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Magnetic structures of the metal monoxides NiO and CoO re-investigated by spherical neutron polarimetry

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Abstract

The metal monoxides NiO and CoO both order antiferromagnetically. In NiO, the moments are perpendicular to the propagation vector. In the case of CoO, some discrepancies exist as far as the direction of the moments is concerned. We have taken advantage of the high sensitivity of the spherical neutron polarimetry as implemented in CRYOgenic Polarization Analysis Device (CRYOPAD) to re-investigate their magnetic structures. The results of these experiments are presented and discussed.

Keywords: Spherical neutron polarimetry; Magnetic structures; Transition metal monoxides

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Monoxides of 3d transition metals form an interesting class of materials. Because of their apparently simple crystal and magnetic structures, they have been chosen as test samples for band theory models, and their electronic properties have been debated for a long time [1]. Indeed, their insulating properties both below and above the Néel temperature are still not understood in the framework of simple band models. It is generally agreed that a large Coulomb interaction is at the origin of this insulating behavior [2], but recent abinitio calculations based on the local spin density approximation, taking into account the magnetic structures, have pointed out the key role played by the unquenched orbital moment [3]. As a result, intense experimental efforts have been made to determine both the nature of the magnetic ordering and the value of the orbital contributions in the whole series [4–6], to validate the different theoretical descriptions.

The magnetic structures of the simple monoxides MnO, NiO, and CoO have been established by neutron diffraction by Shull et al. [7] in their pioneering work. They both order antiferromagnetically with a propagation vector $\mathbf{k} = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. In this structure, ferromagnetic (1 1 1) sheets are antiferromagnetically coupled. Each magnetic moment is parallel to its six in plane nearest neighbors, and antiparallel to the out of plane second nearest neighbors. This ordering is due to the super-exchange interaction between next nearest neighbors via the oxygen p-orbitals, as proposed by Anderson in his model of antiferromagnetism [8]. In NiO and MnO, neutron experiments have shown that the moments are perpendicular to the propagation vector [9,10]. For MnO, the exact direction within the (1 1 1) planes has not yet been resolved. In NiO, the spins are aligned along the three $\langle 1\,\bar{2}\,1\rangle$ directions [11] (Fig. 1). For CoO, the moments are no longer perpendicular to the propagation vector **k**, and different moment directions were reported during the last 40 years. A multi-spin-axis structure that preserves the tetragonal symmetry has also been suggested, but Herrmann-Ronzaud et al. [12], from single-crystal neutron diffraction under various uniaxial stress directions, have concluded that the magnetic structure must be collinear with the moments making an angle of about 8° with the (1 1 1) plane. This angle corresponds to $\varphi = 82^\circ$ in the notation explained below. But later on, CoO has been re-investigated by magnetic X-ray scattering [13]. It has been found that a better agreement was obtained considering a magnetic moment tilted out from the (1 1 1) plane by 8°, but in the opposite direction ($\varphi = 98^\circ$, that is, a mirror image through the (1 1 1) plane) as the one found by Herrmann-Ronzaud et al.

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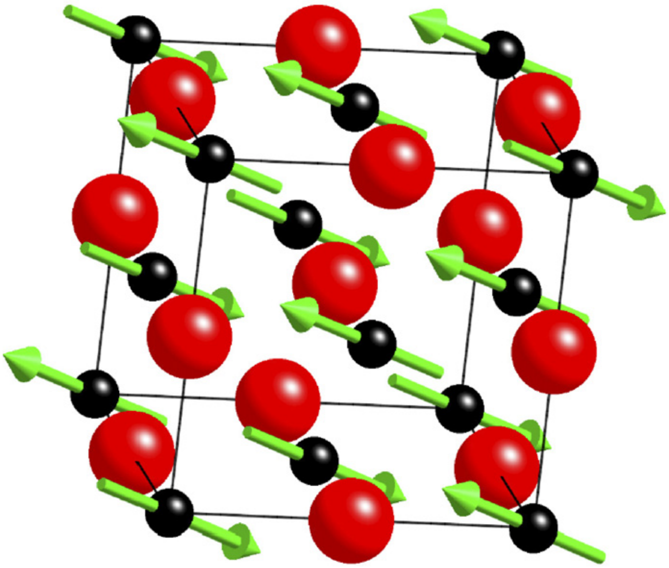

Fig. 1. Crystal and magnetic structure of NiO.

