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The formation of a non-magnetic state for the d^6 electronic system

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Abstract

It has been shown that the crystal–field interactions can produce a non-magnetic singlet ground state for the highly-correlated d^6 system situated in the quasi-octahedral crystal field (CEF) surrounding provided the spin–orbit interactions are correctly taking into account. The spin–orbit interactions in combination with the trigonal distortion of the cubic CEF interactions produce a peculiar energy level scheme with a non-magnetic ground state and highly-magnetic excited states at 11 and 70 meV. The calculated temperature dependence of the magnetic susceptibility exhibits very substantial departure from the Curie law that is due to second-order CEF interactions. The present considerations can be applied to Co^{3+} and Fe^{2+} -ion compounds like LaCoO_3 and FeBr_2 . The derived electronic and magnetic properties mimic very much those found experimentally for LaCoO_3 . © 1999 Elsevier Science Ltd. All rights reserved.

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A proper consistent description of paramagnetic $3d$ ions is still under debate [1–7], though Sir Nevill Mott already in 1949 has realized that it is strong electron correlations that play the fundamental role in the determination of the electronic structure of $3d$ -ion compounds (Mott insulators). The electronic structure governs electronic and magnetic properties. Despite of almost 50 years enormous theoretical research activity in this field Nature once by once shows phenomena that reveal a large shortage of our general understanding of magnetism of $3d$ -ion compounds. Surely properties like these exhibited by LaCoO_3 are challenging. At first, it has a non-magnetic ground state at low temperatures [1–6]. Such the state always draws attention of the magnetic community appealing the question about the nature of the magnetic moment. Secondly, this non-magnetic ground state seems to transform with increasing temperature into a magnetic state as is inferred from an unusual temperature dependence [6,8] of the magnetic susceptibility χ ($\chi \cdot T$ instead of being constant continuously grows up with temperature). These two facts resemble somehow the Kondo problem for the formation of the non-magnetic state of a magnetic impurity. This phenomenon for LaCoO_3 is

discussed, following Raccah and Goodenough [6], by consideration of a model with substantial temperature variation in the population of low- and high-spin Co ions, the latter being randomly distributed in the majority of low-spin Co ions at low temperatures.

Different theoretical approaches for the $3d$ -ion compounds differ in the starting estimation of the strength of $3d$ electron–electron correlations with respect to the strength of crystal–field (CEF) interactions. The spin–orbit (s–o) coupling is usually ignored based on a consensus that the s–o coupling for $3d$ ions is the smallest among these above-mentioned interactions. This consensus is a reason for the misleading, according to us, neglect of the s–o coupling in evaluations of the electronic structure. Our studies indicate that it is just opposite—the smaller the s–o coupling the lower the available energy excitations and the lower the temperatures with anomalies of the electronic properties. Direct calculations confirm that just a weak s–o coupling causes a dramatic change of the electronic structure by producing the fine electronic structure with low-energy excitations even so small as 1 meV ($= 11.6 \text{ K} = 8.0 \text{ cm}^{-1}$).

The aim of this Letter is to study the possibility for the formation of a non-magnetic state on the atomic scale for the d^6 electronic system in case of a predominantly cubic

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surrounding. This paper has been motivated by an unsolved problem of the cause of the non-magnetic ground state of LaCoO_3 [1–8].

In the insulator LaCoO_3 the cobalt atoms occur in the trivalent state anticipated from the charge neutrality $\text{La}^{3+}\text{Co}^{3+}\text{O}_3^{2-}$. The Co^{3+} ion has six d-electrons in the incomplete outer shell and here they will be treated as forming the highly-correlated electron system $3d^6$. Owing to the perovskite-like structure of LaCoO_3 the Co^{3+} ions are situated in the octahedral cubic surrounding that allows the trigonal distortion easily to occur along the cube diagonal.

