Electronic structure of mixed valence transition metal oxides

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I. INTRODUCTION

The character of the charge carriers in oxides of transition metals belongs to the most formidable problems of the solid state physics. In these thesis the attention is focused on a particular, yet broad and important class of these compounds - mixed valence oxides of the $3d$ transition metals. Traditionally oxides were considered to be ionic compounds, in which the oxygen ions have fully occupied $2p$ states, corresponding thus to the valence state O^{2-}. In many cases the valence of the cations was then unambiguously determined by the requirement of the charge neutrality, so in FeO the iron valence is 2+, while it is 3+ in the hematite Fe_2O_3. The mixed valence occurs when such simple calculation results in a nonintegral number, an important example being magnetite Fe_3O_4. Frequently the mixed valence is induced by the substitution - in a 'parent' compound the valence of all kinds of ions is integral and it is dictated by the requirement of the charge neutrality and the stable valence state of cations. If, however, a substitution is introduced with a stable valence different from the one of a substituted ion, the result is an oxide with a mixed valence. Typical example is provided by the mixed valence manganite perovskites $R_{1-x}M_xMnO_3$ where R is trivalent rare-earth ion (R=La, Pr, Nd ...) and M is the divalent alkaline-earth (M=Ca, Sr, Ba). Simple calculation shows that the valence v_{Mn} of the manganese increases linearly with the content of M: $v_{Mn} = 3 + x$ and, writing the valences explicitly, we get $R^{3+}_x M^{2+}_{1-x} Mn^{3+}_{1-x} Mn^{4+}_x O^{2-}_3$. For small x the electron holes that are predominantly localized on the cations thus appear in the system.

Soon after the discovery of the high temperature superconductors it was recognized that the situation is more complex, however. In these layered copper oxides the extra electron holes are localized not on the copper, but on the oxygen so e.g. the valence state of $La_{2-x}Sr_xCuO_4$ may be written as $La^{3+}_{2-x}Sr^{2+}_x Cu^{2+} O^{2-}_{4-x} O^{1-}_x$ rather than $La^{3+}_{2-x}Sr^{2+}_x Cu^{2+}_{1-x} Cu^{3+}_x O^{2-}_4$. Accordingly the parent compounds are classified as the 'Mott-Hubbard' insulators (the electron holes introduced by doping are localized on the cations) or 'charge-transfer' insulators (the electron holes introduced by doping are localized on the oxygen).

Apart from the clasification of the parent compound a number of difficult questions arises, perhaps the most basic one is whether the charge carriers are localized or itinerant. Other problems concern the long-range ordering of the charges introduced by the substitution (charge ordering), ordering of the orbital states (orbital ordering), the phase separation etc.

During my carrier as a solid state theorist I repeatedly tried to understand the physics of the mixed valence transition metal oxides. Number of results was obtained in a close cooperation with the experimentalists, at first using the electron paramagnetic resonance, then switching to the nuclear magnetic resonance in the magnetically ordered compounds. These results are described in the next part and they are arranged according to the crystal structure of the oxides studied. About twenty years ago I began to be interested in the $ab-initio$ calculation of the electronic structure of magnetic systems. Because of the complexity of the mixed valence oxides *ab-initio* calculation of their electronic structure became feasible only recently and we discuss them in the part III.

II. GARNETS

Garnets $c_3a_2d_3O_{12}$ have a cubic crystal structure, the cations occupy three different sublattices: dodecahedral (c), octahedral (a) and tetrahedral (d). Tetrahedral sites are tetragonally distorted with the S_4 axis parallel to one of the cubic edges, octahedral sites are distorted trigonally with the C_3 axis parallel to one of the cube diagonals.

