Chemical Bonding Induced Large Local Magnetic Effects in Li₂[(Li_{1-x}Fe_x)N]

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Introduction

Substitution series of lithium nitridometalates $Li_2[(Li_{1-x}M_x)N]$ (*M* = Mn, Fe, Co, Ni, Cu) crystallize in the hexagonal α -Li₃N (i.e. Li₂[LiN]) structure type [1]. This structure consists of alternating planes (Li₂N) and (Li_{1-x} M_x) that are stacked along the hexagonal axis (Fig. 1). Atoms $(\text{Li}_{1-x}M_x)$ are linearly coordinated by two nitrogen atoms from the (Li₂N) plane above and below, respectively, forming linear one-dimensional chains ...-N-M-N-...-N-Li-N-... In detailed experimental studies [2] (see "Low-Valency Nitridonickelates") only for M = Ni an almost complete substitution according to $Li_2[MN]$ has been achieved until now. Within each substitution series the lattice parameters change linearly with the dopand concentration and the Li atoms at the substitution site are approximately statistically substituted, although some dependence on the detailed preparation conditions has been observed. Analysis of XAS spectra at the K thresholds of the transition metals M = Mn, Fe, Ni, Co, Cu have led to the assignment of a + 1 oxidation state [2], as expected.

In this contribution we will focus on the theoretical explanation of unexpected magnetic effects that were observed for the iron substitution series [3]:

1. Analysis of Mössbauer spectroscopic measurements on samples with small x_{Fe} ($x_{\text{Fe}} = 0.16, 0.21$) resulted in the following assignment of the lines: iron species A, whose lateral surroundings consist of six Li neighbours, shows a very large magnetic hyperfine field ($B_{hf} = 69.6(3)$ T). Successive replacement of Li neighbours by Fe leads to a reduction of the hyperfine field: if one atom is replaced (species B: 5 Li and 1 Fe neighbour) B_{hf} = 65.6(4) T and with two Fe neighbours (species C: 4 Li and 2 Fe neighbours) $B_{hf} = 59.1(15)$ T. Substitution of more than two Li neighbours by Fe results in a much lower hyperfine field and these different species (D - G) with similar B_{hf} cannot be further distinguished by means of the measurements. Comparison of the hyperfine fields ob-



Fig. 1: Part of the crystal structure of $Li_2[Li_{1-x}Fe_x)N]$.

tained for this phase with the well-known standard FeF₃ ($B_{hf} = 61.5$ T, long-time record holder for Fe hyperfine field) reveals that the value obtained for iron species A is distinctly larger. This is a surprising result as for Fe^{III} with octahedral high-spin d^5 configuration the maximum number of unpaired electrons possible for a transition metal is achieved.

2. Magnetic susceptibility measurements on the same samples revealed average magnetic moments per Fe atom being composition-dependent. Surprisingly the magnetization per mole is higher for the compound with the smaller Fe-content: average $\mu_{eff} = 5.8(3) \ \mu_B$ for x = 0.16 and average $\mu_{eff} = 4.4(3) \ \mu_B$ for x = 0.21. Thus, in both samples average μ_{eff} values are lying well above the spin-only values for high-spin d^7 Fe^I ($\mu_{eff} = 3.87 \ \mu_B$). Additionally, in field cooling measurements for x = 0.16 a large saturation magnetization $\mu_{sat} = 5.0(3) \ \mu_B$ has been observed.

In order to understand these surprising experimental results we have performed electronic structure calculations both on various levels of theory and for different structural models. In the following we will report some essential results.

Band Structure Calculations

First principles scalar-relativistic electronic structure calculations on the LSDA-level and beyond were performed using the full potential augmented plane wave plus local orbital (FP-APWLO) program package WIEN2k [4]. In order to account for the experimental effects (see above) two further improvements of the hamiltonian proved to be necessary: spin-orbit coupling was treated using the second variational approach and strong correlation effects had to be taken into account using the LDA+U method. Both methods are implemented in the WIEN2k code. LDA+U calculations are no longer truly first principles ones as they depend on the Hubbard parameter U and exchange parameter J, which are often taken from experiment. Additionally, it is necessary to select a priori the states on which LDA+U will be applied. In the present calculations LDA+U was applied to the 3dstates of iron. The parameters were taken to be those of U and J for Ni in NiO (subsequently referred to as U_2 , J_2), which can be regarded as an upper limit for our iron case. To find out how the values affect the results, all calculations were additionally performed with $U_1 = 1/2U_2$ and $J_1 = 1/2J_2$. The random distribution in the $(Li_{1-x}Fe_x)$ plane was simulated by the supercell method, where we used different supercell models to account for different local surroundings of Fe atoms. For our purpose we can confine the discussion to only one especially illustrative model with hexagonal symmetry (space group P6/mmm). It corresponds to a $0.3 \times$ 0.3×2 supercell of the original hexagonal cell, where the c axis was doubled in order to avoid pure -N-Fe-N- chains along [001] direction, which should exhibit antiferromagnetic coupling (due to 180° superexchange) not being observed. So, the chains along [001] had the sequence -N-Li-N-Fe-N-Li-N-. Inspired by the Mössbauer results, we choose to model that Fe species (species A, called Fe_A in the following), which has six lateral Li neighbours in the plane, and Fe species D (Fe_D), which has 3 Li and 3 Fe neighbours. With this model we will be able to explain both, the mechanisms governing the creation of the high hyperfine fields for species A - C and the reason for dependence of the local magnetic moments and hyperfine fields on the number of lateral Fe neighbours.



