

# Electron densities in relation to magnetism: $\gamma$ -ray diffraction from transition-metal monoxides and difluorides

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In this article, results are described from an area of solid-state physics that heretofore has remained unexplored by Bragg charge-scattering experiments. It is shown that  $\gamma$ -ray electron densities can provide detailed information on magnetic ground-state properties at a subatomic resolution. The use of 316 keV  $\gamma$  radiation has allowed low-order structure factors at better than 0.1% accuracy to be determined and, at the same time, extended data sets to be collected up to high momentum transfer. Prototypic antiferromagnets such as the late  $3d$  transition-metal monoxides and difluorides have been systematically investigated, in most cases both in the paramagnetic and in the fully ordered phase. At transitions with a lowering of symmetry, multidomain formation was suppressed by application of external mechanical stress or magnetic fields. The results are considered in the context of information provided by recent magnetic neutron and X-ray studies.

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## 1. Introduction

Exhaustive  $\gamma$ -ray charge-density studies have been performed in recent years on archetypal antiferromagnets such as the transition-metal difluorides  $\text{MnF}_2$  (Jauch *et al.*, 1999),  $\text{CoF}_2$  (Jauch *et al.*, 2004),  $\text{FeF}_2$  and  $\text{NiF}_2$  (Palmer & Jauch, 1993), as well as on the monoxides  $\text{MnO}$  (Jauch & Reehuis, 2003),  $\text{CoO}$  (Jauch & Reehuis, 2002) and  $\text{NiO}$  (Jauch & Reehuis, 2004).

With the use of 316 keV  $\gamma$  radiation, the high-energy diffraction case (photon energy  $\gg$  binding energy of  $K$ -shell electrons) is fully realized so that fewer corrections and fewer assumptions have to be made in the process of deriving structure factors from the observed integrated intensities, and a structure-factor accuracy better than 0.1% is achievable. The improvement in accuracy is not solely a consequence of the high photon energy but is also brought about by additional favourable experimental conditions, such as the perfect stability, homogeneity and spectral line width ( $\Delta\lambda/\lambda = 10^{-6}$ ) of the incident  $\gamma$ -ray beam. There are thus important advantages to the diffraction conditions met in synchrotron-radiation work as far as systematic error sources are concerned (Jauch, 2001). Because of the relatively low intensity, the  $\gamma$ -ray technique is confined to studies of small-unit-cell systems.

The canonical tools to probe magnetic ground-state properties in crystalline solids on a subatomic scale are neutron and to a lesser extent X-ray magnetic diffraction. It is the purpose of this paper to demonstrate that  $\gamma$ -ray charge scattering can be equally employed to study the consequences of magnetic interactions on the electronic structure. From the experimental model electron-density, quantitative information

is accessible about crystal field effects, spin delocalization, spatial extent of  $d$  electrons, spin-orbit coupling, orbital-to-spin angular momentum ratios *etc.* Comparisons are made between analyses based on modern neutron and X-ray magnetic measurements providing a stringent validation of results. In addition, the chemical bonding states and its implications are discussed. In view of its importance for the field, we will look briefly at the reliability of atomic displacement parameters.

## 2. Background information

The  $3d$  transition-metal difluorides crystallize in the rutile structure. Except for  $\text{NiF}_2$ , which exhibits a canted antiferromagnetic structure, no lowering of symmetry occurs upon magnetic ordering.

The crystal structure of  $\text{MnO}$ ,  $\text{CoO}$  and  $\text{NiO}$  in the paramagnetic phase is of the NaCl type. For  $\text{CoO}$ , the onset of magnetic order results in a large tetragonal distortion, which is accompanied by a very small monoclinic deformation (Jauch *et al.*, 2001). The phase transition is thus of first order. It is of great theoretical interest to establish the nature of the transition. From the behaviour of the magnetic susceptibility, a continuous type has been claimed, which would have conflicted with major predictions of renormalization-group calculations (Srinivasan & Seehra, 1983). In the cases of  $\text{MnO}$  and  $\text{NiO}$ , the structure appears to be rhombohedral in the antiferromagnetic phase. Since the direction of the magnetic moments is perpendicular to the threefold axis, the true

**Table 1**

Néel temperatures and principal structural characteristics of transition-metal monoxides at 10 K.

The distortion parameters refer to the f.c.c. cell.