A. $\mathbf{NaCa_2Mg_2V_3O_{12}}$

In this garnet the monovalent Na^{1+} and divalent Ca^{2+} ions are distributed randomly in the c sublattice, Mg^{2+} occupy the a sublattice and V^{5+} ions enter the sublattice d. All these ions have filled electron shells (electron configuration of V^{5+} is $3d^0$) and consequently the system is nonmagnetic. However, the real compounds exhibit a small nonstoichiometry - either there exist oxygen vacancies or/and Ca:Na ratio is slightly larger than two. As a consequence small part of the vanadium ions is tetravalent. V^{4+} ion represents an extra electron that, at least in principle, can move over the tetrahedral sites. The electron paramagnetic resonance is a convenient tool to study the V^{4+} ion and we published a series of papers on this subject [1–3]. The spectrum taken at 77 K in an external magnetic field along the [001] direction exhibits two groups of lines: the first one ('parallel spectrum') corresponds to the V^{4+} ion on those d sites that have the local S_4 axis along the magnetic field $\vec{B}$, while for the second one ('perpendicular' spectrum) $S_4 \perp \vec{B}$. Vanadium has a nuclear spin $I = 7/2$ and as a consequence each group consists of eight lines corresponding to the allowed transitions $(m_s = -1/2, m_I) \rightarrow (m_s = +1/2, m_I)$; $m_I = -7/2, -5/2... + 7/2$.

The form of the spectrum is unusual - the intensity of lines depends strongly on m_I and for the perpendicular spectrum it even resembles a damped oscilator. Such form is very similar to the spectrum of the V^{4+} ion in the liquids, where it is associated with the tumbling motion [4]. It was thus tempting to associate the anomaly with the motion of an electron over the d sublattice - it would be the first direct experimental evidence for a 'small polaron' - a moving electron associated with the lattice distortion. A detailed investigation revealed, however, that the origin of the anomaly is more prosaic. The extra electrons ($\equiv$ V^{4+} ions) are immobile and the dependence of the amplitude of lines on m_I is well explained as a consequence of the fluctuation of the crystal potential. Evidently due to the random distribution of Na^{1+} and Ca^{2+} ions in the c sublattice each d site experiences a different potential. The electrons are likely to be trapped in deep potential wells formed by six Ca^{2+} nearest c neighbors. The fluctuation of the potential is then associated with a random distribution of Na^{1+} and Ca^{2+} on the second nearest and more distant c sites. We presented both the phenomenological description and a microscopic model in [2]. The explanation was then corroborated by measuring EPR of the V^{4+} impurities on the d sites of garnets with the sublattices occupied by a single type of ion only [3].

B. Yttrium iron garnet doped by silicon

Yttrium iron garnet $Y_3Fe_5O_{12}$ (YIG) is a prototype of a ferrimagnetic garnet. In the stoichiometric compound the c sublattice is occupied by the Y^{3+} ions, while a and d sites are filled by the Fe^{3+} ions. Doping YIG by cations which are divalent (e.g. Ca^{2+}, Pb^{2+} on the c sites) or tetravalent (e.g. Si^{4+}, Ge^{4+} on the d sites) leads to a mixed valence compound. While it is still a matter of discussion whether the extra negative charge of the M^{2+} impurities is compensated by the increased valence of iron ($Fe^{3+} \rightarrow Fe^{4+}$) or by creating the electron hole on oxygen ($O^{2-} \rightarrow O^{1-}$), it is generally accepted that the tetravalent d site impurities are compensated by the extra electrons (Fe^{2+} ions) on the octahedral (a) sublattice. Based on the photo-induced magnetic effects it was concluded that the electrons are immobile at low temperatures, while they can hop between the a sites above ≈120 K (see [5] for a survey).

Convenient and sensitive tool to study the defects and impurities in ferrites proved to be the nuclear magnetic resonance. As we demonstrated on numerous examples (see [6] for a review) the presence of an impurity leads to a modification of the hyperfine field on the nuclei of neighboring Fe ions. For the nearest neighbors, and often also for 2nd nearest and even more distant neighbors, the modification is large enough to give rise to a satellite lines in the NMR spectrum. From the structure and intensity of the satellites conclusion can be made concerning the concentration, location and other properties of the impurity. The sensitivity of the method is remarkable - it allows to study the defects having the concentration as low as 0.01% [6].