Fig. 2: Scalar relativistic LSDA total DOS for the $Li_2[Li_{1-x}Fe_x)N]$ superstructure model used.



Fig. 3: Scalar relativistic LSDA DOS for the minority spin channel of $Fe_A d$ states. Inset: modification of the $M_L = \pm 2$ local DOS by SO coupling (blue) and by LDA+SO+U (red), using $U_1 = 4$ eV and $J_1 = 0.5$ eV.

Results and Discussion

Total density of states (DOS), obtained from scalarrelativistic spinpolarized LSDA calculation, is displayed in Fig. 2. The most important feature is the very sharp DOS peak for the minority spin channel which is intersected by the Fermi energy (E_F). This peak originates from pure Fe_A $3d_{x^2-y^2}$, $3d_{xy}$ states (or, equivalently from $m_l = \pm 2$) as shown in Fig. 3. This may not have been expected as it corresponds to an unusual crystal field (CF) splitting (see



Fig. 4: Crystal field from standard ligand field arguments (left) and actual case (right), which produces an orbitally degenerate state for the $/d_{x^2-y^2} \pm d_{xy}$ 9doublet in the minority spin channel (see ellipse).

Fig. 4): an axial crystal field splits the five d orbital states into a doublet D1 [states (d_{xz}, d_{yz}) , or equivalently ($/m_l = 19 / -19$], a doublet D2 [states ($d_{x^2-v^2}$, d_{xy} , or(/29, /-29] and a singlet S (d_{z^2} , or /09. For the expected $3d^7$ configuration of Fe^I and in the weak CF scheme the majority spin electrons occupy all five orbital states while the distribution for the minority spin electrons depends on the energetic sequence of D1, D2 and S. A simple ligand field picture would predict that, because of the strongly antibonding Fe $3d_{z^2}$ -N $2p_z$ interactions, the singlet S possesses the highest energy. Our electronic structure calculations point to a different sequence. All 3d majority spin energy levels lie below $E_{\rm F}$ in accord with the weak CF scheme. However, in contrast to the ligand field prediction, for the minority spins the energetic sequence is S <D2 < D1 with D2 being intersected by $E_{\rm F}$ and D1 being unoccupied. Detailed analysis shows that the unusual energy scheme is a consequence of an onsite $3d_{z^2}$ -4s mixing [5] which creates covalent Fe_A-N s-bonding contributions. In other words: covalent bonding effects are responsible for the observed energetic orbital sequence. This chemical bonding effect has a dramatic influence on the local magnetic properties. If singlet S were the highest orbital, the resulting state of Fe^I would be orbitally non-degenerate. Instead, the actual situation we observe in our calculations is the occurrence of an orbitally degenerate ground state. Now a further chemical bonding effect comes into play: due to the lack of bonding partners in the (001) plane the Fe_A $(d_{x^2-y^2}, d_{xy})$ states are strongly localized and their peak at $E_{\rm F}$ is narrow (FWHM < 50 meV). Therefore, even the weak spin-orbit (SO) coupling for a 3d transition element is strong enough to split this peak by decreasing the energy of the $/m_l = 29$ state moving it partially below $E_{\rm F}$ and increasing the energy of the /-29 state, which becomes less