Recently, Jauch et al. have studied the crystallographic symmetry of CoO in the antiferromagnetic phase using high-resolution synchrotron powder diffraction. They have found a monoclinic symmetry (space group C2/m) [5]. The neutron powder-diffraction data that they have also collected are compatible with a collinear magnetic structure with the moments in the monoclinic $(\mathbf{a},\mathbf{c})$ plane, but different values of tilting angle could fit equally well the data.

The main difficulty to come to a conclusive answer about the magnetic structure in these oxides arises, in the case of single crystals, from the occurrence of domains. Indeed, with such a propagation vector $\mathbf{k} = (\frac{1}{2},\frac{1}{2},\frac{1}{2})$, four different K-domains exist. In each of these K-domains, because of the symmetry of the (1 1 1) direction and the mirror planes of the $Fm\bar{3}m$ structure, up to six S-domains may occur. It is therefore very difficult, using integrated intensities from unpolarized neutron diffraction data, to sort out all these possibilities and to end up with a reliable and non-ambiguous solution.

On another hand, it has been shown that the vector properties of the neutron beam polarization could provide a much more efficient way to solve magnetic structures. The changes in direction of the neutron spin which take place on scattering in a crystal are highly dependent, and therefore highly sensitive, on the orientation of the magnetic moments. These changes can be precisely measured using a neutron polarimeter which can determine the direction of the scattered polarization for any chosen incident polarization direction. This technique has been named spherical neutron polarimetry (SNP). Using it, it has been possible to solve a number of magnetic structures which were intractable by other means. This technique has been described in several publications, in particular in Ref. [14]. In this work, we have applied it to these monoxides, to see whether it could bring valuable conclusive information about their magnetic structures.

1. Results for NiO

The experiment has been carried out with the newly installed CRYOPAD option [15] of the CRG triple-axis spectrometer IN22, a machine located on the thermal guide H25 of the Institut Laue-Langevin. The incident wavelength, provided by a Heusler monochromator, was $\lambda = 1.5\,\text{Å}$, and the incident polarization, measured on a purely nuclear reflection, was 0.916(2). A Heusler focusing analyzer has been used for analyzing the polarization. The experiment was performed at room temperature, that is, well below $T_N = 523\,\text{K}$. The crystal was mounted with the $\mathbf{a}-\mathbf{c}$ axis vertical, referred to the cubic cell. Thus, two propagation vectors $\mathbf{k}_1 = (\frac{1}{2},\frac{1}{2},\frac{1}{2})$ and $\mathbf{k}_3 = (\frac{1}{2},-\frac{1}{2},\frac{1}{2})$ out of the four existing were in the scattering plane. We have investigated three different reflections $Q_1 = \frac{1}{2},\frac{1}{2},\frac{1}{2}$, $Q_2 = \frac{1}{2},-\frac{3}{2},\frac{1}{2}$, and $Q_3 = \frac{3}{2},-\frac{1}{2},\frac{3}{2}$, which all belong to the domain $\mathbf{k}_1$. For each of these reflections, we have measured the nine polarization matrix terms $P_{\alpha\beta}$, α and β being, respectively, X, Y, or Z in the usual basis set used with CRYOPAD, where X is parallel to the scattering vector, Z is vertical, and Y completes the right-handed set. α denotes the incident polarization direction and β the scattered one. We have measured the scattered polarization for both the α and the $-\alpha$ directions, which leads to 18 data points. This technique is well adapted for estimating the systematic errors due to e.g. a residual magnetic field trapped in the zero-field chamber.