A modern approach to compounds like LaCoO_3 is based on an idea of Mott that it is strong electron correlations that make electrons in the incomplete $3d$ shell to stay rather localized than itinerant (Mott insulators). The physical situation of the $3d^n$ system of a $3d$ -transition-metal ion is here taken to be accounted for by considering the single-ion-like Hamiltonian containing the electron-electron interactions within the $3d$ shell H_{el-el} , the crystal-field H_{CF} , spin-orbit H_{s-o} and Zeeman H_Z interactions [9]:

$$H_d = H_{el-el} + H_{CF} + H_{s-o} + H_Z. \quad (1)$$

The electron–electron and spin–orbit interactions are intra-atomic interactions, whereas crystal–field and Zeeman interactions account for interactions of the unfilled $3d$ shell with the charge and spin surrounding. These interactions are written in a decreasing-strength succession [10].

In a zero-order approximation the electron correlations are accounted for by phenomenological Hund's rules that yield for the $3d^6$ electron configuration the term 5D with $S = 2$ and $L = 2$ as the ground term. Following the intermediate crystal-field approach [11–13] the ground term 5D , under the action of the crystal field of the cubic symmetry, splits into the orbital triplet Γ_5 , denoted also as T_{2g} , and the orbital doublet Γ_3 (E_g). The 5D term is 25-fold degenerated; five-fold degeneration occurs with respect to the orbital degree of freedom. Each orbital state contains the five spin-degree of freedom. The removal of this 25-fold degeneracy can be traced by consideration of the single-ion-like Hamiltonian written for the lowest Hund's rule [LS] term [9,11–13]:

$$H_d = B_4(O_4^0 + 5O_4^4) + k\lambda_o L \cdot S + \mu_B(L + g_e S) \cdot B_{ext}. \quad (2)$$

The first term is the cubic CEF Hamiltonian with the Stevens operators O_n^m that depend on the orbital quantum numbers L, L_z . The second term accounts for the spin–orbit interactions; the coefficient k denotes the change of the s–o coupling in a solid compared to the free-ion value, presumably due to the covalent mixing. The last term accounts for the influence of the magnetic field, externally applied in the present case. The g_e value equals to 2.0023. The calculations of the many-electron states of the $3d^6$ system have been performed by the diagonalization of a 25×25 matrix associated with the Hamiltonian (Eq. (1)) considered in the $[\text{LSL}_z S_z]$ base [14]. Fig. 1 presents a general overview of the effect of CEF and s–o interactions on the 5D term for the

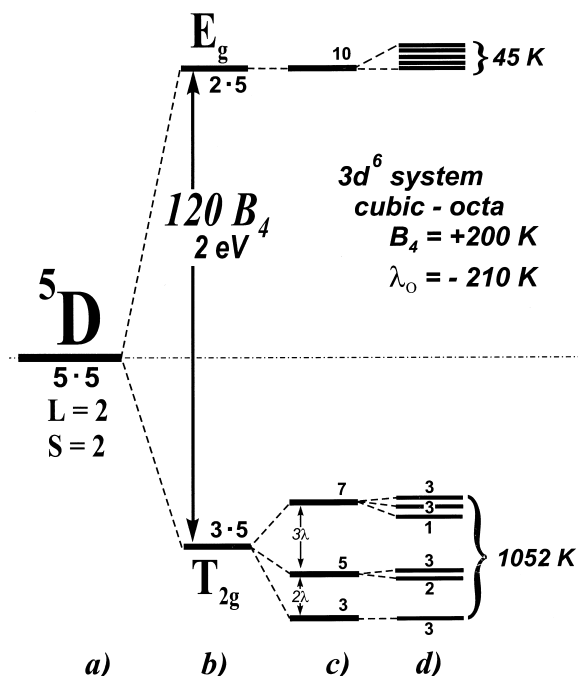


Fig. 1. (a) The 25-fold degenerated 5D term of the $3d^6$ system that is expected to be realized in the $\text{Co}^{3+}/\text{Fe}^{2+}$ ion. (b) The energy level scheme for the $3d^6$ system under the action of CEF interactions of the octahedral symmetry. All the orbital levels have the internal 5-fold spin-degree of freedom, (c) the effect of the spin–orbit interactions on the localized states of the $3d^6$ system according to Abragam and Bleaney [11], fig. 7.19; (d) the effect of the s–o coupling according to the present calculations: additional splittings should be noticed.

