Magnetism and electronic structure of LaMnO$_3$ and LaCoO$_3$

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Abstract

For the description of electronic and magnetic properties of transition metal oxides we have taken into account the fine electronic structure of the Mn^{3+} and Co^{3+} ions, that results from the crystal-field, spin–orbit coupling, local lattice distortions (Jahn–Teller effect). Our model consistently explains the formation of the non-magnetic state of LaCoO$_3$ as due to the non-magnetic Co^{3+}-ion ground state caused by the Jahn–Teller effect via the trigonal lattice distortion and the magnetic insulating state for LaMnO$_3$. Our studies indicate that the orbital moment has to be unquenched in this description of 3d-ion compounds. © 2000 Elsevier Science B.V. All rights reserved.

LaMnO$_3$ and LaCoO$_3$ belong to the class of compounds called Mott insulators. The interest in LaMnO$_3$-based compounds largely increases after discovery of the giant magnetoresistance [1,2]. The interest in LaCoO$_3$ is mostly related to its non-magnetic ground state at low temperatures [3–7].

The aim of this paper is to study the single-ion-like properties of the Mn^{3+} and Co^{3+} ions in LaMnO$_3$ and LaCoO$_3$. We consider the Mn^{3+}/Co^{3+} ions in the octahedral crystal field (CEF) with taking into account the spin–orbit (s–o) coupling. We make use of the fact that both the compounds are isostructural and isoelectronic.

In the insulating LaMnO$_3$ and LaCoO$_3$ compounds the manganese/cobalt atoms are in the trivalent state as anticipated from the compensated valences La^{3+}Mn^{3+}O$_3^{2-}$ and La^{3+}Co^{3+}O$_3^{2-}$. Owing to the perovskite-like structure the Mn^{3+}/Co^{3+} ions are situated in the octahedral cubic surrounding of the oxygen ions. Detailed X-ray studies have revealed extra slight distortion [4]. The Mn^{3+}/Co^{3+} ion has 4/6 d-electrons in the incomplete outer shell and here they are treated as forming the highly correlated electron system 3d^n. In a zero-order approximation these electron correlations within the incomplete 3d shell are accounted for by the phenomenological two Hund's rules. They yield for both the 3d^4 and 3d^6 electron configuration the ground term ^{5}D with $S = 2$ and $L = 2$ (Fig. 1). Under the action of the dominant cubic crystal field, the ^{5}D term splits into the orbital triplet ^{5}T$_{2g}$ and the orbital doublet ^{5}E$_g$. For the 3d^4 configuration the subterm ^{5}E$_g$ is lower whereas the orbital triplet ^{5}T$_{2g}$ is lower for the 3d^6 system.

We have taken into account the intra-atomic spin–orbit coupling and have calculated the low-energy electronic structure, resulting from the Hamiltonian

$$H_{\mathrm{d}} = H_{\mathrm{CF}}^{\mathrm{cub}} + k\lambda_0 LS + B_2^0 O_2^0 + \mu_{\mathrm{B}}(L + g_{\mathrm{e}}S)B_{\mathrm{ext}}. \qquad (1)$$

All symbols have standard meaning, k denotes the change of the s–o coupling in a solid compared to the free-ion value. These terms are written in the decreasing energy sequence: $H_{\mathrm{CF}}^{\mathrm{cub}} = 2$–3 eV, $H_{\mathrm{s-o}} = 0.1$ eV, $H_{\mathrm{t}} = 0.05$ V, $H_z = 0.01$ eV. In our calculations we are treating all terms on the same footing in the same diagonalization procedure. The last term allows the influence of the magnetic field to be calculated. In particular, the temperature dependence of the paramagnetic susceptibility

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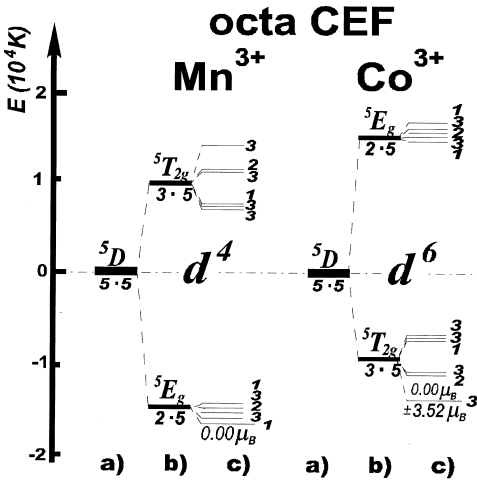*E-mail address:* sfradwan@cyf-kr.edu.pl (R.J. Radwański)

Fig. 1. The fine electronic structure produced by the cubic octahedral CEF interactions in the presence of the spin–orbit coupling for the Mn^{3+} (d^4) and Co^{3+} (d^6) ions (c). Both ions have the ^5D ground term (a) that is 25-fold degenerated in the spin–orbital space. In (b) is shown the splitting of the ^5D term into ^5E_g and $^5T_{2g}$ cubic subterms under the action of the octahedral CEF only.

χ can be calculated. The cubic part of CEF interactions has been separated owing to its usual dominancy.