In a project 'Charge compensation and charge carriers in magnetic oxides' supported by the Grant Agency of the Czech Republic we proposed to study the charge carriers in YIG:Si by analysing the satellites in the NMR spectra associated with the Fe^{2+} impurities (i.e. observing the NMR on Fe^{3+} ions which are neighbors of the Fe^{2+} impurity - to observe NMR directly on the Fe^{2+} impurity is difficult or even impossible due to the short relaxation time). We used the high quality single crystals in which the presence of Fe^{2+} ions was detected by the chemical analysis, by the decrease of the electrical resistivity (compared to stoichiometric YIG by several orders of magnitude) and also by the FMR and NMR [7] relaxation. Despite repeated and careful measurements and despite the fact that the concentration of the Fe^{2+} was much higher than the sensitivity of the method, no satellites which could be attributed to Fe^{2+} impurities were found. I believe that this has a simple explanation - the absence of the satellites may be understood if the extra electron represents an 'extended' defect, having probability to be found on several, possibly many, a sites, even if it is immobile. This, however, contradicts the common viewpoint that the charge carriers in YIG:Si are small polarons. Because of its negative nature it is difficult to prove the above idea and thus we never published it. Nevertheless an analogous dichotomy between Fe^{2+} ion localized on a single site vs dispersed over several sites occurs in the magnetite, where using NMR we were able to confirm the later picture (see the next part). Also our very recent calculation of the electronic structure of the mixed valence (SrLa) hexaferrite points to possible delocalization of the extra electron (see section V F).

III. MAGNETITE

Magnetite Fe_3O_4 is the oldest known magnet, the physics of which was studied by perhaps all possible means. It has spinel crystal structure, in which the tetrahedral (A) sublattice is filled by the Fe^{3+} ions while the formal valence of iron on the B sublattice is 2.5; $Fe^{3+}(A)[Fe^{3+}Fe^{2+}](B)O_4$ is thus a mixed valence compound. In distinction to the garnets discussed above, the mixed valence is not associated with the impurities and Fe_3O_4 possesses the full translation symmetry. At $T_V \approx$ 118-125 K magnetite undergoes a Verwey transition which was interpreted as an ordering of the ferric and ferrous ions on the B sublattice. Below T_V the electrical conductivity drops by three orders of magnitude and the crystal symmetry is lowered from cubic to monoclinic.

We measured and analysed the temperature dependence of the ^{57}Fe NMR in the high quality single crystals of magnetite [8, 9]. Two important results were obtained - first we showed that the NMR spectra below T_V are compatible with the Cc symmetry. This symmetry was found by the X-ray, neutron and electron-diffraction experiments, but earlier NMR measurements by Mizoguchi [10] were seemingly in conflict with the Cc symmetry. Second, and more significant, the temperature dependence of the NMR frequencies and relaxation rates of the 16 magnetically inequivalent B-site irons is similar and these ions definitely can not be divided in two distinct groups, the first consisting of eight Fe^{3+}, the second of eight Fe^{2+} ions. The most probable explanation is the charge density wave on the B sublattice with the charges on individual sites differing much less than a charge of an electron. This conclusion is supported by our analysis of the mean Fe(B)-oxygen distances [8], to which end we used the magnetite crystal structure as determined by neutrons [11].

Of interest are also the exchange interactions in the cubic phase of the magnetite - inbetween the magnetic oxides it has one of the highest Curie temperatures and it has large potential for the application in the spin electronics. Undoubtely the dominating interaction is the superexchange which leads to an antiparallel ordering of the Fe(A) and Fe(B) magnetic moments. The Fe(A)-Fe(A) interaction is also dominated by an antiferromagnetic exchange, while the leading Fe(B)-Fe(B) interaction is ferromagnetic double exchange. To treat double exchange and superexchange on the same footing is a difficult task, we described a possible approach that uses the mean field approximation in [12] and applied it to the magnetite.

