Jahn-Teller-effect formation
of the non-magnetic ground state for the d$^8$ system*

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It is shown that the d$^8$ electron system occurring in the Ni$^{2+}$ ion can have
the non-magnetic ground state in the atomic scale formed by the Jahn-Teller
effect. The tetragonal/trigonal off-cubic lattice distortion for the octahedral
site causes the splitting of the triplet $^3A_2g$ into a singlet-doublet structure
with the non-magnetic singlet lying lower provided the intra-atomic spin-orbit
coupling is taken into account.

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The formation of the non-magnetic ground state of compounds containing Ni$^{2+}$ ions
is one of very challenging problem of the 3$d$ magnetism$^{1-4}$. Such the ground state is re-
ally intriguing because in most of the Ni$^{2+}$-ion containing compounds are magnetic (e.g.
NiO with Neel temperature of 525 K). Many of these compounds are known as Haldane-gap
compounds being extensively studied after Haldane conjecture$^5$ that one dimensional Heisen-
berg magnetic system with the integer spin should possess a nonmagnetic singlet ground
state separated by an energy gap from the excited magnetic triplet state. Compounds like
CsNiCl$_3$, organic compounds Ni(C$_2$H$_8$N$_2$)$_2$NO$_2$(ClO$_4$) and Ni(C$_2$H$_8$N$_2$)$_2$Ni(CN)$_4$ known as
NENP$^{2-3}$ and NENC$^4$ are regarded as being physical realization of the Haldane system with
S=1.

Experimentally, the non-magnetic ground state at lowest temperatures (4.2 K and lower) is inferred from an anomalous temperature dependence of the magnetic susceptibility that exhibits a pronounced rounded maximum, e.g. at 55 K for NENP\textsuperscript{2,3} with the vanishing low-temperature susceptibility. With the increase of temperature this anomalous dependence transforms to the conventional Curie-Weiss behaviour above, say 100 K, with the effective moment of 2.5-3.3 \( \mu_B \). Also a Schottky-like peak in the temperature dependence of the specific heat is often observed, e.g. at 2.5 K for NENC\textsuperscript{4}. These compounds are insulators and contain Ni ions in the divalent state i.e. Ni\textsuperscript{2+} ions. From crystallographic studies it is known that in many compounds the nearest ligand surrounding of the Ni cation is well approximated by the octahedron. A standard crystal-field theory\textsuperscript{6–8} yields for the octahedral site the orbital singlet ground state \( \text{^3A}_2g \). Forming the orbital singlet, the Ni\textsuperscript{2+} ion in the octahedral site is not expected to exhibit the Jahn-Teller (J-T) effect.

The aim of the present paper is to show that the non-magnetic state of the \( d^8 \) electronic system can be formed in the atomic scale by the lattice off-cubic distortion fulfilling the Jahn-Teller theorem provided the intra-atomic spin-orbit coupling is taken into account. The standard crystal-field (CEF) theory largely neglects the spin-orbit (s-o) coupling owing to its weakness in case of 3d ions. Accepting the weakness of the spin-orbit coupling we have treated the spin-orbit coupling on the same foot as crystal-field interactions, even of the low symmetry. It turns out that the \( d^8 \) system exhibits the Jahn-Teller effect, i.e. the spontaneous distortion driven by the lowering of the energy by the removal of the degeneracy of the ground state. It can be theoretically traced provided the spin-orbit coupling is taken into account. The \( d^8 \) system is expected to be realised in Ni\textsuperscript{2+} and Cu\textsuperscript{3+} ions. As we consider the octahedrally coordinated nickel ion the present discussion, in fact, concerns the properties of the NiO\textsubscript{6} complex in a macroscopic solid. Such the complex is very often found in realistic systems, where the macroscopic solid is built from the NiO\textsubscript{6} complexes by sharing the wall, the edge or the corner of the octahedra. For instance, the NaCl structure of the nickel monooxide NiO is built up from the edge-sharing NiO\textsubscript{6} octahedra.
We assume that eight d electrons of Ni$^{2+}$ and Cu$^{3+}$ ions in the unfilled 3d shell form the highly-correlated electron system 3$d^8$ as their orbital and spin movements are strongly correlated within the incomplete outer shell. According to Hund’s rules the $d^8$ system is described by $S=1$ and $L=3$. The resulting 21-fold degeneracy of the lowest term $^3F$ is split by cubic CEF interactions into two orbital triplets $^3T_{1,2}$ and the orbital singlet $^3A_2$, the latter being the ground state in case of the octahedral site (Ref. 6 p. 375; Ref. 8 p. 134). The energy positions of two triplets are usually well above 1.5-2.5 eV (2 eV = 23200K). For further consideration it is worth noting that the lowest orbital singlet is, in fact, the triplet in the $|LSL_ZS_Z⟩$ space that becomes physically relevant after involving the spin-orbit coupling. In this space the triplet can be split by a lattice off-cubic distortion into singlet and doublet.

