self-consistent atomiclike approximation, while valence states were treated scalar relativistically. Increasing the plane-wave cutoff to 24.7 Ry, corresponding to an average of ≈ 159 basis functions per atom, yielded a change in total energy of less than 2.5 mRy/atom in LDA tests. Highly converged special \mathbf{k} -point sets³⁵ were employed consisting of 512 points in the rhombohedral (NM, FM, and AFII) Brillouin zones and 486 points in the tetragonal (AFI) zone. Doubling the number of \mathbf{k} points in each direction yielded a change in total energy of less than 0.15 mRy/atom in LDA tests. LDA and GGA calculations employed the exchange-correlation functionals of Hedin and Lundqvist,³⁶ and Perdew and Wang,³⁷ respectively. As shown in Fig. 2, the LDA calculations predict the ground state to be antiferromagnetic with AFII ordering, consistent with experiment,¹⁸ previous HF calculations,²⁰ and density-

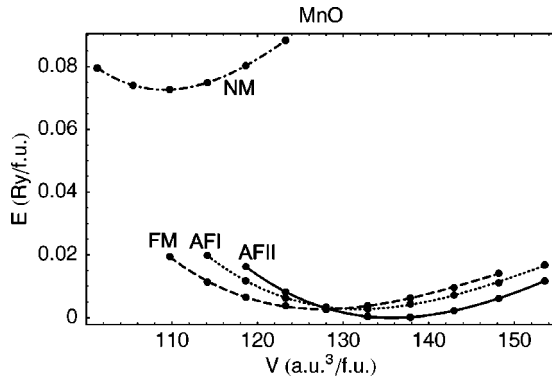


FIG. 2. LAPW-LDA results for energy vs volume of MnO, predicting AFII ground-state magnetic ordering.

functional calculations^{15,23} employing spherical or pseudopotential approximations. The GGA results are qualitatively similar, predicting the correct AFII ground state, but with a lattice constant of 8.38 a.u., much improved from the LDA value of 8.16 a.u. relative to the experimental value of 8.38 a.u.³⁸

Figures 3 and 4(c) show the Brillouin zone and LDA band structure and density of states corresponding to the ground-state AFII ordering. The GGA results are qualitatively similar, but with a larger exchange splitting and gap of ≈ 0.29 Ry and ≈ 0.105 Ry, respectively, compared to LDA values of ≈ 0.27 Ry and ≈ 0.075 Ry, due to lower occupied and higher unoccupied d states relative to O p states. In both cases, the large exchange splitting and narrow e_g band are sufficient to produce an insulator, consistent with experiment¹⁸ and previous calculations.^{9,15,17,20,23,24} Significantly, however, both LDA and GGA calculations predict other configurations to be metallic [Figs. 4(a) and (b)], with the implication that the spin-disordered paramagnetic state would also be metallic, contrary to experiment. These results

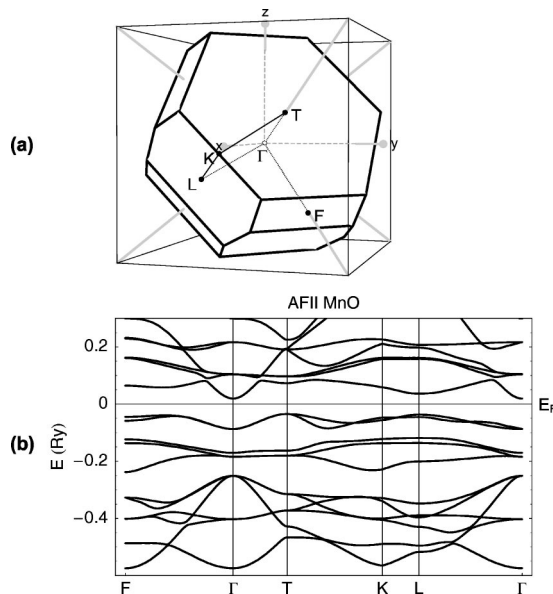


FIG. 3. (a) Rhombohedral Brillouin zone and (b) LAPW-LDA band structure of AFII MnO.