	MnO	CoO	NiO
$T_N$ (K)	118	290	523
Distortion	$\langle 111 \rangle$ $\alpha = 90.62^\circ$	$\langle 001 \rangle$ $c/a = 0.98$	$\langle 111 \rangle$ $\alpha = 90.075^\circ$

**Table 2**

Mean-square vibrational amplitudes in paramagnetic and antiferromagnetic MnO.

$U_{\parallel}$  and  $U_{\perp}$  refer to directions parallel and perpendicular to the threefold axis. Rigid-ion model: Hewat (1972) as reported in Jacobson *et al.* (1973); X-rays: Sasaki *et al.* (1979). The unit of  $U$  is  $\text{Å}^2$ .

		295 K	15 K
Mn	$U_{\parallel}$	0.00563 (1)	0.00238(3)
	$U_{\perp}$		0.00210 (2)
	Rigid-ion model	0.0061	0.0019
	X-rays	0.00781 (6)	
O	$U_{\parallel}$	0.00584 (6)	0.00378 (18)
	$U_{\perp}$		0.00340 (10)
	Rigid-ion model	0.0061	0.0034
	X-rays	0.00912 (25)	

crystallographic symmetry must also be lower than trigonal. A summary of the essential distortion characteristics is presented in Table 1.

The diffraction data have been collected on the  $\gamma$ -ray diffractometer installed at the Hahn-Meitner-Institut where the most intense line of an  $^{192}\text{Ir}$  source ( $T_{1/2} = 73.83$  d) with a wavelength of  $0.0392 \text{ Å}$  (316.5 keV) is used. The sample quality has been examined in a double-crystal arrangement with an angular resolution of  $1.5''$ . Single-crystal studies involving phase transitions with a lowering of symmetry need special precautions to keep the specimen untwinned in the ordered phase. Crystallographic domain formation was suppressed in the present studies by the application of mechanical stress (oxides) or an external magnetic field ( $\text{NiF}_2$ ). It should be noted that the single-domain condition is a severe limitation for the other techniques employed in the measurement of structure-factor data sets.

The multipole refinements were performed with the program system VALRAY (Stewart *et al.*, 2000). The observations were weighted solely by their counting-statistical variances, leading to goodness-of-fit values close to one, indicating that the high accuracy of the data has been practically exhausted. Scattering factors were calculated from analytical Hartree–Fock wavefunctions (Clementi & Roetti, 1974) with the radial valence deformation functions for the transition-metal atoms being constructed from  $3d3d$  orbital products.

### 3. Reliability of atomic displacement parameters

The correct disentanglement of atomic thermal motion and electron-density contributions to the structure factors is a

**Table 3**

Radial scaling parameters and  $3d$ -electron population numbers (electrons) for the monoxides in the paramagnetic (PM) and antiferromagnetic (AFM) phases.

			PM	AFM
MnO	Mn	$\kappa$	1.050 (5)	1.037 (3)
		$P_{3d}$	4.74 (2)	4.75 (2)
	O	$\kappa$	0.980 (4)	0.978 (3)
CoO	Co	$\kappa$	1.018 (6)	1.047 (9)
		$P_{3d}$	6.42 (4)	6.43 (5)
	O	$\kappa$	0.953 (6)	0.954 (7)
NiO	Ni	$\kappa$	1.033 (2)	1.030 (1)
		$P_{3d}$	7.63 (2)	7.65 (1)
	O	$\kappa$	0.973 (2)	0.974 (2)

prerequisite for any reasonable estimate of electronic charge parameters. The case study of MnO will be used to illustrate achievement of this goal (Table 2).

At room temperature,  $U(\text{Mn})/U(\text{O}) = 0.964$  (10), in agreement with a prediction from lattice-dynamical theory that for temperatures above the Debye temperature both atoms of a binary compound in a cubic lattice should vibrate equally, irrespective of their masses (Huiszoon & Groenewegen, 1972). At low temperature, the two atoms vibrate distinctly differently, roughly according to the corresponding mass ratio. For manganese, the anisotropy of zero-point motion is highly significant,  $U_{\parallel}/U_{\perp} = 1.13$  (2).