d^6 system ($\lambda < 0$) in case of cubic CEF interactions of the octahedral surroundings (T_{2g} ground cubic subterm). For the tetrahedral surroundings the CEF structure is reversed yielding the E_g ground state.

As a result of the computation one obtains the energies of the 25 states and the eigenvectors containing information, e.g. about the magnetic properties. These magnetic characteristics are computationally revealed under the action of the external magnetic field, and they are shown in Fig. 2 on the right hand side. Of course, due to the spin–orbit coupling the states are no longer purely cubic orbital states. The calculations have been performed for the spin–orbit constant λ_o for the Co^{3+} ion of -210 K taken after Ref. [11], p. 399 and with $k = 3.0$. Values for B_4 depend on the strength of cubic CEF interactions. The separation Δ of the E_g and T_{2g} states amounts to $120B_4$. The experimentally derived values for Δ are largely inconsistent: 1.2 eV is given in Ref. [3] or 2.4 eV in Ref. [4]. Thus we have chosen for the calculations $B_4 = +200 \text{ K}$ that yields a more reasonable value of Δ of 2.1 eV . The positive sign for B_4 is consistent with the octahedral oxygen surrounding in LaCoO_3 . It yields the orbital triplet T_{2g} cubic subterm as the ground

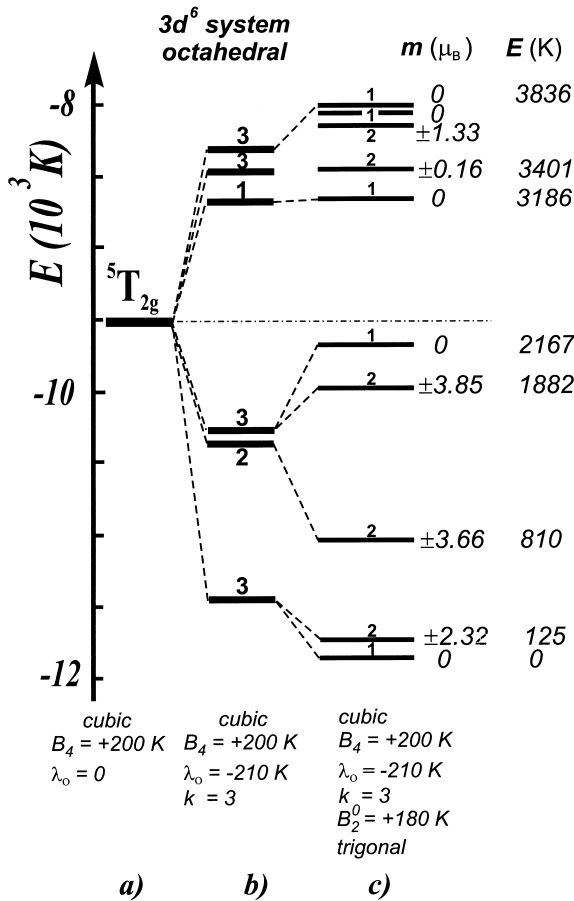


Fig. 2. The influence of the trigonal distortion, $B_2^0 = +180$ K, on the cubic CEF + spin-orbit states ($\lambda_0 = -210$ K, $k = 3.0$, $B_4 = +200$ K) of the 15-fold degenerated orbital-triplet ${}^5T_{2g}$ ground state. The trigonal distortion produces the fine electronic structure with a nonmagnetic singlet ground state and strongly magnetic excited states at 125 K and 810 K (c). The states are labelled with the degeneracy, the respective energy and the magnetic moment.