Our recent $ab-initio$ calculations of the electronic structure of magnetite are described in section five, subsection E.

IV. MANGANITES

In this section the mixed valence oxides with the perovskite structure and the composition $R_{1-x}M_xMnO_3$ where R is the trivalent rare-earth ion (R=La, Pr, Nd ...) and M is the divalent alkaline-earth (M=Ca, Sr, Ba) or monovalent Na^{1+} are considered. During the last decade they were in the focus of attention because of the 'colossal' magnetoresistance these compounds exhibit in vicinity of the Curie temperature in samples with $\approx 30\%$ content of Mn^{4+}. The phase diagrams of manganites is exceptionally rich - depending on temperature and Mn^{4+} content the compounds may be para- antiferro- or ferromagnetic, for some composition a spin glas state is also found. The conductivity proceeds via thermally activated hoping or it could be metallic-like. In addition for some compositions the charge and/or orbital order exists in the Mn sublattice. The crystal structure may accomodate relatively large local distortions, including the Jahn-Teller distortions around the Mn^{3+} ions.

The phase transition may be of the first or second order and often two or even more magnetic phases coexist. The origin of the colossal magnetoresistence is now well understood - ferromagnetic order of the manganese spins make the transfer of the charge easier and it results in a gain in the electron kinetic energy. The ordering is thus connected with a sudden drop of the resistence. The onset of the ordering is influenced by an external magnetic field and thus a large magnetoresistance appears. The number of problems in manganites still remains open - to the most important belongs the nature of the charge carriers in the metallic-like state (band conduction vs polaron hopping), the coexistence of different magnetic states, a connection between the composition and the Curie temperature, character of the phase transition etc. Nuclear magnetic resonance is a suitable tool to address these problems as it probes the manganese ions locally and a wealth of information may be obtained concerning the local magnetic fields and the nuclear spin dynamics. The hyperfine field B_{hf} on the nuclei of the Mn^{4+} ion is smaller by $\approx$ 10 T than B_{hf} of the Mn^{3+}. The hopping $Mn^{4+} \rightleftarrows Mn^{3+}$ results in a 'motionally narrowed' line, providing that the hopping time is shorter compared to the characteristic time of the NMR experiment ($\tau_{NMR} \approx 3.10^{-9}$s). B_{hf} of the motionally narrowed line lies between B_{hf} Mn^{4+} and B_{hf} Mn^{3+} which fact allowed us to follow the delocalization of the electron hole as the temperature is raised by detecting the ^{55}Mn NMR in $Pr_{1-x}Ba_xMnO_3$ [13, 14].

We have found that in the metallic-like manganites the temperature dependence of the ^{55}Mn nuclear relaxation rate is exponential [15]. This rules out the possibility of a band-like, halfmetallic character of the charge carriers (in halfmetals at 0 K all the charge carriers have the same direction of the spin) and we suggested that the charge carriers may be described as spin polarons. The combination of the NMR and dc magnetization measurements is particularly useful for the determination of the character of the magnetic phase transition. We thus showed that the transition is of second order in $La_xNa_{1-x}MnO_3$ system ($x = 0.1, 0.15, 0.2$, corresponding T_C=266, 315, 325 K) [16]. On the other hand in $Pr_{0.7}Ba_{0.3}MnO_3$ (T_C=175 K) and $Pr_{0.7}Ca_{0.15}Sr_{0.15}MnO_3$ (T_C=180 K) [13] we found that the transition is of the first order and the volume of the ferromagnetic phase decreases continuously for $T \rightarrow T_C$. In [17] the different character of the phase transition in different manganites was explained on the basis of the mean field theory of double exchange taking into account spontaneous magnetostriction.