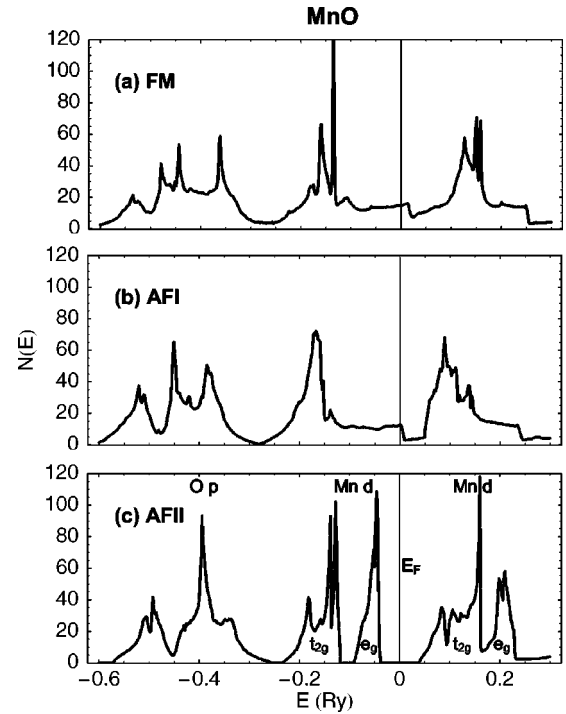


FIG. 4. LAPW-LDA density of states for (a) FM, (b) AFI, and (c) AFII MnO. Only the AFII ordering is predicted to be insulating.

are consistent with the characterization of MnO as a correlated Mott-Hubbard insulator.

III. RHOMBOHEDRAL DISTORTION

Figure 5 shows LDA results for the total energy vs rhombohedral strain in the ground-state AFII ordering at the experimental volume. The GGA results are essentially the same. The rhombohedral strain is determined by a parameter g through the volume conserving strain tensor

$$G = \begin{pmatrix} 1+g & g & g \\ g & 1+g & g \\ g & g & 1+g \end{pmatrix} (1+3g)^{-1/3}.$$

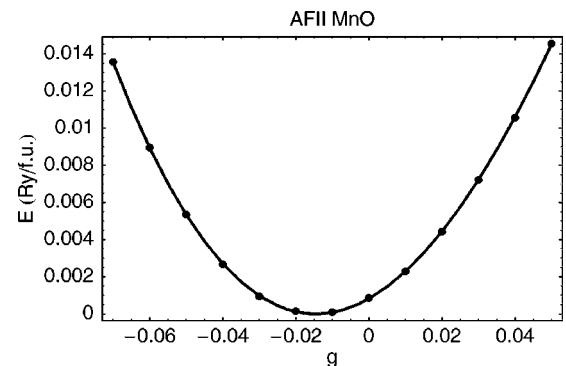


FIG. 5. LAPW-LDA energy vs rhombohedral strain for AFII MnO at the experimental volume. The minimizing strain of $g = 0.01456$ corresponds to a deviation of 1.68° from the ideal cubic angle.

TABLE I. LAPW-LDA and GGA rhombohedral distortion angles for AFII MnO and comparison to previous calculations and experiment.

LDA	LAPW		PWPP-GGA (Ref. 23)	LCAO-HF (Ref. 20)	LAPW-LDA (Ref. 24)	Experiment (Ref. 18)
	GGA					
1.68°	1.69°		≈ 2.0°	0.47°	0.66°	0.62°

As shown in the figure, the calculations predict the ground state to be slightly compressed ($g < 0$) along the [111] direction. A least-squares fit of the results yielded minimizing strains of $g = -0.01456$ and $g = -0.01465$, corresponding to deviations of 1.68° and 1.69° from the 90° cubic angle, for LDA and GGA calculations, respectively. A comparison with experiment and previous calculations is shown in Table I. We find that both LDA and GGA results overestimate the experimental angle somewhat, consistent with recent PWPP-GGA calculations²³ but inconsistent with recent LAPW-LDA calculations.²⁴ On the other hand, Hartree-Fock calculations,²⁰ which produce larger gaps, underestimate the distortion somewhat. Within simple tight-binding pictures, interatomic exchange interactions are inversely related to the gap ($\sim t^2/I$ or $\sim t^2/U$, where t is a hopping parameter and I and U are on-site interactions related to the size of the gap). As discussed below, the distortion is driven by the variation of NN exchange with distance, so the tendency to overestimate the distortion may reflect the incomplete treatment of Hubbard correlations and resulting small gaps associated with the LDA and GGA approximations.

