Noncubic Behavior of Antiferromagnetic Transition-Metal Monoxides with the Rocksalt Structure

S. Massidda
INFM-Dipartimento di Scienze Fisiche, Università degli Studi di Cagliari, I-09124 Cagliari, Italy

M. Posternak and A. Baldereschi
Institut de Physique Appliquée, Ecole Polytechnique Fédérale, PHB Ecublens, CH-1015 Lausanne, Switzerland

R. Resta
INFM-Dipartimento di Fisica Teorica, Università di Trieste, I-34014 Trieste, Italy

(Received 9 April 1998)

We give evidence that some nonmagnetic (i.e., spin-integrated) properties of the antiferromagnetic late transition-metal monoxides (MnO, FeO, CoO, NiO) are substantially noncubic below the Néel temperature even when assuming the ideal rocksalt structure for the ions. Our findings, which are at variance with the currently accepted picture, are based on *ab initio* and model calculations for the case study of MnO. The calculated zone-center optic phonon frequencies and Born effective charge tensor of this material show a significant magnetic-induced anisotropy. [S0031-9007(98)08239-8]

PACS numbers: 75.50.Ee, 63.20.Dj, 75.30.Gw, 77.84.Bw

The late transition-metal monoxides XO, with $X =$ Mn, Fe, Co, and Ni, challenge the theory of electronic states and bonding since several decades. These highly correlated materials feature a Mott insulating character, and a type-II antiferromagnetic (AFM) ordering. They have the rocksalt structure in their paramagnetic phase, while below the Néel temperature T_{N}, a weak structural distortion accompanies the AFM transition. The AFM ordering occurs along any one of the $\langle 111 \rangle$ directions for MnO and NiO, and T_{N} is 117 and 523 K, respectively. The transition is accompanied by a small distortion that transforms the cubic structure into a rhombohedral one: the 90° angle between the lattice vectors increases only [1] by 0.624° and 0.100°, respectively, and therefore experimental data—particularly the lattice dynamical ones [2–4]—are usually interpreted under the assumption of cubic symmetry [5,6], *even* below T_{N}. The present theoretical investigation gives evidence that this assumption is not valid: even assuming a perfectly cubic ionic arrangement below T_{N}, the AFM ordering by itself induces substantial noncubic behavior of some *nonmagnetic* (i.e., spin-integrated) properties. Although the ground-state electronic distribution deviates little from cubic symmetry, its *derivatives* with respect to a symmetry-breaking perturbation can have substantial anisotropy, owing to the strong exchange coupling between electrons. We focus on the half-filled d shell oxide MnO as the most suitable case study, since the available theoretical schemes apply better to this material, and its structural distortion is larger. Qualitatively similar effects should occur also in NiO. Our evidence is based on accurate *ab initio* and semiempirical calculations. We use different one-particle schemes, and compare their results in order to obtain realistic predictions for this highly correlated material. We show that the calculated zone-center phonon frequencies are strongly noncubic, and that this anisotropy is practically induced solely by the magnetic order.

Throughout this study, the ionic positions of the unperturbed MnO crystal are those of the perfect rocksalt structure with the experimental lattice constant 4.435 Å. This ensures that any resulting deviation from cubic symmetry is solely due to AFM ordering. We thus isolate these effects from those due to the tiny structural distortion, which is present in the real material below T_{N}. The AFM spin density is periodic with a magnetic unit cell, whose volume is twice that of the rocksalt cell [7]. The two anions O_1, O_2 and the two cations Mn_1, Mn_2 are equivalent as far as spin-independent observables are concerned. However, due to magnetic order, the crystal has a preferred axis along the AFM direction [111], and anisotropies are in principle expected.

Because of the large value of the on-site $3d$ cationic Coulomb repulsion, the conventional band-structure schemes are inadequate for MnO, and innovative schemes have been proposed in the literature. In this work we use and compare band schemes based on different approximations: traditional ones like unrestricted Hartree-Fock (UHF) and local-spin density (LSD), the recent model GW scheme [8,9], and a further model, designed for the present purpose, which will be described below. They are implemented with identical technical ingredients: the full-potential linearized-augmented plane wave (FLAPW) method [10,11], expanded with local orbitals [12] where appropriate. The atomic-sphere radii for Mn and O are chosen to be 1.7 and 1.8 a.u., respectively. We adopt the Hedin and Lundqvist exchange-correlation functional in the LSD calculations, while the self-energy used in the model GW calculations is the one of Ref. [8]. The Brillouin-zone integrations are particularly critical for the determination of the magnetic anisotropies, and therefore very large special-point sets are used. The Born dynamical charge tensors are evaluated as Berry phases [13].