The  $\gamma$ -ray vibrational parameters are up to 50% smaller than the values reported from an X-ray study (Sasaki *et al.*, 1979). There is abundant evidence for a corresponding relation between X-ray and neutron results,  $U(\text{X-ray}) > U(\text{neutron})$ . The discrepancy has recently been traced back to the wavelength spread of the *Bremsstrahlung* component contained in a graphite-monochromated Mo  $K\alpha$  X-ray beam (Rousseau *et al.*, 2000). Systematic intensity truncation errors increasing with Bragg angle eventually bias the thermal parameters to values that are too large. Surprisingly, the seminal contribution by Rousseau *et al.* has so far not been given due attention by the charge-density community. The handicap of shorter wavelength laboratory X-rays is absent in synchrotron experiments.

Isotropic mean-square amplitudes of vibration have been calculated by Hewat (reported in Jacobson *et al.*, 1973), based on the rigid-ion model of lattice dynamical theory. The calculated values are in close agreement with our experimental results, thus substantiating the high accuracy level.

### 4. Spherical deformation parameters

The refined radial scaling parameters,  $\kappa$ , and  $3d$  population numbers are shown in Table 3 for the monoxide compounds. The  $\kappa$  parameters multiply the radial coordinate and allow for expansion ( $\kappa < 1$ ) or contraction ( $\kappa > 1$ ) of the valence shells relative to the free-atom ground-state density. The spherical deformations should describe an intrinsic solid-state property, which is invariant with respect to the magnetic phase. The monopole parameters are very sensitive to the quality of the data. It is evident from Table 3 that the magnetic phase

**Table 4**

3d-electron population numbers for the difluorides.

	$P_{3d}$
MnF <sub>2</sub>	4.89 (4)
FeF <sub>2</sub>	5.98 (4)
CoF <sub>2</sub>	6.95 (3)
NiF <sub>2</sub>	7.92 (5)

**Table 5**

3d-orbital populations in cubic MnO and CoO.

Orbital	MnO	CoO
$e_g$	2.11 (4)	2.16 (7)
$t_{2g}$	2.63 (5)	4.26 (9)
$e_g/t_{2g}$	0.80	0.51
Ideal ratio	2/3	2/5

invariance is indeed satisfied on a quantitative level. All the radial 3d functions are contracted in the solid. The total number of d electrons on the metal atoms is found to be significantly smaller than the formal integer values. The  $\kappa$  parameters are consistent with the observed charge transfer. The metal atoms are expected to contract in view of the decreased screening of the nuclear charge whereas the O atoms should show an expansion.

MnO is a spin-only magnetism case. The 3d occupation number can therefore be compared straightforwardly with the ordered magnetic moment on manganese, which has been reported as 4.54 (5)  $\mu_B$  (Jauch & Reehuis, 2003) and 4.58 (3)  $\mu_B$  (Cheetham & Hope, 1983). To deduce the absolute moment, the contribution from zero-point fluctuations in spin direction has to be taken into consideration. It was calculated by Lines & Jones (1965) to be 3.0%. The absolute magnetic moment as obtained from neutron diffraction is thus 4.7  $\mu_B$ . The close agreement between the  $\gamma$ -ray and neutron results supports the reliability of the multipole partitioning leading to physically meaningful charge transfer.

In Table 4, the d-electron population numbers for the difluorides are shown. The results are completely different from those observed for the monoxides. Within standard uncertainties, the populations are equal to the formal integer values. In the difluorides, any charge transfer between the atoms is thus absent in the solid.

## 5. d-orbital population analyses

### 5.1. Paramagnetic MnO and CoO

The fivefold degenerate d orbitals of the free atom are strongly affected by the cubic crystalline electric field and are separated into a doublet  $e_g$  ( $z^2, x^2 - y^2$ ) pointing towards the ligands and a triplet  $t_{2g}$  ( $xy, yz, xz$ ) pointing in between them. d-orbital populations of the metal atom can be calculated from the multipole population coefficients (Holladay *et al.*, 1983). Results are given in Table 5.

Surprisingly, the experimental  $e_g/t_{2g}$  populations are considerably larger than the ideal ratios corresponding to

**Table 6**

3d-orbital populations in antiferromagnetic CoO; x, y and z are pointing towards the ligands; the z axis is along the short Co–O bond.

Also shown are the independent-atom populations in a cubic crystal field and the distribution of unpaired electrons inferred from the orbital analysis (the integers come about by rounding within error margins).