The internal energy of the crystal can be partitioned into elastic and exchange parts. The elastic part is symmetric with respect to small rhombohedral distortions of the ideal cubic structure. Thus, it is sufficient to consider the exchange part to understand the mechanism of the observed compression along [111]. Within the model, the size of the distortion is just due to the competition of the exchange part that favors distortion and the non-spin-order dependent elastic energy, given in the harmonic approximation by the shear elastic constant c_{44} for the non-spin-ordered case. To set the energy scale we calculated $c_{44} = 66$ GPa using the LDA at the experimental cell volume with a ferromagnetic ordering. Experimentally, the two terms cannot be readily separated, but above the magnetic-ordering temperature a value of c_{44} near 75 GPa is measured with very strong temperature dependence in the region of T_N .³⁹ We now show that the exchange part can be understood in terms of a Heisenberg Hamiltonian with distance dependent NN and NNN interactions determined from *ab initio* calculations. Let

$$H = \sum_{NN} J_1 \mathbf{S}_i \cdot \mathbf{S}_j + \sum_{NNN} J_2 \mathbf{S}_i \cdot \mathbf{S}_j. \quad (1)$$

Considering a single formula unit, the above Hamiltonian reduces to

$$H^{\text{FM}} = (6J_1 + 3J_2)S^2, \quad (2)$$

$$H^{\text{AFI}} = (-2J_1 + 3J_2)S^2, \quad (3)$$

and

$$H^{\text{AFII}} = -3J_2S^2, \quad (4)$$

where S is the magnitude of the cation spin for FM, AFI, and AFII orderings, respectively. We deduce the exchange constants from the above expressions and *ab initio* total energies for each ordering at the experimental volume, with $S = 5/2$. Our results are shown in Table II, along with previous *ab initio*^{13,14,30} and semiempirical^{28,40,41} results for comparison. While there are still significant differences, our *ab initio* results agree in sign and order of magnitude with the semiempirical ones and are generally closer to the semiempirical ones than previous *ab initio* results employing the CPA and/or spherical approximations, implying better consistency with thermal and spin-wave data. Still, a significant difference exists, perhaps reflecting the role of Hubbard correlations, which might reduce the effective values of J via larger band gaps (recall that in the density-functional calculations the ferromagnetic case is metallic). In any case, we find both NN and NNN interactions to be antiferromagnetic, consistent with the Goodenough-Kanamori rules^{13,42} and experiment. We note that since these calculations involve energy differences on the order of a few mRy, large \mathbf{k} -point sets were required in order to attain sufficient convergence. The above results were calculated using 4096 special \mathbf{k} points in the full zone. Reduction of this set to 1728 points yielded differences of less than 0.003 mRy and 0.001 mRy for J_1 and J_2 , respectively, in LDA tests. Convergence with respect to plane-wave cutoff was also checked. Increasing the cutoff from 18.9 Ry to 24.7 Ry yielded a difference of less than 0.002

TABLE II. Exchange constants (in K) for MnO based on LAPW-LDA and GGA calculations and comparison to other *ab initio* and semiempirical results.

	LAPW		LMTO-ASA-LDA (Refs. 13 and 14)	ASW-LDA (Ref. 30)	Semiempirical (Ref. 28)	Semiempirical	
	LDA	GGA				(Ref. 40)	(Ref. 41)
J_1	9.8	18.8	24.5	30	10	8.9	8.5
J_2	24.5	33.0	43.6	30	11	10.3	9.6
J'_1	12.3	21.3				10.0	9.9
J''_1	7.4	16.4				7.9	7.5

mRy for both J_1 and J_2 in LDA tests. Calculated Mn moments varied by less than 2.2% over all magnetic orderings in both LDA and GGA tests.

We deduce the distance dependence of the interactions from calculations on distorted structures. For a small compression along [111], adjacent-plane NN's move closer together and in-plane NN's move farther apart, so that $J_1 \rightarrow J_1'$ for adjacent-plane NN's and $J_1 \rightarrow J_1''$ for in-plane NN's; while for a volume conserving strain, NNN distances remain unchanged to first order.²⁷ Considering again a single formula unit, the preceding Hamiltonians (2), (3), and (4) then become

$$H^{\text{FM}} = (3J_1' + 3J_1'' + 3J_2)S^2, \quad (5)$$

$$H^{\text{AFI}} = (-J_1' - J_1'' + 3J_2)S^2, \quad (6)$$

and

$$H^{\text{AFII}} = (-3J_1' + 3J_1'' - 3J_2)S^2 \quad (7)$$

for FM, AFI, and AFII orderings, respectively. We deduce the exchange constants as before from the above expressions and *ab initio* total energies corresponding to the appropriate magnetic orderings at the experimental volume and distortion. Our results are shown in Table II, along with semiempirical values for comparison. As the table shows, our *ab initio* results predict the same distance dependence as the semiempirical ones: whatever the nature of the NN interactions, whether direct or indirect, their strength decreases with distance on the relevant scale, as may be expected.