All four schemes predict the insulating character of MnO. In Fig. 1 we display the band structures along the Γ-Z direction which corresponds to one-half of the Γ-L direction of the paramagnetic fcc Brillouin zone. The shaded areas correspond to valence states. Dashed lines represent both the nonbonding O $2p$ valence states, and the free-electron-like Mn $4s$/O $3s$ conduction states; solid lines in the neighborhood of the fundamental gap represent Mn $3d$/O $2p$ bands. The one-electron bands calculated within the different schemes differ considerably from each other. As usual, the UHF gap (12.7 eV) is much larger than the experimental one (3.8–4.2 eV), while the LSD gap (0.8 eV) is too small. The model *GW* provides the best value (4.5 eV) [8]. The same trend applies to the energy separation between occupied and empty d states, which is due to the on-site interaction U between cation $3d$ states. LSD gives an unphysically low separation, while UHF implies an essentially unscreened $U \approx 2$ Ry. Within the model *GW* scheme, the antibonding e_g states (highest valence band) gain substantial O $2p$ character relatively to the LSD case (at Γ, 17% p occupancy in each of the two O spheres vs 7% in LSD), at the expense of the d occupancy of both Mn atoms: charge from the Mn_1 sphere (45% vs 57% in LSD) is transferred to lower occupied states, while charge from the Mn_2 sphere (7% vs 12%) is transferred to the e_g unoccupied conduction states whose occupancy is 73% vs 65% within LSD. The charge of the lowest empty state, having mostly Mn $4s$/O $3s$ character, is basically unaffected switching from LSD to model *GW*. These findings confirm the picture which places MnO in the intermediate charge-transfer/Mott-Hubbard regime.

For reasons which are explained below, it is expedient to devise a simplified model, intermediate between LSD and UHF, which reproduces the model *GW* results. To this purpose, we add to the one-electron LSD potential a spin- and angular-momentum-dependent term acting only on minority-spin Mn d orbitals, thus discriminating chemically the two Mn atoms. The modification is $V(l = 2) \rightarrow V(l = 2) + \overline{U}$ inside $\mathrm{Mn}_1^{\uparrow}$ and $\mathrm{Mn}_2^{\downarrow}$ spheres. This procedure (called "fake" LSD in the following) is similar in spirit to other schemes such as LSD + U [14] and LSD constrained-occupancy [15] methods. In our fake LSD approach the perturbation has by construction the AFM symmetry, but it is important to note that it introduces a difference between the *bare* potentials of the two Mn atoms, while within the model *GW* the difference stems from electron-electron interactions. Choosing $\overline{U} =$ 0.3 Ry, the fake LSD band structure (see the third panel of Fig. 1) reproduces well the model *GW* one. The gap has essentially the LSD value, as the lowest conduction band is unaffected by the perturbation, but the empty d states are raised at about the energy they have in the model *GW* band structure. The valence band ordering is also similar to the model *GW* one. Furthermore, all the relevant atomic-sphere occupancies within the fake LSD are very similar to the model *GW* ones (discussed above): for instance, we get 16% p occupancy in the O sphere for the upper e_g state at Γ. Such a value would be *imposed* in a LSD constrained-occupancy calculation.

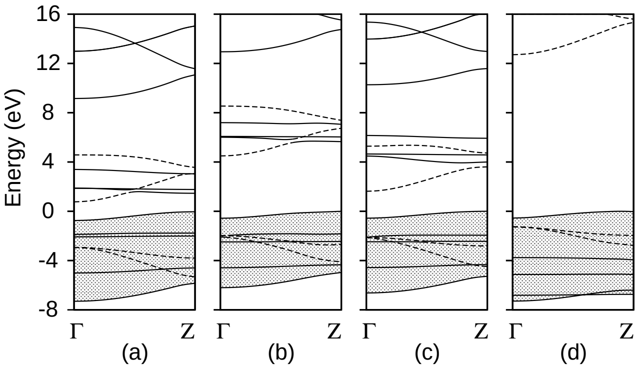

FIG. 1. Energy bands of antiferromagnetic MnO calculated along the Γ-Z line of the rhombohedral magnetic zone assuming that the ions occupy perfect rocksalt sites and using four different schemes: (a) Local-spin-density approximation, (b) model *GW*, (c) "fake" LSD (see text), and (d) unrestricted Hartree-Fock. All symbols are explained in the text.