The low-energy many-electron structure of the 3$d^8$ system, the splitting of the $^3F$ term and the formation of the singlet non-magnetic ground state, can be quantitatively traced by studying the single-ion-like Hamiltonian containing the electron-electron correlations, the crystal field, the spin-orbit and Zeeman interactions:

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

These interactions have been written in the decreasing-strength succession. The electron-electron correlations $H_{el-el}$ within the incomplete 3d shell are taken to be accounted for by the first two Hund’s rules. Accepting them to be realized in the reality we are in the LS space. Then considerations are confined to the $^3F$ term and the Hamiltonian 1 takes the tractable form

$$H'_d = B_4(O^0_4 + 5O^1_4) + \lambda L \cdot S + B^0_2O^0_2 + \mu_B(L + g_eS) \cdot B_{ext}(2).$$

The first term is the CEF Hamiltonian with the Stevens operators $O^m_n$ that depends on the orbital quantum numbers $L$ and its z-component $L_Z$. It is separated into the cubic part and an axial term written as $B^0_2O^0_2$ term. The cubic part is usually dominant due to the crystal structure with 6 nearest neighbours forming a distorted octahedron. The second
term accounts for the spin-orbit coupling; $\lambda$ is negative for the Ni$^{2+}$ ion. The last term accounts for the influence of the magnetic field, the externally applied in the present case. $g_e$ amounts to 2.0023. The calculations of the many-electron states of the 3$d^n$ system have been performed\(^9\) by the diagonalization of a $(2L+1) \cdot (2S+1)$ matrix associated with the Hamiltonian (2) considered in the $|LSL_Z S_Z\rangle$ base. As a result of the diagonalization the energies and the eigenvectors of the $(2L+1) \cdot (2S+1)$ states are obtained. The latter ones contain information about the magnetic properties.

The direct calculations of the Hamiltonian (2) have confirmed that the inclusion of the second-order CEF parameter $B_0^2$, appearing due to an axial distortion, causes the splitting of the lowest three-fold degenerated $^{3}A_{2g}$ state into the singlet and the doublet. Physically, the singlet-doublet sequence of states depends on the sign of the distortion, i.e. the elongation or the shrinkage (compression) of the octahedron along the cube diagonal. The kind of the distortion is related with the sign of the $B_0^2$ parameter, as shown in Fig. 1.

The performed calculations with the cubic parameter $B_4^4=+4.5$K, the spin-orbit coupling $\lambda=-480$K and the tetragonal-distortion parameter $B_2^0=+100$K reveal the singlet ground state and the singlet-doublet gap $\delta$ of $81$ K. The same value of the trigonal-distortion parameter $B_2^0$ causes the gap of $187$ K. The parameters used are physically relevant. For the $d^8$ system placed in the octahedral ligand surrounding $B_4$ is positive though a bigger value of 20-40 K is expected owing to the $^{3}A_{2g}$ - $^{3}T_{2g}$ separation of 1.5-2.5 eV often found for 3d-ion compounds in optical experiments. This smaller value has been taken here for the illustration reason associated with the energy scale. The relative positions of the CEF states are of course preserved.