Orbital	Experimental	Cubic	Unpaired
$d(z^2)$	0.40 (8)	1	0.40 (8)
$d(x^2 - y^2)$	1.10 (8)	1	1
$d(xz) = d(yz)$	1.55 (6)	1.5	1
$d(xy)$	1.83 (9)	2	0
Total	6.43 (5)	7	2.40 (8)

**Table 7**

3d-orbital populations in antiferromagnetic MnO.

$a_g$  is along the threefold contraction axis and  $e'_g$  is pointing towards the ligands. Also shown are the independent-atom populations in a cubic crystal field.

	Experimental	Cubic
$e'_g$	1.25 (8)	2
$e_g$	2.23 (8)	2
$a_g$	1.27 (4)	1
$e_g e'_g$	-0.78 (8)	0

spherical high-spin atoms in a cubic crystal field. Our results are in qualitative agreement with recent theoretical work (Pickett *et al.*, 1998), where it follows that the charge rearrangement between  $e_g$  and  $t_{2g}$  leads to a reduction of the large value of the on-site 3d Coulomb repulsion.

### 5.2. Antiferromagnetic CoO

In the pseudotetragonal phase, the two apical O atoms are shifted towards Co, and the degeneracy of  $e_g$  and  $t_{2g}$  is lifted, the energy of  $d(z^2)$  becoming higher than for  $d(x^2 - y^2)$ . Similarly,  $d(xy)$  should be stabilized relative to  $d(xz)$ . Table 6 reflects the corresponding charge rearrangement. The  $d(z^2)$  orbital is only partially occupied and about 0.4 electrons are moved into  $d(xy)$ , which is now fully occupied. The  $d(xz, yz)$  orbitals are degenerate and contain a single hole. The number of unpaired electrons is thus found to be 2.40 (8). Consequently, the spin magnetic moment considerably deviates from the isolated-atom value of 3  $\mu_B$ .

### 5.3. Antiferromagnetic MnO

On the lowering of the symmetry from cubic to trigonal, the  $t_{2g}$  orbitals split into a single  $a_g$  with its lobes pointing along the threefold axis and a doubly degenerate  $e_g$  level, whereas the original  $e_g$  orbitals retain their symmetry characteristic and are now termed  $e'_g$ . The four symmetry-allowed multipoles transform into three self products and an additional cross-product term that is related to the extent of  $e_g/e'_g$  mixing.

The experimental results are shown in Table 7. In the rhombohedral phase, the Mn–O distance is elongated by only 0.005 Å relative to the cubic phase. According to crystal field theory, the  $e'_g$  orbitals pointing towards the ligands should therefore show little difference in population compared to the

cubic phase. Actually, it is found that 0.9 electrons are removed from  $e'_g$  into  $e_g$ . The cross term is highly significant, which reflects the considerable amount of orbital mixing. The observed anisotropy in electron subshell population is at variance with the common view according to which lower than cubic effects can be ignored in antiferromagnetic MnO.

## 6. Separation of spin and orbital magnetic moments

### 6.1. Orbital magnetism in CoO

From neutron powder diffraction, the ordered total magnetic moment (proportional to  $2S + L$ ) on Co has been determined as  $\mu_{\text{total}} = 3.98$  (6)  $\mu_B$  (Jauch *et al.*, 2001). If we combine this value with the spin moment estimated from the  $3d$ -orbital analysis, the orbital magnetic moment is as large as  $\mu_L = 1.6$  (1)  $\mu_B$ , which leads to an orbital-to-spin angular momentum ratio of  $L/S = 1.3$  (1) (as compared with  $L/S = 2$  for the free atom). It has been demonstrated by numerical calculations that the orbital moment is indeed parallel to the spin (Solovyev *et al.*, 1998). From magnetic X-ray scattering, the ratio  $L/S = 0.95$  has been reported (Neubeck *et al.*, 2001), and from photoemission spectra  $L/S = 1.14$  was found (Ghiringhelli *et al.*, 2002). There is thus reasonable consistency amongst the values extracted by completely different experimental methods.