state. It is 15-fold degenerated in the LS space. The spin-orbit interactions largely remove the 15 or 10-fold degeneracy of the T_{2g} and E_g subterms as is seen in Figs. 1(d) and 2(b). As we are mostly interested in the ground state as it determines properties at low temperatures we would like to point out that the lowest triplet state, in the orbital + spin space, can be split by electrostatic interactions as is shown in Fig. 2(c). We have checked that a trigonal or tetragonal distortion, described by the leading term $B_2^0 O_2^0$, removes the three-fold degeneracy of the lowest cubic CEF + s-o state producing the singlet and the doublet. The positive B_2^0 term along the cube diagonal (the trigonal distortion) realizes the Jahn–Teller theorem, i.e. makes the singlet to be energetically lower. This discussion is relevant to LaCoO_3 as it undergoes [6] a trigonal (rhombohedral) distortion at a temperature of 1210 K.

Fig. 2 presents the influence of the spin-orbit coupling

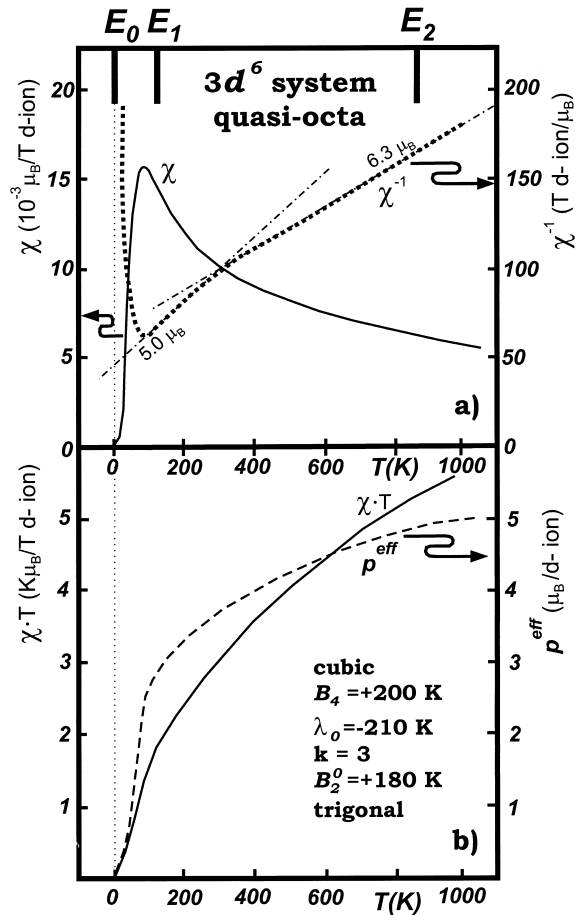


Fig. 3. (a) The calculated temperature dependence of the magnetic susceptibility χ (the solid line) for the $3d^6$ system situated in a trigonally distorted cubic octahedral site. It does not follow the Curie law having a sharp rounded peak at ~ 90 K. Two distinctly different regions in the χ^{-1} vs T plot (the dot-dashed line) are seen: below 300 K with $p^{\text{eff}} = 5.0 \mu_B$ and above 400 K with p^{eff} of $6.3 \mu_B$. The χ^{-1} vs T dependence mimics the Curie–Weiss behaviour though this anomalous susceptibility dependence is purely CEF effect associated with the substantial second-order CEF term. The susceptibility calculated without the B_2^0 distortion almost follows the Curie law with a mean value of $p^{\text{eff}} = 5.84 \mu_B$. In the top the energy positions of the three lowest states are shown. (b) Temperature dependence of the $\chi \cdot T$ (the solid line). A continuous increase indicates departure from the Curie law. It could be misleadingly attributed to the temperature-induced increase of the effective paramagnetic moment, shown by the dashed line, if one misleadingly uses the Curie-law expression $p^{\text{eff}} = \sqrt{3\chi \cdot T}$. This picture is in nice agreement with experimental data presented in Fig. 4 of Ref. [15].

