Research Article

Relativistic effects in the electronic structure for the 3d paramagnetic ions♠

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It has been shown that relativistic spin-orbit effects have enormous influence on the electronic structure of the correlated electron systems $3d^n$. The s-o coupling produces the fine electronic structure with a large number of low-energy, <10 meV, localized states. These states affect enormously electronic and magnetic properties of 3d-ion compounds at low- and room-temperature regions. It is inferred that the relativistic s-o effects and the multiplet structure on individual atoms are indispensable for the proper evaluation of the electronic structure of paramagnetic 3d-ion compounds.

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The 3d-paramagnetic-ion compounds are the subject of continuous interest [1–17] despite of more than 60 years of intensive theoretical and experimental studies. The relativistic spin-orbit (s-o) coupling is usually ignored in calculation of the electronic structure of the 3d ions

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in solids basing on a general consensus that the s-o coupling is for $3d$ ions relatively weak. We have argued [18] that it is just opposite - the weak s-o coupling causes dramatic change of the electronic structure by producing the fine electronic structure with low-energy excitations even so small as 1 meV (=11.6 K = 8.0 cm^{-1}).

The aim of this Letter is to present the influence of the spin-orbit coupling on the localized states of the highly-correlated d^n electronic system produced by crystal-field interactions of the cubic octahedral symmetry. The present approach is an extension of an approach known as an intermediate crystal-field approach [17]. One can be surprised, but the influence of the spin-orbit coupling has not been systematically studied [19] despite of a quite simple form of the s-o Hamiltonian $H_{s-o} = \lambda L \cdot S$. It turns out that the spin-orbit coupling has to be taken into account for any meaningful analysis of electronic and magnetic properties of $3d$-ion compounds due to the presence of the fine electronic structure.

The modern approach to a $3d$-ion compound is based on an idea of Mott that it is strong electronic correlations that make electrons in the incomplete $3d$ shell to stay rather localized than itinerant (Mott insulators). The physical situation for 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 $d-d$ interactions H_{el-el}, the crystal-field H_{CF}, spin-orbit H_{S-O}, and Zeeman H_Z interactions [20]

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

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 surroundings. These interactions are written in the decreasing- strength succession [18].

In a zero-order approximation the electron-electron correlations are accounted for by phenomenological Hund's rules (the maximal value of L provided the maximal value of the spin S is realized). They yield for the $3d^n$ electron configuration the ground term $|LS\rangle$ that is (2L+1)·(2S+1) degenerated, see Table 1. Strong intra-atomic Hund's-rule correlations allows one to work in the $|LSL_ZS_Z\rangle$ space. In this space the effect of the crystal-field, of the spin-orbit coupling and of the (internal/external) magnetic field is accounted for by considering the single-ion Hamiltonian of the $3d^n$ system of the $3d$-transition-metal ion of the form [14]:

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

n	S	L	Free ion		Octa cubic CEF			s-o coupling	
			Ground		Ground				
			Term	deg.	Subterm	deg.	B_4 (K)	λ (K)	deg.
d^1	$\frac{1}{2}$	2	^{2}D	10	$^2T_{2g}$	6	+200	+220	4
d^2	1	3	^{3}F	21	$^3T_{1g}$	9	-40	+150	2
d^3	$\frac{3}{2}$	3	^{4}F	28	$^4A_{2g}$	4	+40	+125	4
d^4	2	2	^{5}D	25	^5E_g	10	-200	+120	1
d^5	$\frac{5}{2}$	0	^{6}S	6	-	6	-	-	6
d^6	2	2	^{5}D	25	$^5T_{2g}$	15	+200	-140	3
d^7	$\frac{3}{2}$	3	^{4}F	28	$^4T_{1g}$	12	-40	-260	2
d^8	1	3	^{3}F	21	$^3A_{2g}$	3	+40	-480	3
d^9	$\frac{1}{2}$	2	^{2}D	10	^2E_g	4	-200	-1200	4
d^{10}	0	0	^{1}S	1	-	1	-	-	1

Table 1. Spin S and orbital L quantum numbers of the ground term for the highly-correlated $3d^n$ electronic systems with the total degeneracy in the LS space. The ground term and the degeneracy in the octahedral cubic crystal field with the respective values of the cubic CEF parameter B_4. Next, the spin-orbit coupling parameter λ and the degeneracy resultant from the spin-orbit coupling in the presence of the octahedral cubic CEF interactions. These values of B_4 and λ have been used for calculations of Fig. 1.

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 last term accounts for the influence of the magnetic field, the externally applied in the present case. g_s value is taken as 2.0023. The computations of the many-electron states of the $3d^n$ system have been performed by consideration of the Hamiltonian (2) in the $|LSL_ZS_Z\rangle$ base [21]. As a result of the diagonalization one obtains the energies of the (2L+1)·(2S+1) 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 B_{ext}.