### 6.2. The seemingly anomalous behaviour of CoF<sub>2</sub>

A pure spin magnetic moment of  $\mu_S = 2.21$  (2)  $\mu_B$  was determined in CoF<sub>2</sub> using high-energy magnetic X-ray diffraction (Stremper *et al.*, 2004). It is considerably smaller than the isolated-atom value of 3  $\mu_B$ . In view of the integer  $d$ -electron populations deduced for the difluorides, the spin reduction cannot be related to a charge-transfer effect, and therefore seemingly contradicts the scenario for the monoxides. There exists, however, a further possible reason for the large spin deviation, and that is the presence of single-ion anisotropy due to spin-orbit interaction. From molecular-field theory, a spin moment of 2.18  $\mu_B$  has been calculated (Lines, 1965), which is remarkably close to the observed one. The ordered total magnetic moment was determined from neutron powder diffraction as  $\mu_{\text{total}} = 2.60$  (4)  $\mu_B$  (Jauch *et al.*, 2004). Despite the strong deviation from the unperturbed spin value, there is thus still an appreciable orbital contribution to the local magnetic moment,  $\mu_L = 0.4$   $\mu_B$ , and hence  $L/S = 0.4$ .

The case for CoF<sub>2</sub> should be contrasted with FeF<sub>2</sub> for which no moment deficit due to spin-orbit interaction should occur (Lines, 1967). High-energy magnetic X-ray scattering yielded the ideal value of the spin moment,  $\mu_S = 4.01$  (5)  $\mu_B$  (Stremper *et al.*, 2001). From the charge-density study, the absence of charge transfer was inferred. The conclusions from magnetic and charge scattering are thus fully consistent with each other. These findings are in contradiction to results from Brown *et al.* (1990), who suggested a spin transfer of at least 10% from Fe onto the ligands in order to explain polarized neutron diffraction data.

**Table 8**

Selected bond-critical-point properties.

Values of  $\rho$  in  $e \text{ \AA}^{-3}$ ,  $\nabla^2\rho$  in  $e \text{ \AA}^{-5}$ .  $G$ ,  $G/\rho$  and  $V$  are given in atomic units. Data for NaF are taken from Abramov (1997).

	$\rho(\mathbf{r}_c)$	$\nabla^2\rho(\mathbf{r}_c)$	$G(\mathbf{r}_c)$	$G(\mathbf{r}_c)/\rho(\mathbf{r}_c)$	$V(\mathbf{r}_c)$
MnF <sub>2</sub>	0.38	7.9	0.079	1.40	-0.076
FeF <sub>2</sub>	0.24	8.2	0.067	1.88	-0.050
CoF <sub>2</sub>	0.40	10.1	0.096	1.62	-0.087
NiF <sub>2</sub>	0.37	10.5	0.095	1.73	-0.081
MnO	0.31	5.0	0.0517	1.13	-0.0513
CoO	0.39	7.3	0.0753	1.30	-0.0748
NiO	0.40	7.3	0.0761	1.28	-0.0769
NaF	0.37	11.2	0.100	1.82	-0.094

## 7. A comparison with polarized neutron diffraction

The classical way to study the detailed spatial distribution of magnetization in crystalline solids is polarized neutron diffraction, where the magnetic structure factors are obtained from the flipping ratios between the intensities for the two polarization states of the incident beam (provided that nuclear and magnetic scattering coincide in mixed reflections, thereby excluding most antiferromagnets). Kernavanois *et al.* (2003) have performed such a study on paramagnetic CoO with the magnetization aligned by an external field of 9.6 T. Thus, a unique opportunity is offered to directly compare the results inferred from magnetic scattering with those from charge scattering.

The magnetic structure factors were analysed by a parameterized model consisting of the  $L/S$  ratio, the spin momentum on Co and O atoms, the  $3d$  radial scaling parameter  $\kappa$  and the fraction  $\alpha$  of unpaired electrons in  $e_g$  orbitals. The best fit was obtained with the ratio  $L/S$  fixed to the value of 1.3 from the charge-density analysis, leading to  $\kappa = 1.03$  (1),  $\alpha = 0.79$  (3), and a significant magnetization on the O atom. Whereas agreement with the spherical deformations from Table 3 is obvious, the above authors claim their value of  $\alpha$  to be 'in complete contradiction with the charge-density work', which they wrongly conclude to yield  $\alpha = 0.50$ . Application of Hund's first rule is straightforward for antiferromagnetic CoO (see Table 6), this is not the case, however, for the cubic phase. Both the high degree of degeneracy and the fractional orbital populations prevent a corresponding direct assortment (see Table 5). Since the number of unpaired electrons will be same for both phases, an educated guess is  $\alpha = 2/2.40$  (9) = 0.83 (3) in perfect accordance with the polarized neutron result.