The results are shown in part c of Fig. 1. There are 25 orbital states spread over 2–3 eV. Some of the states are very close to the ground state. For instance, for the Mn^{3+} ion 10 states are confined to 2 meV only; the off-cubic distortion causes further, but still small spreading of the ^5E_g subterm up to, say, 5–7 meV (in the presence of $B_4 = -200$ K and λ of $+120$ K). It turns out the existence of so many states helps in the development of the magnetic state as is observed for $LaMnO_3$ with T_N of 140 K. Obviously, for description of the magnetic state we have to involve the spin-dependent inter-site interactions – such studies are, however, beyond the scope of present considerations. From the studies of rare-earth compounds we know that the existence of the fine electronic structure in the energy window below 10 meV causes anomalous temperature behaviour of many physical properties [8]. It is illustrated in Fig. 2 for the Co^{3+} ion where the calculated temperature dependence of the paramagnetic susceptibility is shown. Clearly, the appearance of the trigonal distortion completely breaks down the Curie law. $\chi(T)$ reveals the low-temperature non-magnetic state and exhibits the pronounced maximum of the susceptibility at 90 K with the Curie–Weiss law at temperatures above 130 K. Such a shape of $\chi(T)$ is in good agreement with experimental data of Ref. [6]. Such particular dependence results from the singlet–doublet low-energy spectrum, which is the effect of the trigonal off-cubic distortion that splits the lowest
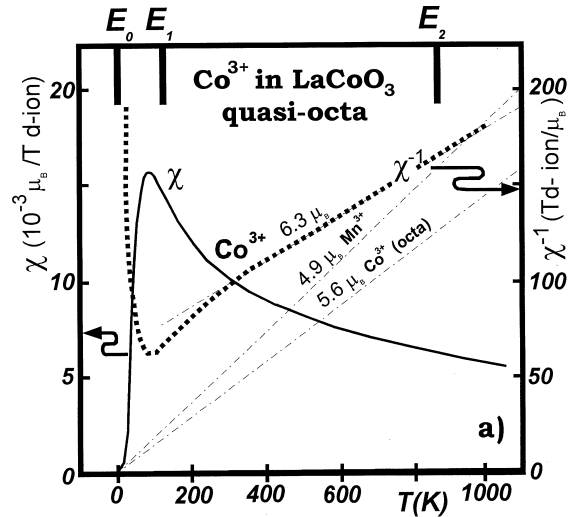

Fig. 2. The calculated temperature dependence of the paramagnetic susceptibility χ for the Co^{3+} (the solid line) and Mn^{3+} (dotted–dashed line) ion in the distorted octahedra in $LaCoO_3$ and $LaMnO_3$. The dashed line shows $\chi(T)$ of the Co^{3+} ion in the purely octahedral crystal field that fulfils the Curie law. On the top the energy position of the three lowest states for $LaCoO_3$ is shown.
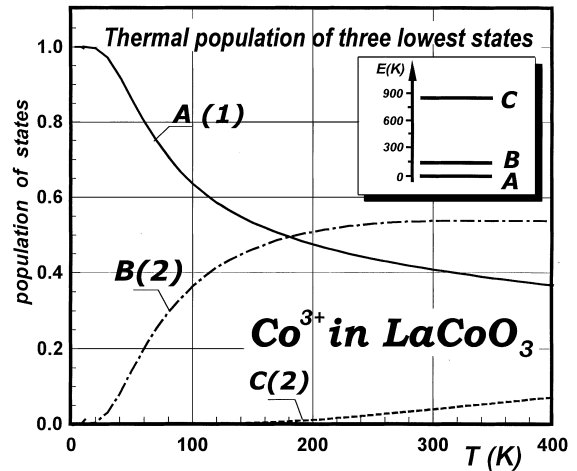

Fig. 3. The temperature dependence of population of the three lowest states of the Co^{3+} ion in the distorted octahedral crystal field in $LaCoO_3$.

spin + orbital triplet state. The trigonal distortion term H_t with B_2^0 of $+175$ K yields for the $LaCoO_3$ a spin-like gap of 11 meV (in the presence of $B_4 = +200$ K and λ of -630 K). With increasing temperature higher states become populated according to the Boltzmann-distribution function. The population of the three lowest states for $LaCoO_3$ is shown in Fig. 3. Quite similar occupation has been inferred in Ref. [6] on the

basis of experimental studies. The E_g–T_{2g} splitting of 2–3 eV, that is largely determined by the cubic CEF interactions ($= 120B_4$) is in good agreement with optical data [3,4].

In conclusion, the fine electronic structure with 25 orbital states is expected to exist in $LaMnO_3$ and $LaCoO_3$ as originating from the Mn^{3+} and Co^{3+} ions. The diamagnetic state of $LaCoO_3$ is associated with the non-magnetic singlet ground state of the Co^{3+} ion being situated in the slightly trigonally-distorted octahedral crystal field in $LaCoO_3$ and, in fact, is the physical realization of the Jahn–Teller theorem. Magnetism of $LaMnO_3$ appears, despite the singlet ground state of the Mn^{3+} ion, because of particularities of the electronic structure. There are two-closely lying singlets, that behave like magnetic Kramers doublet. Our model explains in a very natural way the insulating state of $LaMnO_3$ and $LaCoO_3$ – in fact, $LaCoO_3$ is one of the best insulators (ρ at 77 K amounts to 10^7 Ω m, Ref. [6]). The present calculations prove the importance of the s–o coupling and off-cubic lattice distortions for the description of low-temperature properties of compounds containing 3d ions.

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