occupied (Fig. 3). As a consequence a large orbital momentum appears. The unquenched orbital momentum is usually accompanied by a large magnetocrystalline anisotropy. Using the force theorem [6] and the LSDA method we calculated the magnetocrystalline anisotropy and obtained $E_c - E_a =$ -10.5 meV/(unit cell), where E_c and E_a are the total energies for magnetization $\parallel c$ axis and $\parallel a$ axis, respectively. The hexagonal c axis therefore is the easy direction for magnetization and the anisotropy is very large for a 3d metal compound. All subsequent calculations with SO coupling were performed with $M \parallel c$. Within LDA+SO the projection of the orbital momentum onto the hexagonal axis yields $8l_z = 0.75$. The orbital momentum obtained so far is further enhanced by LDA+U, because the energy of states with larger (smaller) occupation is increased (decreased). The splitting of the D2 peak is shown in the inset of Fig. 3. This figure suggests that the resulting value of $8l_2$, 9 should be almost independent of the values of U and J, providing these are kept within reasonable limits. Indeed, increasing the value of U from $U_1 = 4$ eV to $U_2 =$ 8 eV increases $8l_2$ 9 from 1.37 to 1.45.

The hyperfine field on the Fe nuclei may be written as $H_{\rm hf} = H_{\rm cont} + H_{\rm orb} + H_{\rm dip} + H_{\rm latt}$, where $H_{\rm cont}$ is the Fermi contact term, $H_{\rm orb}$ and $H_{\rm dip}$ are contributions from the on-site interaction of the nuclear magnetic momentum with the electronic orbital and the spin momentum, respectively. H_{latt} corresponds to the interaction with other electronic magnetic moments and was neglected here. This is justified as the model is constructed for the case of strong dilution of magnetic centers. The results for Fe_A can be summarized as follows: H_{cont} (LDA+SO: 6 T, LDA+SO+ U_1 : 8 T; LDA+SO+ U_2 : 10 T) is always smaller than H_{orb} (LDA+SO: 52 T; LDA+SO+ U_1 : 96 T; LDA+SO+ U_2 : 102 T), so that the sign of the hyperfine field is negative. Recently, this prediction has been confirmed by magnetic field-dependent Mössbauer measurements performed by our coworkers [7]. The field on Fe_A (H_{hf} = 86 T or 88 T, for U_1 , U_2 , respectively) comes out larger in LDA+U than observed ($H_{\rm hf} = 69.6$ T). This is not surprising because the contact field on iron nuclei is underestimated in current DFT calculations [8] which seems to be mainly caused by self-interaction of the core states [9]. As H_{cont} and $H_{\rm orb}$ have opposite signs the total field comes out too high.



Fig. 5: DOS for minority spin channel $M_L = \pm 2$ projection. Comparing the effect of SO coupling (red) on the scalar relativistic LSDA curve (blue) for species Fe_A with Fe_D . Only for Fe_A SO coupling results in a distinct splitting.

Having answered the question about the microscopic mechanism responsible for the creation of the observed unexpected local magnetic effects in $Li_2[(Li_{1-x}Fe_x)N]$, we now turn to the mechanism responsible for their subsequent destruction on going from iron species A, B, C (all of which show high orbital momentum) to species D with low orbital momentum. For this purpose analysis of species Fe_D in our model is well suited. The electronic situation for Fe_D is similar to Fe_A and for both species the minority spin D2 doublet is intersected by $E_{\rm F}$. However for Fe_D the bonding interaction with the three lateral iron neighbours causes a significant broadening of the D2 doublet (Fig. 5). This chemical bonding effect leads to a significantly smaller orbital momentum $8l_7$ 9 upon switching on spin-orbit coupling $(8l_z 9 = 0.26)$ and strong intra-atomic correlation $(8l_2 9= 0.14, 0.06, \text{ for } U_1,$ U_2 , respectively).

In summary, we observed a peculiar new feature for a 3*d* metal compound: it is generally accepted that CF quenches a part or all of the orbital momentum of the free 3*d* ion. For cubic symmetry a maximum L = 1 is possible and a reduction of symmetry leads to further quenching of *L*. For the compound studied we showed that due to special chemical bonding effects, orbital moments of up to L = 2 may be observed in an axial CF. The chemical bonding features responsible for this behavior are *i*) the formation of covalent s-bonding Fe—N interactions, *ii*) bonding interactions between neighbouring iron atoms within the (001) plane and *iii*) the apparent inability of the Li⁺ species to act as a Lewis acid towards Fe⁺ ions.

All these chemical and physical effects could be realistically modelled within a relativistic LDA+U scheme. Theoretical and experimental work to understand the magnetic behavior for the other members of the series Li₂[(Li_{1-x} M_x)N] (M = Mn, Co, Ni, Cu) is currently in progress. For these compounds a serious discussion of chemical bonding in real space using the Electron Localization Function (ELF) is not feasible yet as strong correlation and relativistic effects play an important role. The inclusion of correlation effects into the methological framework of ELF is currently being developed (see "*Electron Localizability*") within the Chemical Bonding Group (see "*Chemical Bonding*").

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