In a number of our papers the problem of the coexistence of different magnetic phases in manganites is addressed. Of particular interest is the coexistence of two different ferromagnetic phases that we showed is rather general feature of the ferromagnetic manganites [18, 19]. In an electron-doped system $Ca_{1-x}Pr_xMnO_3$ [20] the antiferromagnetism and ferromagnetism coexist for $x \leq 0.1$. In a recent paper [22] the ferromagnetic, but insulating manganites were studied and the coexistence of insulating and metallic regions possessing different NMR spectra and nuclear-spin dynamics was found. Very interesting situation occurs in $La_{1-x}Sr_xMnO_3$ for a small concentration of Sr $x = 0.16$. System is ferromagnetic, exhibiting a metal-insulator transition at ≈ 160 K. NMR on ^{55}Mn nuclei revealed that at low temperatures the charge density wave exists [22]. A brief survey of our results on manganites obtained by NMR is given in [23].

V. *AB-INITIO* CALCULATIONS

The explanation of virtually all the results described above was based on the 'effective hamiltonian' method. In this method the relevant degrees of freedom of the system are first identified. Next the effective hamiltonian H_{eff} is constructed as a function of corresponding operators. The number of terms in H_{eff} is limited by symmetry, but usually it is too large and additional meaningful approximations are necessary. As a rule the parameters of H_{eff} were determined by fitting the calculated results to experiments. An example of H_{eff} is the spin hamiltonian, we used to explain the EPR results in the vanadium containing garnets [1–3]. The relevant operators are the electronic and nuclear spins of the V^{4+} ion and H_{eff} consists of the Zeeman and hyperfine interactions:

$$H_{eff} = \mu_B \vec{S}\hat{g}\vec{B} + \vec{I}\hat{A}\vec{S}, \tag{1}$$

where $\vec{B}$ is the external magnetic field, $\vec{S}, \vec{I}$ are electronic and nuclear spins, $\hat{g}, \hat{A}$ are the g-tensor and hyperfine coupling tensors that are determined by fitting the theory to EPR spectra.

In the magnetic systems the exchange interaction must be included in H_{eff}. Often it is necessary to incorporate also the orbital degree of freedom i.e. the crystal field and/or the anisotropy of the exchange. The effective hamiltonian approach certainly remains a valuable tool of theoretical solid state physics. It is based on an intuition, however, and, with increasing number of terms in H_{eff}, it is less and less manageable. It thus became apparent that this method should be suplemented or even replaced by a more fundamental approach. Such a possibility became realistic with an advance of the *ab-initio* calculation of the electronic structure of crystals. Ideally no free parameters are needed, the only information being the atomic number of the constituing atoms and the geometry of the crystal structure. Most of the calculations is based on the density functional theory (DFT) employing the local spin density approximation (LSDA) or generalized gradient approximation (GGA). One of the most robust implementation of the DFT-based electronic structure calculations is represented by the Full Potential Linearized Augmented Plane Wave (FPLAPW) method [24]. There exist several FPLAPW program packages, the one used probably most frequently (several hundreds of users all over the world) is WIEN that was developed on the Vienna Technical University in the group of K. Schwarz. The present release WIEN2k [25] uses a sophisticated dual basis and beside the electron structure calculation it allows also to determine a number of physical quantities (hyperfine field, electric field gradient, elastic constants, optical and phonon spectra etc.).

We were inbetween the first WIEN users and we collaborated actively on its development. When applied to the magnetic oxides and in general to systems with a strong electron correlation we encountered several difficulties that are briefly described below.