## 8. Characterization of the atomic interactions and its implications

According to Bader (1990), atomic interactions may be characterized by the values of  $\rho(\mathbf{r}_c)$  and  $\nabla^2\rho(\mathbf{r}_c)$  at the bond critical points in electron density. Unshared-electron interactions (ionic bond) are characterized by a low value of  $\rho(\mathbf{r}_c)$  and  $\nabla^2\rho(\mathbf{r}_c) \gg 0$ . Additional, more quantitative, information about the bond type can be obtained by consideration of local energetic properties. The Laplacian function of the electron density is related, through the local virial theorem, to the

electronic kinetic energy density,  $G(\mathbf{r})$ , and the electronic potential energy density,  $V(\mathbf{r})$ :  $2G(\mathbf{r}) + V(\mathbf{r}) = (\hbar^2/4m)\nabla^2\rho(\mathbf{r})$ . The kinetic energy per electronic charge, the ratio  $G(\mathbf{r}_c)/\rho(\mathbf{r}_c)$ , should be less than unity for covalent interactions and greater than unity for ionic interactions (when expressed in atomic units).

Table 8 lists a selection of bond critical-point properties, as obtained from the  $\gamma$ -ray studies. For comparison, values for a prototypic ionic crystal, NaF, are also included. The kinetic energy densities at the bond critical points,  $G(\mathbf{r}_c)$ , were calculated using the approximation of Abramov (1997). The potential energy contribution and consequently the total electronic energy density,  $H(\mathbf{r}_c) = G(\mathbf{r}_c) + V(\mathbf{r}_c)$ , follow from the local virial theorem. From inspection of the corresponding parameters, the bonding state in all the magnetic compounds is evidenced as purely ionic. Cremer & Kraka (1984) suggested that, in ionic bonding interactions,  $G(\mathbf{r}_c)$  should dominate over  $V(\mathbf{r}_c)$ , resulting in positive values of  $H(\mathbf{r}_c)$ . However, our experimental results,  $H(\mathbf{r}_c) \simeq 0$ , indicate that the ionic bond is characterized rather by the balance of the two local energy densities. Inspection of the Laplacian along the bond paths manifested the typical shape expected for ionic interactions.

The spin coupling in antiferromagnetic insulators is generally interpreted by an indirect mechanism called superexchange in which the magnetic ions are effectively coupled by means of higher-order perturbation interactions involving the intervening diamagnetic ligands. Partially covalent metal–ligand bonds are inherent to the superexchange mechanism. In the molecular-orbital covalent model, the  $d$  orbitals are assumed to mix with the ligand  $s/p$  orbitals to form bonding and antibonding orbitals. In view of the absence of any charge buildup between the nuclei, the presence of  $\sigma$  metal–ligand bonding can be excluded. Antibonding orbitals produce charge depletion between the nuclei, and a contraction of the  $d$  wavefunctions is predicted, which should always be present. Only in the oxides, however, has such a contraction been observed. Moreover, the ligand-to-metal distance for MnO is 0.13 Å larger than for NiO so that the increasing importance of antibonding should find a correspondence in increased contraction, which is not the case (see Table 3). Furthermore, the strong increase in the magnetic transition temperature for the sequence MnO through NiO should arise from a corresponding increase in superexchange coupling, and one would expect some related order according to their degree in covalent character. From Table 8, the failure of this matching is obvious. Virtual hopping of electrons from a site to its neighbour and return favours antiferromagnetic correlations but it is not an observable phenomenon. Further study seems to be needed before the origin of superexchange can be considered a settled question.

## 9. Concluding remarks

It has been demonstrated that high-quality charge-scattering studies enable valuable insights into the interplay between electronic structure and magnetism, thereby supporting and

complementing results from direct magnetic diffraction techniques. Novel information has emerged from these studies including evidence for distinct anisotropies in the antiferromagnetic monoxides, contrary to the common view that symmetry breaking is negligible for basic properties such as the electronic ground state. In contrast to the oxide series, there is no indication for spin transfer in the case of the difluoride series.

