The orbital moment in CoO

R. J. Radwanski

Center for Solid State Physics, S\textsuperscript{nt}Filip
5,31-150Krakow,Poland.

Z. Ropka

Center for Solid State Physics, S\textsuperscript{nt}Filip
5,31-150Krakow,Poland.

email: sfradwan@cyf-kr.edu.pl, http://css-physics.edu.pl

The orbital and spin moment of the Co\textsuperscript{2+} ion in CoO has been calculated within the quasi-atomic approach with taking into account the intra-atomic spin-orbit coupling. The orbital moment of 1.38 $\mu_B$ amounts at 0 K, in the magnetically-ordered state, to more than 34% of the total moment (4.02 $\mu_B$) and yields the L/S ratio of 1.04, close to the experimental value.

PACS No: 71.70.E; 75.10.D

Keywords: 3d magnetism, crystal field, spin-orbit coupling, orbital moment, CoO

CoO attracts a large attention of the magnetic community by more than 50 years. Despite of its simplicity (two atoms, NaCl structure, well-defined antiferromagnetism (AF) with $T_N$ of 290 K) and enormous theoretical and experimental works the consistent description of its properties, reconciling its insulating state with the unfilled 3$d$ band is still not reached.

The aim of this short Letter is to report the calculations of the magnetic moment of CoO. The direct motivation was a just published paper of Ref. [9]. In our approach we attribute the moment of CoO to the Co\textsuperscript{2+} ions. We have calculated the moment of the Co\textsuperscript{2+} ion in the CoO\textsubscript{6} octahedral complex, its spin and orbital parts, and the orbital moment as large as 1.38 $\mu_B$ at 0 K has been found. The approach used can be called the quasi-atomic approach [10,11] as the starting point for the description of a solid is the consideration of the atomic-like low-energy electronic structure of the constituting atoms/ions, in the present
case of the Co$^{2+}$ ions.

We have treated the 7 outer electrons of the Co$^{2+}$ ion as forming the highly-correlated electron system $3d^7$. The correlations among electrons in the unfilled $3d$ shell are approximated by two Hund’s rules, that yield the ground-term quantum numbers $S=3/2$ and $L=3$, i.e. the ground term $^3F$ [12,13]. Such the localized highly-correlated electron system interacts in a solid with the charge and spin surroundings. The charge surrounding has the octahedral symmetry owing to the $NaCl$-type of structure of CoO. We take into account the small tetragonal distortion as is experimentally observed [3]. The tetragonal distortion is important for the detailed formation of the AF structure and influences the spin and orbital moments but the most essential physical interaction is the intra-atomic spin-orbit coupling. Our Hamiltonian for CoO consists of two terms: the single-ion-like term $H_d$ of the $3d^7$ system and the $d$-$d$ intersite spin-dependent term, important for the formation of the magnetic state. The calculations follow those, that we have performed for the description of FeBr$_2$ and NiO [10,11,14]. For the quasi-atomic single-ion-like Hamiltonian of the $3d^7$ system we take into account the crystal-field interactions of the octahedral symmetry (the octahedral CEF parameter $B_4=-40$ K), the spin-orbit interactions with the spin-orbit coupling $\lambda_{s-0}=-260$ K and the tetragonal distortion approximated by the term $B_{0}^{2}=-10$ K. The calculated single-ion states under the octahedral crystal field and the spin-orbit coupling (the CoO$_6$ complex) are presented in Fig. 1.

The ground-state doublet characterized by the total moment of $\pm 2.21 \mu_B$ is built up from the orbital and spin moments of $\pm 0.70$ and $\pm 1.84 \mu_B$, respectively. It, however, fully cancels in the paramagnetic state and reveals itself only in the presence of the magnetic field, external or internal in case of the magnetically-ordered state, that polarizes two doublet states. This doublet is the Kramers doublet. The intersite spin-dependent interactions cause the (antiferro-)magnetic ordering. They have been considered in the mean-field approximation with the molecular-field coefficient $n$ acting between magnetic moments as $-40T/\mu_B$. It means that the Co moment in the magnetic state at 0 K experiences the molecular field of 161 T. It causes the spin-like gap of 40 meV.
The calculated value of the magnetic moment at 0 K in the magnetically-ordered state amounts to 4.02 $\mu_B$. It is built up from the spin moment of 2.64 $\mu_B$ ($S_z=1.32$) and the orbital moment of 1.38 $\mu_B$. The increase of the orbital moment in comparison to the paramagnetic state is caused by the polarization of the ground-state eigenfunction by the molecular magnetic field. The orbital moment is quite substantial being more than 34% of the total moment. Our theoretical outcome, revealing the substantial orbital moment is in nice agreement with the very recent experimental result of 3.98$\pm$0.06 $\mu_B$ for the Co moment [8]. The magnetic x-ray experiment has revealed the $L/S$ ratio of 0.95 [13]- the calculated by us values lead to $L/S$ ratio, in fact their $z$ components, of 1.04. In NiO we have calculated the $L/S$ ratio as 0.54 at 0 K [14].

The calculated temperature dependence of the total moment, together with the orbital and spin moments, is shown in Fig. 3. These moments disappear above $T_N$ - in the paramagnetic region the derived moment is the effective moment, that bears the information about $J^2$ or $S^2$.

We would like to point out that the evaluation of the orbital moment is possible provided the spin-orbit coupling is taken into account. It confirms the importance of the spin-orbit coupling for the description of the 3d-ion compounds. The present model allows, apart of the ordered moment and its spin and orbital components to calculate many physically important properties like temperature dependence of the magnetic susceptibility, temperature dependence of the heat capacity, the spectroscopic $g$ factor, the fine electronic structure in the energy window below 4 eV with at least 28 localized states.