Considering the deviations from cubic symmetry of the ground-state electronic distribution, we find that they are very small indeed: when partitioning the valence electronic charge into a cubic term and a noncubic one, the latter is less than 0.2% of the total. We have also verified that a correspondingly small anisotropic stress is present when the ground state is evaluated (as we do here) in the cubic structure, which is not the equilibrium one [16].

In this Letter we consider two basic linear-response properties of the electronic ground state: the Born dynamical charge tensor, and the $\mathbf{k} = \mathbf{0}$ optic phonons. Since the four atoms in the magnetic cell are equivalent in pairs, the eigenmodes at $\mathbf{k} = \mathbf{0}$ are uniquely determined by symmetry: the optic phonons we focus on correspond to the in-phase vibration of the two Mn atoms against O atoms. Phonon measurements [3,4] have been invariably interpreted under the *a priori* hypothesis of cubic symmetry. Contrary to this common use, it is important to realize that below T_{N} our material, despite having a cubic ionic arrangement and a practically cubic electron density, has a noncubic electronic response, and low-symmetry perturbations could strongly enhance the weak anisotropy of the responding system. One should therefore expect a cylindrical Born tensor, and optic phonon frequencies at $\mathbf{k} = \mathbf{0}$ that depend on the polarization being parallel or perpendicular to the AFM direction [111].

We start by discussing the LSD results. Although this scheme predicts correctly the insulating character of MnO, the underlying physical approximations lead to an underestimate of the electron-electron interactions. The calculated frequency of the mode polarized along the [111] direction (symmetry C_{3v}) is 3.04 THz, while the (doubly degenerate) mode polarized in the plane orthogonal to [111] (symmetry C_s) appears to be soft, with an almost vanishing restoring force. This result is in contrast with experimental data both below [4] and above T_{N} [3], which indicate a frequency of 7.86 THz. The disagreement is a direct consequence of the underestimate of electron-electron repulsions in LSD which leads to a too small energy separation between occupied and empty d bands. Although quantitatively incorrect, the LSD results carry an important qualitative message: below T_{N}, there is no reason for expecting threefold-degenerate optic frequencies at $\mathbf{k} = \mathbf{0}$, and a very cautious attitude in interpreting experimental data is in order.

Next we have studied the Born dynamical charge tensor Z^*, which governs the infrared activity and the splitting of zone-center optic modes. In a cubic binary compound with the rocksalt structure, the $\mathbf{k} = \mathbf{0}$ optic frequency is threefold degenerate and coincides with the long wavelength TO frequency for any $\mathbf{k}$ direction. Furthermore, the Born tensor is isotropic, and the LO–TO splitting is given by $\omega_{\mathrm{LO}}^2 - \omega_{\mathrm{TO}}^2 \propto |Z^*|^2/\varepsilon_\infty$, where ε_∞ is the electronic dielectric constant. Using the experimental data for MnO [3,4], the cubic model gives $|Z^*|$ values in the range 2.1–2.6: since for binary oxides the "nominal" rigid-ion value is $|Z^*| = 2$, the present important deviation is a clear fingerprint of high electronic polarizability. However, a novel qualitative effect, hitherto uninvestigated, occurs in AFM oxides. The Born tensors of Mn_1 and Mn_2 are indeed identical, as required by the equivalence of the two atoms with respect to nonmagnetic properties, but magnetic order lowers the symmetry of the tensor from spherical, as in nonmagnetic rocksalt solids, to cylindrical along the [111] direction [17]. We will refer to this additional effect—solely due to d unpaired electrons—as to "magnetic anisotropy." Since the current interpretation of low temperature experimental data neglects totally this effect, no information is available on its actual magnitude.

We show in the first row of Table I the calculated LSD eigenvalues of the Mn_1 Born tensor. Looking at the spin-integrated values, one notices important deviations from both the nominal value and the isotropy: this points out the dependence on AFM ordering of this observable. Although LSD predicts a quite reasonable value for the average $\overline{Z^*}$, we argue that it exaggerates the anisotropy, and the results of schemes other than LSD are required for comparison.