The observed compression along [111] now follows straightforwardly from the above established distance dependence and antiferromagnetic nature of the interactions. For a small compression angle $\delta > 0$,

$$J_1' = J_1(1 + c\delta),$$

$$J_1'' = J_1(1 - c\delta),$$

and, for a volume conserving strain, J_2 remains unchanged to first order, where $J_1 > 0$ (antiferromagnetic NN interactions) and $c > 0$ (strength decreases with distance) as established above. Thus, for the AFII structure,

$$H_{\text{strained}}^{\text{AFII}} - H_{\text{unstrained}}^{\text{AFII}} = -6S^2J_1c\delta < 0;$$

and so the compression lowers energy. Physically, for a small compression, the antiparallel-spin NN's move closer together and the parallel-spin NN's move farther apart, while NNN distances remain unchanged. And so, since the NN interaction is antiferromagnetic and decreases with distance, the energy is lowered. Thus, while decisive in determining the magnetic ordering,¹⁵ the strong NNN coupling through the oxygens has nothing (to first order) to do with the observed rhombohedral distortion. Rather, it is the weaker antiferromagnetic NN coupling that is decisive.

TABLE III. LAPW-LDA and GGA EFG's (in 10^{21} V/m²) for various conformations of MnO. The last row corresponds to the observed rhombohedrally distorted ground state. The asymmetry parameters vanish in all cases.

		LDA	GGA
AFI	Mn	1.31	0.65
	O	0.18	0.13
AFII	Mn	-0.13	-0.05
	O	0.22	0.27
AFII (distorted)	Mn	0.10	0.20
	O	-0.12	-0.08

IV. MAGNETIC-ORDER-INDUCED CHARGE ANISOTROPY

The electric-field gradient (EFG) tensor, the second derivative of the Coulomb potential at the atomic position,⁴³ provides a sensitive probe of the electronic charge distribution, and due to this sensitivity, very accurate distributions are required in order to calculate EFG's reliably. Blaha *et al.*^{44,45} were the first to show that the LAPW method could be used to calculate accurate EFG's with no adjustable parameters. In subsequent work⁴⁶ it was shown that, due to the extreme sensitivity of the EFG's to inaccuracies in the density, the local orbital extension of the method (LAPW + LO),³⁴ as we employ here, is sometimes required in order to obtain reliable results.

Massidda *et al.*²⁴ have investigated magnetic-order-induced anisotropies of two nonmagnetic (spin-independent) linear-response properties of MnO, finding significant anisotropies in the zone-center optic phonon frequencies and Born effective charge tensor despite the fact that the atomic positions had cubic symmetry, so that the only noncubic ingredient was in the spin channel. Since strong Hubbard correlations are thought to separate charge and spin degrees of freedom in general, measurements of such couplings in comparison with density-functional calculations can be particularly illuminating. Here, we consider magnetic-order-induced anisotropy in a static, nonmagnetic quantity: the charge density itself. Since the EFG (the largest-magnitude eigenvalue of the EFG tensor) depends sensitively on the charge density and vanishes for cubic symmetry, it provides a sensitive measure of such anisotropy. And using this measure, our calculations show that magnetic ordering can induce significant charge anisotropy in MnO—on the order of that associated with noncubic crystal structure in some cases. Table III shows our LDA and GGA results for MnO in various magnetic and structural conformations. Cubic AFI and AFII structures show significant (up to $\approx 1.3 \times 10^{21}$ V/m²) EFG's, indicating significant anisotropy due solely to the magnetic ordering, with an order-of-magnitude difference in the Mn EFG's in the AFI and AFII orderings. Generally speaking, GGA calculations are thought to provide a better description than corresponding LDA results for the ground-state properties of materials which contain light elements and are not strongly correlated. For example, GGA equilibrium lattice