The existence of the spin-like gap $\delta$ and the (highly-magnetic) excited doublet state cause interesting temperature dependence of the heat capacity and the magnetic susceptibility. The heat capacity exhibits a Schottky-type peak centered at temperature of $0.42 \cdot \delta$ with the maximal heat of $6.3$ J/K mol. The similar maximum is seen in the temperature dependence of the paramagnetic susceptibility $\chi$ as is presented in Fig. 2. The parameters used are: $B_4=+30$ K, $\lambda=-480$ K and $B_2^0=+1000$ K. The overall shape of this $\chi(T)$ plot is in very
good agreement with that experimentally observed\textsuperscript{3} for NENP. The maximum occurs at 50 K with the value of $18 \cdot 10^{-3} \mu_B/T$ ion. For NENP the maximum of the susceptibility amounts to $7.2 \cdot 10^{-3}$ emu/mol that can be recalculated with the use of the Avogadro number to $13 \cdot 10^{-3} \mu_B/T$ ion. Here is a need for the comment. In the approach shown above we calculate the contribution to the susceptibility from the one Ni\textsuperscript{2+} ion placed in the octahedral complex being the part of the macroscopic solid. The experimental susceptibility is always derived for the macroscopic system. In the recalculation it is assumed that each Ni atom contributes equally. This is surely not always the case. Even in the case of the perovskite structure the orientation of the octahedral MO\textsubscript{6} complexes is not parallel forming a zig-zag structure. It will cause that the experimentally derived susceptibility is lower. Knowing this fact we consider the obtained agreement as remarkably good, though we would like to remind that the exact reproduction of the specific data was not the intention of this paper.

The main purpose of Fig. 2 is to show the influence of the off-cubic lattice distortion on the overall temperature dependence of the susceptibility $\chi(T)$ by comparing with the $S=1$ behavior. In case of the purely octahedral crystal field and despite the presence of the s-o coupling $\chi(T)$ follows the Curie law quite well (the curve 2 in Fig. 2) - the $\chi^{-1}(T)$ plot is practically the straight line yielding the effective moment of 3.18 $\mu_B$. This value can be transformed into the spectroscopic $g$ factor of 2.24 for the effective spin $S=1$. It means that our approach allows for the calculations of the $g$ factor - in many theoretical papers it is simply an assumed parameter basing on experimental observations (about 2.20 $\mu_B$). It is worth noting that despite of the non-magnetic ground state and the anomalous low-temperature behavior the curve 1 mimics the Curie-Weiss behavior at quite low ambient temperatures, already above, say 150 K.

Finally we would like to point out that the singlet-doublet sequence depends on the sign of the lattice distortion. The formation of the singlet ground state is preferred by Nature going spontaneously because then the system gains energy fulfilling the theorem formulated already in 1937 by Jahn and Teller. Moreover, the bigger effectiveness of the trigonal distortion in the realisation of the J-T splitting, visible in Fig. 1, is the predicted
effect that can be experimentally checked. The realisation of the singlet ground state is also consistent with the Kramers theorem that states that the singlet ground state can be formed by electrostatic interactions for the electron system with an even number of electrons. On the other hand we know a great number of Ni compounds that are magnetically-ordered. Apparently then, by the formation of the magnetic state the system gains more energy than by the lattice distortion. The lattice distortion is always eventually prohibited by the elastic energy.