TABLE I. Eigenvalues of the Z^* tensor corresponding to a Mn_1 displacement. In the fake LSD scheme, a repulsive potential confined to Mn spheres is added, acting only upon d radial wave functions of minority spin. $\Delta Z^* = |Z_\parallel^* - Z_\perp^*|/\overline{Z^*}$ measures the anisotropy of Z^* in percent, where $\overline{Z^*} = 1/3\,\mathrm{Tr}\,Z^*$.

Scheme	$Z_\parallel^{*\uparrow}$	$Z_\parallel^{*\downarrow}$	$Z_\parallel^*$	$Z_\perp^{*\uparrow}$	$Z_\perp^{*\downarrow}$	$Z_\perp^*$	ΔZ^*
LSD	3.93	−1.61	2.32	4.06	−1.29	2.77	17.2
GW	3.83	−1.40	2.43	3.84	−1.30	2.54	4.4
Fake	3.75	−1.51	2.24	3.72	−1.37	2.34	4.3
UHF	3.70	−1.47	2.23	3.60	−1.34	2.26	1.3

The UHF scheme, which in a sense is the extreme approximation, opposite to LSD, provides a much too ionic description of the chemical bonding, and therefore its results can be considered as a lower bound to the effects considered in this work. The results for Z^* are reported in the last row of Table I: inspection shows that within UHF the anisotropy is 1 order of magnitude smaller than within LSD, while the deviation from the nominal value remains appreciable, though smaller than experimentally measured.

A successful scheme for MnO is the model *GW* [8,9]: it has been able to predict both energy and intensity of all one-particle features of the photoemission spectra; it also gives a good value of the magnetic moment and of the on-site interaction [8]. It is therefore expected to give a rather accurate picture of the electronic response. We have calculated the Born dynamical-charge tensor within this scheme: results are reported in the second row of Table I. It is easily noticed that these values are—as expected from the underlying physical approximation—intermediate between the LSD and UHF ones. We believe that values of this order are realistic and reliable. In particular, a Z^* anisotropy of about 5%, solely induced by the AFM ordering, is to be expected from measurements in the real material. As for the average $|Z^*|$ value, we get 2.50, which compares well with the experimental data.

We also wish to give an order-of-magnitude estimate of the AFM-induced splitting of the optic phonon frequencies at $\mathbf{k} = \mathbf{0}$, better than the LSD one which is obviously not trustworthy. Unfortunately, the present implementation of our most realistic scheme, the model *GW*, does not yet allow us to evaluate the total energy: we use therefore the fake LSD scheme described above, whose total energy is variational, and which "mimics" the most relevant features of the electronic system as predicted by the model *GW*. We first check that the Z^* values calculated with the two schemes are very close to each other, as shown in the third row of Table I. We then perform standard frozen-phonon calculations at $\mathbf{k} = \mathbf{0}$ within the fake LSD: the calculated frequency of the mode polarized along the [111] direction is 8.27 THz, while the one of the (doubly degenerate) mode polarized in the orthogonal plane is 6.97 THz, leading to an average value of 7.40 THz. The low temperature experimental data [4] indicate, as already stated, a frequency of 7.86 THz: such a dramatic improvement over the LSD result owes to the gap opening: the effect of the interelectronic coupling across the gap, exaggerated by the LSD scheme, is thus reduced to a realistic value [18]. The quantitative agreement supports the reliability of the fake LSD in describing the electronic response of our material. Furthermore, we also believe that a propagation-vector dependent zone-center splitting, of the order of the calculated one, experimentally unnoticed so far in MnO [4] (and even in NiO [3]), may be expected below T_N as due to AFM ordering.

We have emphasized throughout this Letter the role of the AFM order on nonmagnetic properties, and, in particular, the magnetic-induced anisotropies in the electronic response. This effect correlates monotonically with the separation energy between occupied and empty d bands, which is too small within LSD, too high within UHF, and about the correct value within both model *GW* and fake LSD. As a double check of this physical picture, we have performed a further series of fake LSD calculations, where the $\overline{U}$ parameter is taken as infinitely large: the empty d bands are thus repelled at very high energy, and the magnetic anisotropy should be killed. Not surprisingly, the resulting Z^* tensor is very close to the UHF one (anisotropy 1.3%). The splitting of the optic phonon frequencies at $\mathbf{k} = \mathbf{0}$ reduces to about 3%, which we believe is a lower bound for the real effect.