parameters and structural coordinates are frequently in better agreement with experiment than LDA results for such materials. However, while one may conjecture that this should also be the case for EFG's, this is not well established yet because the error bars on the experimental numbers are often larger than the LDA-GGA differences due to the uncertainty in the nuclear quadrupole moments (note that in most cases relative LDA-GGA differences are not as large as in the present case). In fact, comparisons of calculated density-functional EFG's with experimental quadrupole splittings were even used to obtain a more accurate value for the quadrupole moment of the Fe-57 nucleus.⁴⁷ In strongly correlated systems, Coulomb correlations differentiate the orbitals more than LDA calculations. In open-shell materials, this generally would lead to larger EFG's. For example, a strong effect of this type was demonstrated for the plane Cu site in YBa₂Cu₃O₇.⁴⁸ On the other hand, in closed-shell systems (like MnO), the effect may be opposite due to the suppression of charge degrees of freedom relative to spin, i.e., a lowering of the EFG. The last row of Table III corresponds to the AFII structure with the observed rhombohedral distortion and so constitutes our prediction for the observed EFG's. These values should be amenable to experimental measurement and, as mentioned, comparison with density-functional predictions should prove quite useful.

V. SUMMARY AND CONCLUSIONS

We have calculated the structural, electronic, and magnetic properties of MnO from first principles, using the LAPW method, with both LDA and GGA approximations to

exchange and correlation. In both the LDA and GGA, we found the ground state to be of rhombohedrally distorted *B1* structure with compression along the [111] direction, antiferromagnetic with AFII ordering, and insulating, consistent with experiment and previous HF and density-functional calculations employing spherical, pseudopotential, and/or strictly LDA approximations. The GGA was shown to yield a much improved lattice constant. However, highly converged LDA and GGA results were shown to overestimate the observed rhombohedral distortion, consistent with one recent PWPP-GGA calculation but inconsistent with others, including recent LAPW-LDA calculations. We showed that the distortion can be understood in terms of a Heisenberg model with distance dependent NN and NNN interactions determined from first principles, obtaining exchange constants in better agreement with semiempirical values than previous *ab initio* results employing the CPA and/or spherical approximations, but still somewhat larger in general. Whereas the NNN coupling plays the decisive role in the magnetic ordering, the weaker NN coupling was shown to play the decisive role in the structural distortion. Finally, we showed that magnetic ordering can induce significant charge anisotropy, on the order of that associated with noncubic structure in some cases, and gave density-functional predictions for EFG's in the observed rhombohedrally distorted structure.

ACKNOWLEDGMENTS

Support from the Office of Naval Research and the National Research Council is gratefully acknowledged.

-
- ¹J. Zaanen, G.A. Sawatzky, and J.W. Allen, *Phys. Rev. Lett.* **55**, 418 (1985).
- ²A. Fujimori, N. Kimizuka, T. Akahane, T. Chiba, S. Kimura, F. Minami, K. Siratori, M. Taniguchi, S. Ogawa, and S. Suga, *Phys. Rev. B* **42**, 7580 (1990); A.E. Bocquet, T. Mizokawa, T. Saitoh, H. Namatame, and A. Fujimori, *ibid.* **46**, 3771 (1992).
- ³P. Hohenberg and W. Kohn, *Phys. Rev.* **136**, B864 (1964); W. Kohn and L.J. Sham, *Phys. Rev.* **140**, A1133 (1965).
- ⁴*Theory of the Inhomogeneous Electron Gas*, edited by S. Lundqvist and N.H. March (Plenum, New York, 1983).
- ⁵A. Svane and O. Gunnarsson, *Phys. Rev. Lett.* **65**, 1148 (1990).
- ⁶Z. Szotek, W.M. Temmerman, and H. Winter, *Phys. Rev. B* **47**, 4029 (1993).
- ⁷M.R. Norman, *Phys. Rev. B* **44**, 1364 (1991).
- ⁸V.I. Anisimov, J. Zaanen, and O.K. Andersen, *Phys. Rev. B* **44**, 943 (1991).
- ⁹J. Hugel and M. Kamal, *Solid State Commun.* **100**, 457 (1996).
- ¹⁰T. Kotani and H. Akai, *Phys. Rev. B* **54**, 16 502 (1996); T. Kotani, *J. Phys.: Condens. Matter* **10**, 9241 (1998).
- ¹¹S. Massidda, A. Continenza, M. Posternak, and A. Baldereschi, *Phys. Rev. Lett.* **74**, 2323 (1995).
- ¹²T.M. Wilson, *Int. J. Quantum Chem., Symp.* **3**, 757 (1970).
- ¹³T. Oguchi, K. Terakura, and A.R. Williams, *Phys. Rev. B* **28**, 6443 (1983).
- ¹⁴T. Oguchi, K. Terakura, and A.R. Williams, *J. Appl. Phys.* **55**, 2318 (1984).
- ¹⁵K. Terakura, T. Oguchi, A.R. Williams, and J. Kübler, *Phys. Rev. B* **30**, 4734 (1984).
- ¹⁶D.C. Langreth and J.P. Perdew, *Phys. Rev. B* **15**, 2884 (1977); *Phys. Rev. B* **21**, 5469 (1980).
- ¹⁷P. Dufek, P. Blaha, V. Sliwko, and K. Schwarz, *Phys. Rev. B* **49**, 10 170 (1994).
- ¹⁸D. Seino, *Phys. Rev. B* **38**, 11 901 (1988).
- ¹⁹M. Belkhir and J. Hugel, *Solid State Commun.* **70**, 471 (1989).
- ²⁰M.D. Towler, N.L. Allen, N.M. Harrison, V.R. Saunders, W.C. Mackrodt, and E. Aprà, *Phys. Rev. B* **50**, 5041 (1994).
- ²¹W.C. Mackrodt, E.-A. Williamson, D. Williams, and N.L. Allan, *Philos. Mag. B* **77**, 1063 (1998).
- ²²R.E. Cohen, I.I. Mazin, and D.G. Isaak, *Science* **275**, 654 (1997).
- ²³Z. Fang, I.V. Solovyev, H. Sawada, and K. Terakura, *Phys. Rev. B* **59**, 762 (1999).
- ²⁴S. Massidda, M. Posternak, A. Baldereschi, and R. Resta, *Phys. Rev. Lett.* **82**, 430 (1999).
- ²⁵J. Kanamori, *Prog. Theor. Phys.* **17**, 197 (1957).
- ²⁶S. Greenwald and J.S. Smart, *Nature (London)* **166**, 523 (1950).
- ²⁷D.S. Rodbell and J. Owen, *J. Appl. Phys.* **35**, 1002 (1964).
- ²⁸M.E. Lines and E.D. Jones, *Phys. Rev.* **139**, A1313 (1965).
- ²⁹M.E. Lines, *Phys. Rev.* **139**, A1304 (1965).