In conclusion, it has been shown that the non-magnetic singlet ground state of the highly-correlated \( d^8 \) electronic systems can be formed on the atomic scale by the off-cubic lattice distortion provided the spin-orbit coupling is correctly taking into account. By the realization of the non-magnetic singlet ground state the \( \text{NiO}_6 \) system fulfils the Jahn-Teller theorem. The highly-correlated \( d^8 \) electronic system is thought to be realised in \( \text{Ni}^{2+} \) and \( \text{Cu}^{3+} \) ions even then when they are the part of a solid. The good reproduction of the experimental data indicates that this atomic-like structure is largely preserved in the \( \text{Ni}^{2+} \)-ion containing compounds. The splitting of the lowest orbital singlet by the lattice distortion via the spin-orbit coupling offers clear physical mechanism compared e.g. to spin-Hamiltonian considerations where the splitting, known as a zero-field splitting results from the spin interactions with the effective spin and to the Haldane-type mechanism where the gap results from the inter-site spin interactions also with the effective spin and the neglect of the s-o coupling. For the present calculations the spin-orbit coupling is essentially important as the splitting of the original orbital singlet ground state cannot be obtained if the s-o coupling is not taken into account. Our approach proves the existence of strong correlations between the local magnetic moment of the 3\( d \) ion and its local symmetry.

A note added during the referee process. The referees argued that the J-T theorem does not apply to the system considered in this paper, the ground state of which is the orbital singlet. A message of this paper is that this text-book knowledge is not correct - in the \( 3d^8 \) electronic system realized in the \( \text{Ni}^{2+} \) ion the lattice distortion removes the degeneracy of the ground state orbital singlet that is, in fact, the triplet in the spin-orbital
space [10]. This paper can be also understood as an argument that the spin-orbital space is physically adequate for description of electronic and magnetic properties of 3d-ion containing compounds. We add, that our understanding of the J-T theorem for the d^8 system is consistent with its understanding for the rare-earth systems. The clue of the J-T effect relies in the fact of the removal of the degeneracy by lattice distortions with formation of the singlet state, if possible.

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**Figure Captions:**

Fig. 1.) The splitting of the 21-fold degenerated $^3F$ term of the $3d^8$ system. b) The energy level scheme of the $3d^8$ system under the action of CEF interactions of the cubic symmetry, produced by octahedrally arranged ligands, $B_4^0 > 0$, with the orbital-singlet $^3A_{2g}$ ground state. All the orbital levels have the internal 3-fold spin-degree of freedom, c) the effect of the s-o coupling according to the present calculations, d and e show the splitting of the 3-fold degenerated ground state $^3A_{2g}$ by the tetragonal and trigonal distortion. The formation of the singlet ground state by the given $B_2^0$ parameters should be noticed. The shown splitting of the lowest orbital-singlet $^3A_{2g}$ fulfils the Jahn-Teller theorem because thanks distortion the system lowers the energy.

Fig. 2. Influence of the lattice off-cubic trigonal distortion (curve 1) on the temperature dependence of the paramagnetic susceptibility $\chi(T)$ of the $d^8$ electron system in the octahedral crystal field and in the presence of the spin-orbit coupling. The parameters used: $B_4=+30$ K, $\lambda = -480$ K and the trigonal distortion $B_2^0=+1000$ K that yield the electronic structure as shown in the inset, i.e. with non-magnetic ground state and the magnetic doublet excited state $(m=\pm 2.03 \mu_B)$. The curve 2 shows the susceptibility in the absence of the distortion - it follows the Curie law though with the effective moment of 3.18 $\mu_B$, i.e. 12 % larger than expected for the purely S=1 system.
$3d^8$ system

Ni$^{2+}$/Cu$^{3+}$ ion

octa

\[ \begin{aligned}
\text{cubic CEF} & : B_4 = +4.5 \text{ K} \\
\lambda & = 0
\end{aligned} \]

\[ \begin{aligned}
\text{cubic CEF} & : B_4 = +4.5 \text{ K} \\
\lambda & = -480 \text{ K}
\end{aligned} \]

\[ \begin{aligned}
\text{tetragonal} & : B_2^0 = +100 \text{ K}
\end{aligned} \]

\[ \begin{aligned}
\text{trigonal} & : B_2^0 = +100 \text{ K}
\end{aligned} \]
$T(K)$

magnetic susceptibility ($\mu_B/T$ d-ion)

$3d^8$ system

$A_{2g}$

$\delta = 64 K$

$1$ $2$