## References

- Abramov, Yu. A. (1997). *Acta Cryst.* **A53**, 264–272.  
 Bader, R. F. W. (1990). *Atoms in Molecules. A Quantum Theory*. New York: Oxford University Press.  
 Brown, P. J., Figgis, B. N. & Reynolds, P. A. (1990). *J. Phys. Condens. Matter*, **2**, 5297–5308.  
 Cheetham, A. K. & Hope, D. A. O. (1983). *Phys. Rev. B*, **27**, 6964–6967.  
 Clementi, E. & Roetti, C. (1974). *At. Data Nucl. Data Tables*, **14**, 177–478.  
 Cremer, D. & Kraka, E. (1984). *Croat. Chem. Acta*, **57**, 1259–1281.  
 Ghiringhelli, G., Tjeng, L. H., Tanaka, A., Tjernberg, O., Mizokawa, T., de Boer, J. L. & Brookes, N. B. (2002). *Phys. Rev. B*, **66**, 075101-1–7.  
 Holladay, A. M., Leung, P. & Coppens, P. (1983). *Acta Cryst.* **A39**, 377–387.  
 Huiszoon, C. & Groenewegen, P. P. M. (1972). *Acta Cryst.* **A28**, 170–172.  
 Jacobson, A. J., Tofield, B. C. & Fender, B. E. F. (1973). *J. Phys. C. Solid State Phys.* **6**, 1615–1622.  
 Jauch, W. (2001). *J. Phys. Chem. Solids*, **62**, 2103–2108.  
 Jauch, W. & Reehuis, M. (2002). *Phys. Rev. B*, **65**, 125111-1–7.  
 Jauch, W. & Reehuis, M. (2003). *Phys. Rev. B*, **67**, 184420-1–8.  
 Jauch, W. & Reehuis, M. (2004). Unpublished results.  
 Jauch, W., Reehuis, M., Bleif, H.-J., Kubanek, F. & Pattison, P. (2001). *Phys. Rev. B*, **64**, 052102-1–3.  
 Jauch, W., Reehuis, M. & Schultz, A. J. (2004). *Acta Cryst.* **A60**, 51–57.  
 Jauch, W., Schultz, A. J. & Stewart, R. F. (1999). *Phys. Rev. B*, **59**, 373–380.  
 Kernavainis, N., Ressouche, E., Brown, P. J., Henry, J. Y. & Lelièvre-Berna, E. (2003). *J. Phys. Condens. Matter*, **15**, 3433–3443.  
 Lines, M. E. (1965). *Phys. Rev.* **137**, A982–A993.  
 Lines, M. E. (1967). *Phys. Rev.* **156**, 543–551.  
 Lines, M. E. & Jones, E. D. (1965). *Phys. Rev.* **139**, A1313–A1327.  
 Neubeck, W., Vettier, C., de Bergevin, F., Yakhou, F., Mannix, D., Ranno, L. & Chatterji, T. (2001). *J. Phys. Chem. Solids*, **62**, 2173–2180.  
 Palmer, A. & Jauch, W. (1993). *Phys. Rev. B*, **48**, 10304–10310.  
 Pickett, W. E., Erwin, S. C. & Ethridge, E. C. (1998). *Phys. Rev. B*, **58**, 1201–1209.  
 Rousseau, B., Maes, S. T. & Lenstra, A. T. H. (2000). *Acta Cryst.* **A56**, 300–307.  
 Sasaki, K., Fujino, K. & Takeuchi, Y. (1979). *Proc. Jpn Acad. Ser. B*, **55**, 43–48.  
 Solov'yev, I. V., Liechtenstein, A. I. & Terakura, K. (1998). *Phys. Rev. Lett.* **80**, 5758–5761.  
 Srinivasan, G. & Seehra, M. S. (1983). *Phys. Rev. B*, **28**, 6542–6544.  
 Stewart, R. F., Spackman, M. A. & Flensburg, C. (2000). *VALRAY User's Manual*. Carnegie-Mellon University, Pittsburgh, USA, and University of Copenhagen, Denmark.  
 Strempler, J., Rütt, U., Bayrakci, S., Brückel, T. & Jauch, W. (2004). *Phys. Rev. B*, **69**, 014417-1–9.  
 Strempler, J., Rütt, U. & Jauch, W. (2001). *Phys. Rev. Lett.* **86**, 3152–3155.