Fig. 1 presents the calculated general overview of the CEF and spin-orbit effect on the Hund's rule term for the d^n systems. In figures b the splitting of the ground term by the octahedral cubic CEF interactions is shown for different number of n. Figures c show the splitting due to

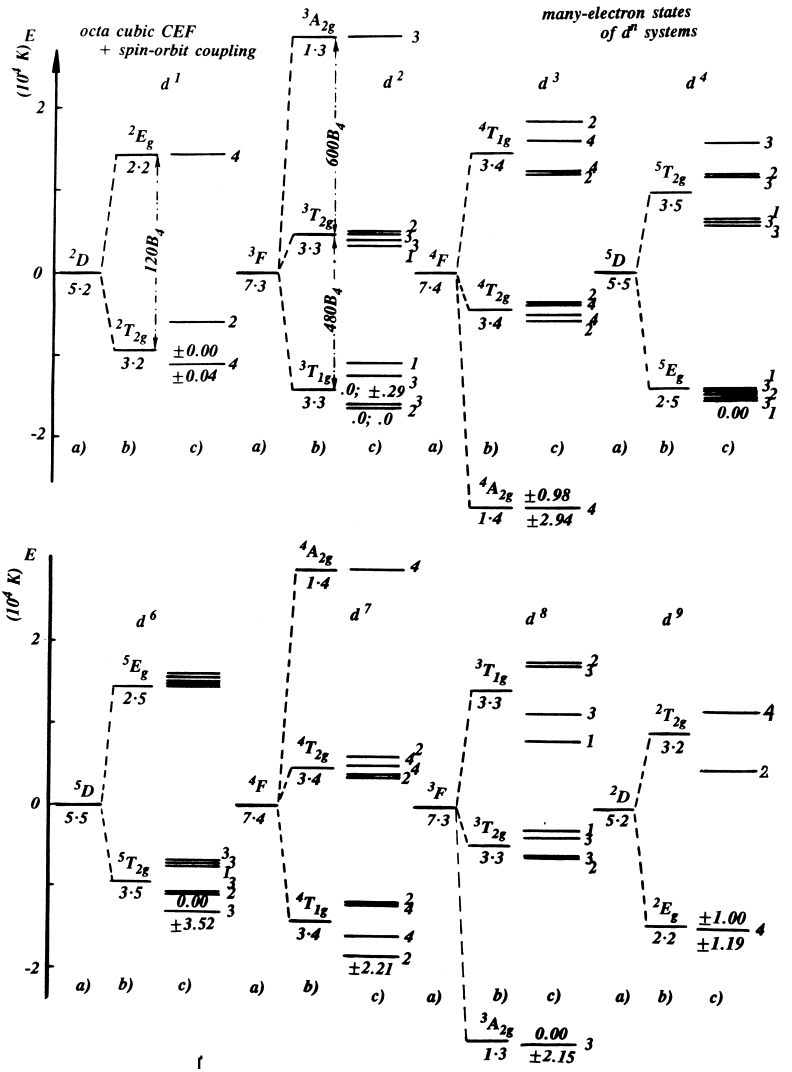

FIG. 1: The general overview of the splitting of the Hund's rules ground term of the 3d^n electronic systems by octahedral crystal-field interactions (b) and the spin-orbit coupling (c). Levels in (c) are labeled with degeneracies in the LS space whereas in (b) the degeneracy is shown by the orbital spin degeneracy multiplication. The spin-orbit splittings are drawn not in the energy scale that is relevant to CEF levels shown in figures b. On the lowest localized level the magnetic moment (in μ_B) is written. The shown states are many electron states of the whole system d^n. At zero temperature only the lowest state is occupied. The higher states become populated with the increasing temperature.

the spin-orbit interactions. The parameters used are collected in Table 1. They have been chosen in order to have the CEF splitting of about 2 eV in agreement with the quite frequent experimental observations of the $d-d$ excitations in the optically visible energy range [1–9].

Figure 1 is full of information. One can see the similarities, but also the differences, between the CEF effect and s-o interactions on, for instance, the ^{2}D and ^{5}D terms for the d^1 ($\lambda > 0$) and d^6 ($\lambda < 0$) terms. The particle-hole symmetry can be studied for the d^n/d^{10-n} systems. We mention here only a few most important points.

1. For $3d$ ions there are only D and F terms as L can be only 2 and 3. The spin degeneracy depends on the number of electrons involved. The total degeneracy as large as 15 can be realized.