A. Electron correlation

LSDA and GGA proved to be immensely valuable for understanding of the magnetic properties of solids. Yet there are well documented shortcomings when they are applied to the systems with a strong electron correlation. The gap in the energy spectrum is underestimated and in many cases (particularly in magnetic oxides) the compounds are often predicted to be metallic in a clear contradiction to the experimentally found insulating state. Partial remedy of this unsatisfactory situation is represented by the so called LDA+U method. In this method one begins by selecting the states most influenced by the strong correlation (usually the $3d$ states of the iron group atoms or $4f$ states of the rare-earth). Next the exchange-correlation energy corresponding to this subspace, that is already contained in the energy functional ('double counting' term), is subtracted. Finally a Hartree-Fock-like exchange correlation energy is added. The correlation is taking into account by screening the coulomb parameter U and exchange parameter J on which the added term depends. The value of the gap increases and in insulators where the metallic state was predicted the desired insulating state is obtained, but there is price to pay:

- The method is no longer truly *a*b-initio as it depends on the parameters U and J. These might either be calculated using the restricted DFT or they may be taken from an experiment. Rather than relying on their particular values, reasonable upper and lower limits should be considered.

- The method is ambiguous as several variants of the LDA+U method that differ in form of the 'double counting' term exist.

- Often there are several solutions of the selfconsistent procedure and it is not straightforward to decide which of them is the true one.

Despite these reservation the LDA+U method proved to be a useful tool when studying the magnetic oxides, but a care is neede when applying it. We implemented in the WIEN package the rotationally invariant form of the LDA+U method [26] with an option to choose between several different versions.

B. Disordered systems, impurities

The mixed valence in the magnetic oxides is often connected with the presence of two kinds of ions in the same sublattice (e.g. Na^+, Ca^{2+} in the dodecahedral sublattice of the $NaCa_2V_3O_{12}$ garnet). The distribution of these ions is presumably random and thus the system does not possess the translational symmetry. To model this situation three different approaches may be used:

- The coherent potential approximation (CPA). This method is not implemented in the WIEN code, note, however that CPA is implmented in the Full Potential Localized Orbitals package that became available recently [27].
- Supercells. The unit cell of the crystal is enlarged so that the sites of sublattice in question may be occupied by the two kinds of ions. To model the disorder large enough supercells are needed.
- Virtual atoms [28]. In the FPLAPW method the electron states are divided in two groups: core states that are completely contained within the nonoverlaping atomic spheres and valence states that participate in the chemical bonding. Consider typical mixed valence oxide $(La^{3+}_{1-x}Ca^{2+}_{x})MnO_3$, where we emphasized that the valence of both lanthanum and calcium is stable. For x=0 all manganese ions are trivalent and number of the valence electrons per formula unit is integer. Introducing the calcium removes x valence electron per formula unit. In the virtual atom approach the number of atoms in the unit cell and the symmetry are kept unchanged. To compensate for the positive charge of the x electron holes (i.e. to keep the system neutral) La is treated as the 'virtual atom' with a fractional atomic number 57-x. Note that this method is only useful when we are not concerned with the La or Ca states. An alternative to the virtual atom approach is to add a homogeneous negative charge. In both methods any effect of the disorder is suppressed.

C. Complexity of system

The FPLAPW is a reliable and robust method that is, however, demanding on computer time and memory. At early ninetieth, when the first WIEN package was released the limit for a number N_A of the atoms in unit cell was between ten and twenty. With continuous improvement of the code and, especially thanks to the increased computer power, this limit increased by an order of magnitude so that at present $N_A \sim$ 100-200. Maximum N_A depends on the kind of atoms, transition metal compounds required larger memory and computer time. Also crystal symmetry is important - especially lack of the inversion center makes the calculation demanding as the complex instead of real eigenvalue problem must be solved. The mixed valence magnetic oxides are complicated compounds and until recently calculation of their electronic structure was beyond the reach of WIEN. As documented on several examples below this is no longer true.