Finally, we would like to point out that our approach should not be considered as the treatment of an isolated ion only - we consider the Co$^{2+}$ ion in the oxygen octahedron. The physical relevance of our discussion to CoO is obvious - the NaCl structure is built up from the edge sharing Co$^{2+}$ octahedra and the similar electronic structure occurs at each Co site.

In conclusion, the orbital and spin moment of the Co$^{2+}$ ion in CoO has been calculated within the quasi-atomic approach taking into account the intra-atomic spin-orbit interactions. The orbital moment of 1.38 $\mu_B$ amounts at 0 K, in the magnetically-ordered state,
to more than 34% of the total moment (4.02 $\mu_B$). Our atomic-like approach provides the discrete energy states for 3$d$-electrons in CoO and calculates, apart of the spin moment, the orbital moment. This orbital moment is completely ignored in most of modern solid-state physics theories. Our studies indicate that it is the highest time in solid-state physics to "unquench" the orbital moment in the description of 3$d$-atom containing compounds, the more that it becomes visible in recent advanced experiments.

[1] M. R. Norman, Phys. Rev. B 44, 1364 (1991).
[2] V. J. Asimov, J. Zaanen and O. K. Anderson, Phys. Rev. B 44, 943 (1991).
[3] P. Wie and Z. Q. Qi, Phys. Rev. B 49, 10864 (1994).
[4] P. Dufek, P. Blaha, V. Slivko, and K. Schwarz, Phys. Rev. B 49, 10170 (1994).
[5] J. Hugel and M. Kamal, Solid State Commun. 100, 457 (1996).
[6] I. V Solovyev, A. I. Liechtenstein, and K. Terakura, Phys. Rev. Lett. 80, 5758 (1998).
[7] T. Bredow and A. R. Gerson, Phys. Rev. B 61, 5194 (2000).
[8] W. Jauch, M. Reehuis, H. -J. Bleif, F. Kubanek, and P. Pattison, Phys. Rev. B 64, 052102 (2001).
[9] W. Jauch and M. Reehuis, Phys. Rev. B 65, 125111 (2002).
[10] R. J. Radwanski, R. Michalski, and Z. Ropka, Acta Phys. Pol. B 31, 3079 (2000).
[11] Z. Ropka, R. Michalski, and R. J. Radwanski, Phys. Rev. B 63, 172404 (2000); http://xxx.lanl.gov/abs/cond-mat/0005502
[12] A. Abragam and B. Bleaney, in: Electron Paramagnetic Resonance of Transition Ions (Clarendon, Oxford) 1970, ch.7.
[13] C. J. Ballhausen, in: *Ligand Field Theory* (Mc-Graw-Hill Comp.) 1962.

[14] R. J. Radwanski and Z. Ropka, Acta Phys. Pol. A 97, 963 (2000).

[15] W. Neubeck, C. Vettier, F. de Bergevin, F. Yakhou, D. Mannix, L. Ranno, and T. Chatterji, J.Phys.Chem. Solids 62, 2173 (2001).

Figure captions.

**Fig. 1.** The electronic structure of the Co$^{2+}$ ion in CoO. a) the free-ion $^4F$ term, b) the effect of the octahedral crystal field, c) the electronic structure resulting from the octahedral crystal field and the intra-atomic spin-orbit interactions.

Fig. 2. The splitting of the ground-state Kramers doublet in the magnetically-ordered state of CoO.

Fig. 3. Temperature dependence of the Co$^{2+}$-ion moment in CoO. At 0 K the total moment of 4.02 $\mu_B$ is built up from the orbital and spin moment of 1.38 and 2.64 $\mu_B$, respectively. The calculations have been performed for the quasi-atomic parameters with the octahedral crystal-field parameter $B_4= -40$ K, the spin-orbit coupling constant $\lambda_{s-o}= -260$ K, the intersite spin-dependent interactions given by the molecular-field coefficient $n = -40$ T/ $\mu_B$ and the tetragonal distortion parameter $B_2^0$ of -10 K.
\[3d^7 \text{ Co}^{2+}\]

\[\begin{array}{cc}
& 4A_{2g} \\
\hline
4 & 1 \cdot 4 \\
\hline
\end{array}\]

\[B_4 < 0\]
\[\lambda < 0\]

\[\begin{array}{cc}
& 4T_{2g} \\
\hline
4 & 3 \cdot 4 \\
\hline
\end{array}\]

\[640K\]

\[\begin{array}{cc}
& 4F \\
\hline
7 \cdot 4 \\
\hline
\end{array}\]

\[\begin{array}{cc}
& 4T_{1g} \\
\hline
3 \cdot 4 & 2 \\
\hline
\end{array}\]

\[\pm 2.21 \mu_B\]

\[1600K\]

a) b) c)

\[B_4 = -40K\]
\[\lambda = -260K\]
$3d^7 \text{Co}^{2+}$

- $T_N = -40 \text{K}$
- $\lambda = -260 \text{K}$
- $n = -40 \text{T}/\mu_B$
- $B_2^0 = -10 \text{K}$

- $<L_z> = 1.38$
- $<S_z> = 1.32$
- $0.85 \mu_B$
- $4.02 \mu_B$
- $\pm 2.54 \mu_B$
Co\textsuperscript{2+} ion in CoO

- $B_4^0 = -40$ K
- $\lambda = -260$ K
- $n = -40$ T/$\mu_B$
- $B_2^0 = -10$ K

Magnetic moment (µ$_B$/Co-ion):
- Total
- Spin moment
- Orbital moment

T (K)