2. The pairs d^1/d^6, d^2/d^7, d^3/d^8 and d^4/d^9 of systems have the same orbital ground state. The spin-orbit effect is, however, entirely different due to different values of S, the reversal of the s-o constant λ and the transformation of non-Kramers ions into Kramers ions (even $\Longleftrightarrow$ odd number of d electrons).

3. The adoption or the loss of the one electron draws the full reconstruction of the fine electronic structure.

4. The spin-orbit coupling removes largely the degeneracy in all cases apart of the spin-only d^5 system, see Table 1 as well as Fig.1. In case of the d^4 system it yields a singlet ground state [18], but there are 10 closely lying levels.

5. The s-o coupling produces a fine electronic structure with excitations below 10 meV. These low-energy excitations can be detected by specific-heat experiments, for instance.

6. There is splitting of the ^5E_g cubic state [22], the fact that is of particular importance for the d^4 system as it becomes the ground state.

7. There is also the extra second-order splitting of the T_{2g} originated states in comparison to the perturbation method.

8. The ground-state magnetic moment, shown in Fig.1, substantially differs from the spin-only value. A very small moment has been revealed for the d^1, d^2 and d^4 systems. In all cases it differs much from an integer value.

9. The states shown are **many-electron states** of the whole $3d^n$ system. At **0 K only the lowest state is occupied. Higher excited states become populated with increasing temperature.**

10. The population of higher states manifests in temperature variation of electronic and magnetic properties like the specific heat and the magnetic susceptibility. Detailed calculations of χ(T) have been presented already for the d^6 system.

From physical point of view the most important seems to be the point 9 and 3. It shows the fundamental difference with the very often recalled one-electron picture with subsequent occupation of the t_{2g} and e_g states. In the many-electron picture at 0 K only the lowest state is occupied, i.e. one can say that all n electrons as the whole d^n system are put on the lowest level. In the one-electron picture electrons are put subsequently [6–13] on the 10 CEF levels without the reconstruction of the electronic structure in contrast to the present results, see point 3. The evaluation of the fine electronic structure, with the given energy and magnetic characteristics, allows for the calculation of temperature dependence of many physical properties like specific heat or the paramagnetic susceptibility similarly to the description used for the rare-earth compounds [23].

According to us this many-electron picture is widely confirmed though the one-electron picture is often recalled in discussion of 3*d*-ion compounds [6–13]. Here we mention EPR experiments, where -provided the experiment is performed at, at least, helium temperature - the ground-level properties can be revealed. For the Ni^{2+} ion, where the d^8 system is realized, the spectroscopic g-value of 2.15-2.35 ([17] AB p. 449; it corresponds to the same value of the magnetic moment in μ_B as S=1) is commonly found for the octahedral interstice. It is close to the value of 2.15 shown in Fig. 1 for the d^8 system. Larger values can be obtained by slightly different values for B_4, λ and by a lattice distortion. Also a value of 3.52 calculated for the $3d^6$ system seems to have been seen in Fe^{2+} impurities in MgO (the octahedral interstice), where value of 3.43 has been reported ([17] AB p. 444). In ref. [14] the g-factor experimentally observed for the Cu^{2+} ions has been calculated reaching very good agreement.

The present calculations are the exact calculations. Up to now the s-o coupling, if discussed, has been taken into account by the perturbation method, with the first-order effect in λ.

In conclusion, large influence of the spin-orbit coupling on the localized states of the d^n system has been revealed. The present

approach treats n d electrons as the **whole highly-correlated d^n system.** The s-o coupling, in combination with crystal-field interactions, produces the fine electronic structure with a large number of low-energy, < 10 meV, localized states. These states affect enormously electronic and magnetic properties of 3d-ion compounds at low- and room- temperature regions. The present calculations prove that the weaker s-o coupling the smaller energy region for the fine low-energy electronic structure and the lower temperatures with the occurrence of anomalies in physical properties. On basis of these studies it is inferred that the relativistic s-o effect and the multiplet structure on individual atoms are indispensable for the proper evaluation of the electronic structure of paramagnetic 3d ions. It is believed that the found fine local electronic structure is essential for the low-and room-temperature properties of 3d-ion compounds and have to be incorporated in modern band-structure calculations.