To summarize, we have investigated theoretically the anisotropies induced—solely by AFM ordering—in the vibrational spectrum of MnO. We find important anisotropy both in the $\mathbf{k} = \mathbf{0}$ optic phonon frequencies and in the dynamical charge tensor. We also provide an order-of-magnitude quantitative estimate for this hitherto undetected qualitative effect. In order to set upper and lower bounds, up to four different theoretical schemes have been used. We expect ε_∞ to be anisotropic as well [6]. Neglecting the latter effect, our most trustworthy theoretical schemes indicate that the low-frequency zone-center optic modes of MnO should exhibit an anisotropic splitting as large as 10% of their energy. Such a splitting and its anisotropy are possibly hidden in the experimental spectra of MnO and NiO, and should prompt further experimental verification below T_N in both materials.

We are grateful to V.I. Anisimov, D. Catti, and D. Singh for very useful discussions.

---

[1] W. L. Roth, Phys. Rev. **110**, 1333 (1958); G. A. Slack, J. Appl. Phys. **31**, 1571 (1960).

[2] B. C. Haywood and M. F. Collins, J. Phys. C **4**, 1299 (1971).

[3] W. Kress *et al.,* in *Lattice Dynamics,* edited by M. Balkanski (Flammarion, Paris, 1978), p. 77.

[4] M. Yokogawa, K. Taniguchi, and C. Hamaguchi, J. Phys. Soc. Jpn. **42**, 591 (1977).

[5] B. R. K. Gupta and M. P. Verma, J. Phys. Chem. Solids **38**, 929 (1977).

[6] We are aware of only one paper where anisotropy in a spin-independent response function of MnO is detected: M. S. Seehra, R. E. Helmick, and G. Srinivasan, J. Phys. C **19**, 1627 (1986). The temperature dependence of the dielectric constant is measured therein. However, since anisotropic strain is applied in order to enforce monodomain orientation, it is difficult to disentangle the "intrinsic" anisotropy due to magnetic ordering from the one due to the applied strain.

[7] Since we neglect spin-orbit terms in the Hamiltonian, our calculations and results are independent of the particular crystallographic orientation of the spin of Mn ions. Under this assumption, the magnetic space group is D_{3d}^5 ($R\overline{3}m$) and the unit cell is rhombohedral.

[8] S. Massidda, A. Continenza, M. Posternak, and A. Baldereschi, Phys. Rev. Lett. **74**, 2323 (1995).

[9] S. Massidda, A. Continenza, M. Posternak, and A. Baldereschi, Phys. Rev. B **55**, 13 494 (1997).

[10] H. J. F. Jansen and A. J. Freeman, Phys. Rev. B **30**, 561 (1984).

[11] S. Massidda, M. Posternak, and A. Baldereschi, Phys. Rev. B **48**, 5058 (1993).

[12] D. Singh, Phys. Rev. B **43**, 6388 (1991).

[13] R. D. King-Smith and D. Vanderbilt, Phys. Rev. B **47**, 1651 (1993); R. Resta, Rev. Mod. Phys. **66**, 899 (1994).

[14] V. I. Anisimov, J. Zaanen, and O. K. Andersen, Phys. Rev. B **44**, 943 (1991).

[15] P. H. Dederichs, S. Blügel, R. Zeller, and H. Akai, Phys. Rev. Lett. **53**, 2512 (1984); M. S. Hybertsen, M. Schlüter, and N. E. Christensen, Phys. Rev. B **39**, 9028 (1989).

[16] The anisotropic stress has been evaluated by finite differences, performing a series of additional calculations for *noncubic* geometries. We find a structural minimum in the rhombohedral structure, whose angle is very close to the experimental one (90.624°), both within standard LSD (90.66°) and within our fake LSD (90.31°).

[17] From a symmetry viewpoint, this situation is similar to the one found in II-VI compounds, which exist in both the wurtzite and the zinc-blende structures. In fact, (i) the unit cell of the low-symmetry structure contains two equivalent formula units, and (ii) the axial symmetry in wurtzite, combined with the nonanalyticity of the dynamical matrix, is responsible for discontinuous phonon dispersion curves at the zone center. See, e.g., the study of wurtzite CdS by A. Debernardi *et al.,* Solid State Commun. **103**, 297 (1997).

[18] We have repeated the phonon calculations for the case of the theoretical, equilibrium rhombohedral structure. Frequencies change by less than 1%, confirming that the resulting anisotropy is insensitive to small variations of the rhombohedral angle.