- ³⁰I.V. Solovyev and K. Terakura, Phys. Rev. B **58**, 15 496 (1998).
- ³¹A.I. Liechtenstein, M.I. Katsnelson, V.P. Antropov, and V.A. Gubanov, J. Magn. Magn. Mater. **67**, 65 (1987).
- ³²S.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), and references therein.
- ³³Sphere radii of 2.07 a.u. and 1.61 a.u. were used for Mn and O atoms, respectively.
- ³⁴D. Singh, Phys. Rev. B **43**, 6388 (1991).
- ³⁵A. 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).
- ³⁶L. Hedin and B.I. Lundqvist, J. Phys. C **4**, 2064 (1971).
- ³⁷J. P. Perdew, in *Electronic Structure of Solids 1991*, edited by P. Ziesche and H. Eschrig (Akademie, Berlin, 1991); J.P. Perdew and Y. Wang, Phys. Rev. B **45**, 13 244 (1992).
- ³⁸L.F. Mattheiss, Phys. Rev. B **5**, 290 (1972).
- ³⁹D. Seino, J. Magn. Magn. Mater. **28**, 55 (1982).
- ⁴⁰M. Kohgi, Y. Ishikawa, and Y. Endoh, Solid State Commun. **11**, 391 (1972).
- ⁴¹G. Peppy, J. Phys. Chem. Solids **35**, 433 (1974).
- ⁴²See, e.g., P.W. Anderson, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1963), Vol. 14, p. 99.
- ⁴³For a review, see M.H. Cohen and F. Reif, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1957), Vol. 5, p. 322.
- ⁴⁴P. Blaha, K. Schwarz, and P. Herzig, Phys. Rev. Lett. **54**, 1192 (1985).
- ⁴⁵P. Blaha, P. Dufek, K. Schwarz, and H. Haas, Hyperfine Interact. **97-98**, 3 (1996).
- ⁴⁶P. Blaha, D.J. Singh, P.I. Sorantin, and K. Schwarz, Phys. Rev. B **46**, 1321 (1992).
- ⁴⁷P. Dufek, P. Blaha, and K. Schwarz, Phys. Rev. Lett. **75**, 3545 (1995).
- ⁴⁸D.J. Singh, K. Schwarz, and P. Blaha, Phys. Rev. B **46**, 5849 (1992).