and of the trigonal distortion on the cubic CEF subterm ${}^5T_{2g}$. The resulting electronic structure, shown in Fig. 2(c), is quite peculiar. It has (i) a non-magnetic ground state and (ii) the highly magnetic excited state; in fact even two highly-magnetic doublets. The magnetic moment of the

first and the second excited states amounts to $\pm 2.32 \mu_B$ and $\pm 3.66 \mu_B$. The Jahn–Teller splitting depends on the value of the trigonal distortion B_2^0 . The calculated temperature dependence of the magnetic susceptibility is shown in Fig. 3(a). It exhibits a very special behaviour with a large maximum at the temperature of ~ 90 K. In fact, the trigonal distortion B_2^0 of $+180$ K and the three-fold increase of the s–o coupling have been chosen in order to have this maximum at 90 K. For smaller values B_2^0 and k , this maximum occurs for lower temperatures. Obviously, the special behaviour $\chi(T)$ results from the peculiarities of the local electronic structure. χ does not follow the Curie law even at higher temperatures what is clearly seen in the χ^{-1} vs T plot presented in Fig. 3(a). It mimics a Curie–Weiss (C–W) behaviour with a quite large value of the paramagnetic Curie temperature θ . θ is, however, largely temperature-dependent varying from 270 to 600 K. This substantial departure from the Curie law, mimicing the C–W law, is purely the CEF effect associated with the second-order CEF interactions. There is an apparent change of the slope of the $\chi^{-1}(T)$ plot at 300 K that mimics somehow the one found experimentally in LaCoO_3 [6]. An effective moment calculated from this slope in the temperature interval 150–300 K yields $5.0 \mu_B$ and $6.3 \mu_B$ if calculated from the 400–1000 K interval. This change of the effective moment is even more visible in the plot $\chi \cdot T$ vs T that is presented in Fig. 3(b). It is the standard plot for the presentation of the Curie law in the physical chemistry [15]. The departure from the constancy of $\chi \cdot T$ signals the temperature variation of the effective moment like it was in case of LaCoO_3 [8,6]. Using the Curie-law formula $p^{\text{eff}} = \sqrt{3\chi \cdot T}$ one gets 0, 2.63, 3.56, 5.00 μ_B at 0, 100, 300 and 1000 K, respectively (see also Fig. 3b). Values of 2.82 and 4.90 μ_B one finds from the theoretical spin-only expression for $S = 1$ and $S = 2$, respectively. It means that this purely CEF effect can be misleadingly attributed to a temperature-induced low-spin–high-spin transformation. Finally it is worth noting that the calculated results in Fig. 3(b) are in nice agreement with very detailed experimental data presented in Ref. [15], Fig. 4.

In conclusion, it has been shown that the crystal-field interactions can produce a non-magnetic singlet ground state for the highly-correlated d^6 system situated in the quasi-octahedral crystal-field surrounding provided the spin–orbit interactions are correctly taking into account [16]. The s–o coupling produces for the d^6 system the fine electronic structure with 15 available energy states below 0.3 eV. The spin–orbit interactions in combination with the

trigonal distortion of the cubic CEF interactions produce a peculiar energy level scheme with a non-magnetic ground state and highly-magnetic excited states at 11 meV and 70 meV. The calculated temperature dependence of the magnetic susceptibility exhibits very substantial departure from the Curie law. In such a case one can misleadingly evaluate the effective paramagnetic moment and reveal its strong temperature variation. The present considerations about the d^6 system can be applied to compounds containing Co^{3+} , Fe^{2+} , Rh^{3+} and Ru^{2+} ions. The derived electronic and magnetic properties mimic very much those found experimentally in LaCoO_3 . The natural explanation for the insulating state of LaCoO_3 , the evaluation of the fine electronic structure and the possibility for calculations of the influence of temperature on electronic and magnetic properties are great advantages of the presented approach.

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