In NiO, according to Baruchel et al. [11], the spin lies in the plane perpendicular to the propagation vector and is parallel to a $\langle 1\,\bar{2}\,1 \rangle$ direction. There are three such directions for each K-domain giving rise to three S-domains. A magnetic reflection can therefore be assigned to a single K-domain, but contains superimposed contributions from each of the three associated S-domains. The 54 data points (3×18) collected were thus refined using a least-square procedure adapted to this model. Only the relative populations of the three S-domains, constrained to have a sum equal to 1, were free to vary in a first refinement. Fig. 2 shows the result of this refinement. The following populations have been obtained: $p_1 = 0.339(1)$, $p_2 = 0.323(1)$, and $p_3 = 1 - p_1 - p_2 = 0.338$, with $\chi^2 = 17.6$. In a second step, the angle φ that makes the magnetic moment in the mirror plane between the $\langle 1\,1\,1 \rangle$ and $\langle 1\,\bar{2}\,1 \rangle$ directions was let free to vary ($\varphi = 90^\circ$ corresponds to a moment aligned along $\langle 1\,\bar{2}\,1 \rangle$). The refinement led to the same populations $p_1 = 0.339(1)$, $p_2 = 0.324(1)$, and $p_3 = 1 - p_1 - p_2 = 0.337$. The refined angle was $\varphi = 89.0(6)^\circ$, and the χ^2 was unchanged. This experiment on NiO thus confirmed unambiguously the result obtained by Baruchel et al.: the magnetic moments are perpendicular to the propagation vector, and point toward a $\langle 1\,\bar{2}\,1 \rangle$ direction, within the accuracy provided by CRYOPAD. Further-

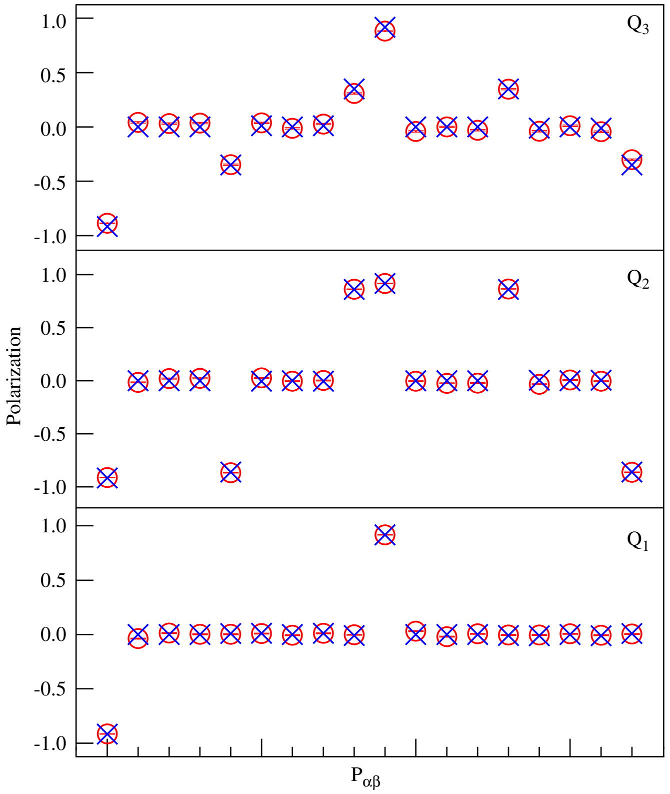

Fig. 2. The different terms $P_{\alpha\beta}$ of the polarization matrix measured in NiO for the three different reflections Q_1, Q_2, and Q_3 (open circles), and the corresponding calculated values (crosses). These terms are plotted in the order: $P_{xx}, P_{xy}, P_{xz}, P_{yx}, \ldots, P_{zz}, P_{\bar{x}x}, P_{\bar{x}y}, P_{\bar{x}z}, P_{\bar{y}x}, \ldots, P_{\bar{z}z}$.

more, in our sample, the three S-domains have roughly the same volume.