D. $(\mathbf{Y}_{2-x}\mathbf{M}_x)\mathbf{BaNiO}_5$ (M=Ca, Sr)

This was the first mixed valence transition metal oxide which we considered [29]. The implementation of LDA+U method in the WIEN code was described, although a number of improvements and modifications was introduced since. For nonzero x the virtual atom method was used, but its validity was tested for x=0.5 by comparing the results with the supercell calculation.The dependence of the electronic structure on the parameter U was studied in detail by varying U from zero to 8 eV (accepted value for the nickel monoxide). The calculated oxygen K edge X-ray absorption spectra were found to be in a good agreement with the experiment.

E. Magnetite

The calculation of the electronic structure of magnetite in the cubic symmetry (temperature above the Verwey transition) is relatively simple as the unit cell comprises easily manaegable fourteen atoms. We calculated the magnetic moments and magneto-optical Kerr spectra using the LDA+U method [31]. In a recent paper [32] a self-interaction corrected method of Lundin and Eriksson [30] was applied to calculate the contribution of the core electrons of iron ions to the contact hyperfine field.

The calculations for the low symmetry Cc symmetry ($T < T_V$) are still outside the reach of the WIEN package. However, recent X-ray synchrotron diffraction study [34] showed that the crystal structure can be refined using the monoclinic cell with an additional orthorhombic

Pmca pseudosymmetry constraint. The simplified unit cell comprises eight Fe_3O_4 molecules and we used it to study the possibility of charge ordering [33]. For the first time the coulomb parameter U was calculated within the FPLAPW method. Using the calculated U we obtained a charge ordering along the c-axis in the monoclinic structure of Fe_3O_4 that is in very good agreement with the experiment [34].

F. SrLa hexaferrite

M-type hexaferrites $MFe_{12}O_{19}$ (M=Sr, Ba, Pb) are suitable and inexpensive materials for the hard magnets. At the same time these systems represent a unique possibility to study iron in the same compound but in different ligand polyhedra, as Fe enters five different sublattices - three with octahedral, one with tetrahedral and one with bipyramidal coordination. Substitution of M^{2+} ion by a trivalent rare earth leads to a mixed valence compound. A natural question arises whether an extra electron that occurs because of the substitution exhibits a preference for some of the five Fe sublattice. This question is difficult to answer experimentally though, to explain the anisotropy in (SrLa) hexaferrite, it was assumed that the electron is localized on the $2a$ sites - one of the octahedral sublattices [35]. This hypothesis contradicts, however, recent NMR results on this system [36]. We performed a calculation of the electronic structure of this system using the GGA+U method [37] and the 'virtual atom' approach. The results support the NMR results - the extra electron is smeared over the interstitial region and the iron sublattices, the exception being the tetrahedral iron sites that remain intact by the substitution.

VI. CONCLUSIONS AND OUTLOOK

I believe that the results described above show convincingly how diverse and exciting is the physics of the mixed valence transition metal oxides. In particular we showed that the charge carriers

- are localized in $NaCa_2Mg_2V_3O12$ garnet,
- behave like spin-polarons in metallic-like manganites,
- are likely to represent 'extended defects' in yttrium iron garnet and (SrLa) hexaferrites.

Both the NMR in Fe_3O_4 and the $ab-initio$ calculations points to the fact that the difference of charge between 'bivalent' and 'trivalent' iron (or tri- and tetravalent Mn in manganites) is much smaller than its nominal value.

Because of their great practical application capacity and also because of the chalenge they represent for the solid state physics, these systems undoubtely will remain in the focus of interest also in the future. While the number of papers on manganites and cuprates seems to level out, there is an increased interest in cobaltites where another degree of freedom comes in play - the 'low', 'intermediate' and 'high' spin state of cobalt ions. Another interesting system represent ruthenates with a formidable interplay of superconductivity and magnetism.

The $ab-initio$ calculations are likely to play ever increasing role in understanding, modelling and predicting the properties of the compounds in question. New, better methods for the strongly correlated systems are being developed (e.g. the dynamical mean field theory), though the possibilities of 'generalized density functional theory' based methods (among them the LDA+U method) are still far from being exhausted. Evidently an important factor will also be rapidly increasing computer power.

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