Note added during the referee process. The presently-published calculations of properties of 3d-ion compounds do not take the s-o coupling into account, e.g. Phys. Rev. B **54** (1996) 5309 on p. 5315 right column, line 12 bottom; Phys. Rev. B **53** (1996) 7158 on p.7164, left column, line 16 bottom. Those authors say that in their approaches the s-o effect is small. Our results are completely different. Arguments of the referee, that "the results presented do not appear to be useful, in the sense that they might explain phenomena in particular 3d systems that have not been understood" and that "the effects predicted occur at small energy and no case has been made by the author that they influence importantly the physical properties of a know system" are incorrect. These results e.g. explain non-integer values of the 3d magnetic moment, enable evaluation of the orbital moment and enable calculation of temperature dependence of the paramagnetic susceptibility that turns out to be very anomalous. All of these outcomes are in agreement with experimental results. The energy splitting of, say, the $^3T_{1g}$ state for the d^2 system amounts to 3λ. It means that in the energy window of 450 K (40 meV) 9 levels are expected. Thus we expect that a d^2 system will show anomalies at low and room-temperature regions. These temperature regions are of great importance for the solid-state physics.

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intra-atomic spin-orbit coupling. Part of this paper has been presented at VII Polish Conf. on High-Tc superconductivity in Miedzyzdroje 1-3.09.1997 (Poland, organized by H. Szymczak *et al.*) but also did not get appreciation of the Scientific Committee chaired by H. Szymczak. This paper has been distributed as the Report of Center for Solid State Physics CSSP-4/97.

[1] D. D. Sarma, N. Shanthi, S. R. Barman, N. Hamada, H. Sawada, and K. Terakura, Phys. Rev. Lett. **75**, 1126 (1995).
[2] E. Muller-Hartmann and E. Dagotto, Phys. Rev. B **54**, R6819 (1996).
[3] D. I. Khomskii and G. A. Sawatzky, Solid State Commun. **102**, 87 (1997).
[4] J. Hugel and M. Kamal, Solid State Commun. **100**, 457 (1996).
[5] P. Mahadevan, N. Shanthi, and D. D. Sarma, J. Phys. Condens. Matter **9**, 3129 (1997).
[6] P. M. Raccah and J. B. Goodenough, Phys. Rev. **155**, 932 (1967).
[7] M. A. Senaris-Rodriguez and J. B. Goodenough, J. Solid Phys. Chem. **116**, 224 (1995); **118**, 323 (1995).
[8] J. B. Goodenough, in: Magnetism and the Chemical Bond, Interscience, New York, 1963; J. B. Goodenough and Longo, in: Landolt-Bornstein, 1970, vol. III/4a.
[9] J. M. D. Coey, M. Viret, and L. Ranno, Phys. Rev. Lett. **75**, 3910 (1995).
[10] M. Abbate, R. Potze, G. A. Sawatzky, and A. Fujimori, Phys. Rev. B **49**, 7210 (1994).
[11] M. Itoh, M. Sugahara, I. Natori and K. Motoya, J. Phys. Soc. Jap. **64** 3967 (1995).
[12] E. Iguchi, K. Ueda, and W. H. Jung, Phys. Rev. B **54**, 17431 (1996).
[13] K. Terakura, T. Oguchi, A. R. Williams, and J. Kübler, Phys. Rev. B **30**, 4734 (1984).
[14] R. J. Radwanski, Molecular Physics Reports **15/16**, 113 (1997).
[15] P. Dufek, P. Blaha, V. Sliwko, and K. H. Schwarz, Phys. Rev. B **49**, 10170 (1994).
[16] Z.-X. Shen, R. S. List, D. S. Dessau, B. O. Wells, O. Jepsen, A. J. Arko, R. Barlett, C. K. Shin, F. Parmigiani, J. C. Huang, and P. A. P. Lindberg, Phys. Rev. B **44**, 3604 (1991).
[17] A. Abragam and B. Bleaney, in: *Electron Paramagnetic Resonance of Transition Ions*, (Clarendon Press, Oxford) 1970; B. N. Figgis, in: *Introduction to Ligand Fields* (Interscience, New York) 1966; C. J. Ballhausen, in: *Ligand Field Theory* (McGraw, New York) 1962.
[18] R. J. Radwanski, Report of Center of Solid State Physics, CSSP-7/96, to be published.
[19] In ref. 11 authors have tried to consider the s-o coupling for the d^6 system, but in a very invalid approximate way within an effective Hamiltonian with L'=1 instead of L=2.

[20] R. J. Radwanski - Report of Center of Solid State Physics, CSSP-8/96, to be published.
[21] the computer program is available on the written request to the author.
[22] The splitting of the ^5E_g state is a surprising finding - the author has in hands a statement of a referee of one of the most prestigious physical journal, that ^5E_g state is not affected by the s-o coupling [evidence for this statement see Acta Physica **9-10**, 27 (2007)]. It is true for the ^2E_g state but not for the ^5E_g state.
[23] R. J. Radwanski, N. H. Kim-Ngan, F. E. Kayzel, J. J. M. Franse, D. Gignoux, D. Schmitt, and F. Y. Zhang, J. Phys. Condens. Matter **4**, 8859 (1992).