2. Results for CoO

Two different experiments were then performed on CoO, on the same spectrometer IN22, in the same conditions. Each time, a constraint was applied along the $\langle 1\,1\,1\rangle$ direction above $T_N = 290\,\mathrm{K}$ before cooling down, in order to unbalance the domain populations. The two different experiments correspond to two different constraints. In both experiments, the crystal was mounted with the $\mathbf{a}-\mathbf{c}$ axis vertical as for NiO, and the same three reflections Q_1, Q_2, and Q_3 were investigated. For each of these reflections, we have measured the same 18 components $P_{\alpha\beta}$. The corresponding 54 data points have been refined using the same least-square procedure. In each case, the relative populations of the three S-domains, constrained to have a sum equal to 1, and the angle φ already defined were free to vary. In the first case, we have obtained $p_1 = 0.523(2)$, $p_2 = 0.272(2)$, $p_3 = 1 - p_1 - p_2 = 0.205$, $\varphi = 88.6(3)^\circ$ ($\chi^2 = 11.2$) and in the second case $p_1 = 0.012(1)$, $p_2 = 0.305(1)$, $p_3 = 1 - p_1 - p_2 = 0.683$, $\varphi = 94.2(2)^\circ$ ($\chi^2 = 32$). Fig. 3 shows the result of the last refinement.

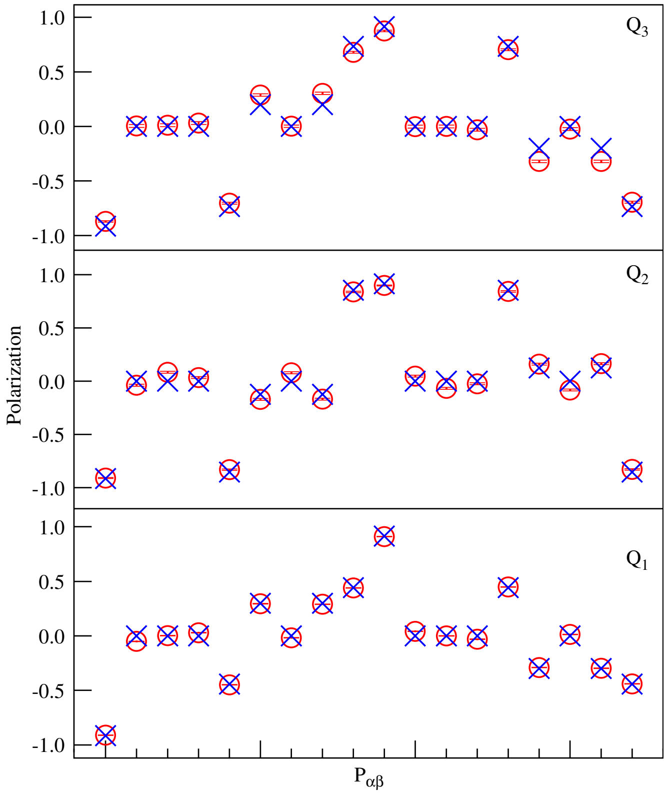

Fig. 3. CRYOPAD measurements in CoO.

The first remark that can be done concerns the effect of a uniaxial stress: such a constraint is able to completely unbalance the repartition of the S-domains within one K-domain. This observation confirms the result already found by Herrmann-Ronzaud et al. that the structure is collinear and single-K, and not multi-K. Concerning the direction of the moments, we find two different values (resp. $\varphi = 89^\circ$ and 94°) that are on both sides of $\varphi = 90^\circ$, the solution for NiO which means that the moments are perpendicular to the propagation. It should be emphasized that the error bars given from the refinements are purely statistical, does not take into account systematic errors such as a misalignment of the crystal on the spectrometer, and are for sure underestimated. Nevertheless, these results seem to suggest that the moments are closer from 90° than previously reported. All the attempts to fix the angle to the values $\varphi = 82^\circ$ or 98° led indeed to poorer χ^2. Further experiments are in progress to bring a definitive conclusion to this old problem.

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