Electronic structure of the V^{3+} ion in V_2O_3♠

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We have attributed magnetism and electronic structure of V_2O_3 to
the V^{3+} ions. We claim that the V^{3+} ion in V_2O_3 should be considered
as described by the quantum numbers $S=1$ and $L=3$. Such quantum
numbers result from two Hund's rules. The resulting electronic struc-
ture is much more complex than considered up to now, but it describes,
e.g. the insulating ground state and the lowered magnetic moment,
of 1.2 μ_B. It turns out that the intra-atomic spin-orbit coupling is
indispensable for the physically adequate description of electronic and
magnetic properties of V_2O_3.

I. INTRODUCTION

V_2O_3 attracts the substantial scientific interest by more than 50 years
[1]. Despite of it there is still strong discussion about the description
of its properties and its electronic structure. There is a long-standing
controversy between a $S=1$ model without an orbital degeneracy [2] and
the $S=1/2$ orbitally degenerate model of Castellani et al. [3]. Recently
an "orbitally degenerate spin-1 model for the insulating V_2O_3" has been

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proposed in Refs [4, 5] whereas spin-1 model with three degenerate orbitals quite recently was worked out by Di Matteo [6].

In all of these considerations it is agreed that V_2O_3 is an insulating antiferromagnet with the Neel temperature of 160 K. At that temperature also the low-temperature insulating state transforms to a metallic state without long-range magnetic order. V_2O_3 has basically the rhombohedral corundum Al_2O_3 structure. It is agreed that V ions in the corundum structure sit predominantly in the oxygen octahedron with some further distortions, Fig. 1 of Refs [4, 5]. It is also agreed that the V^{3+} ion has two d electrons, i.e. that the charge fluctuations are practically absent [2–4]. The basis for all theories is the description of the V^{3+} ion and its electronic structure.

The aim of this paper is to point out that the V^{3+} ion in V_2O_3 should be described by the quantum numbers $S=1$ and $L=3$.

II. THEORETICAL OUTLINE

The V^{3+} ion has two $3d$ electrons. According to us these two electrons form the highly-correlated atomic-like electronic system $3d^n$ ($n=2$) that is described by the resultant quantum numbers $S=1$ and $L=3$. Its electronic structure contains 21 discrete states. According to the Quantum Atomistic Solid State Theory, QUASST, these states are preserved also when the paramagnetic ion becomes the full part of a solid [7]. The resultant quantum numbers $S=1$, $L=3$ and ^3F ground term, Fig. 1a, come out from two Hund's rules (two, i.e. 1° the maximal S and 2° the maximal L for two d electrons). Hund's rules reflect strong intra-atomic interactions. Thus, the demand for keeping the Hund rules is equivalent to an idea that the paramagnetic atom preserves much of their internal atomic structure being the part of a solid. Such the atomic-like $3d^n$ system interacts with the charge and spin surrounding in the solid. The interaction with the charge surrounding we approximate by means of the crystal-field interactions. The symmetry of the crystal-field interactions depends on the local symmetry and in the corrundum structure is predominantly octahedral. The calculated discrete electronic structure in the octahedral crystal field, Fig. 1b, and in the presence of the intra-atomic spin-orbit coupling is shown in Fig. 1c. To such electronic structure we superimpose the spin-dependent interactions to account for the magnetic state. The self-consistent calculations are performed similarly to that presented in Ref. [8] for $FeBr_2$. Having the electronic structure, both in magnetic and paramagnetic state, we can calculate the free Helmholtz energy and the resulting thermodynamical properties by means of the statistical physics.
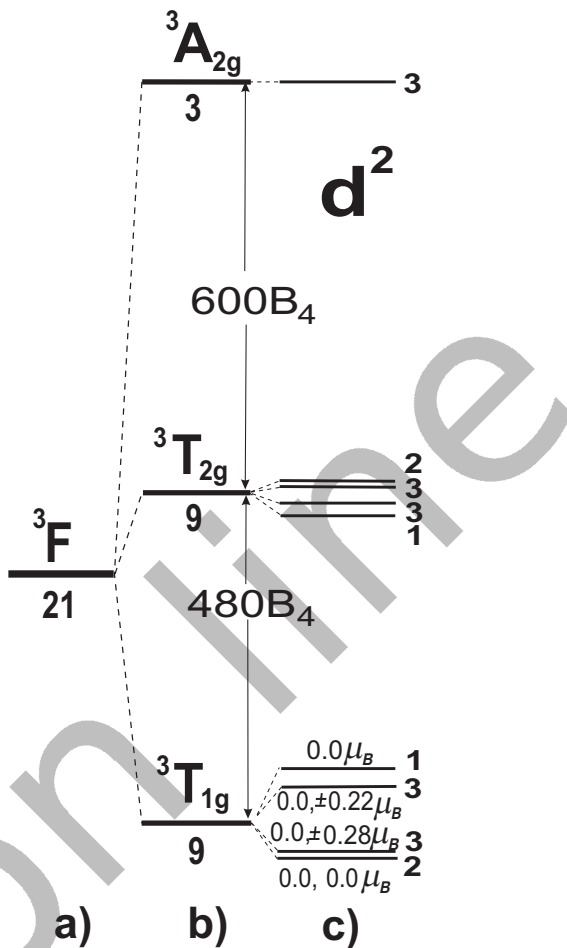
FIG. 1: Electronic structure of the highly-correlated $3d^2$ electronic system occurring in the V^{3+} ion calculated with the octahedral CEF parameter $B_4^0 =$ -40 K and the spin-orbit coupling λ_{s-o}=+150 K. According to the QUASST theory such the electronic structure is expected to be largely preserved in a solid. In real V_2O_3 this structure is slightly modified by off-octahedral distortions and magnetic interactions.

III.   RESULTS AND DISCUSSION

The shown energy level scheme of the $3d^2$ system in the octahedral crystal field and in the presence of the spin-orbit coupling, with the octahedral crystal field dominating the intra-atomic spin-orbit coupling, contains 21 states. As seen from Fig. 1c the dominating octahedral crystal field leaves 9 lowest states well separated from others. These 9 states are spread over 60 meV and their eigenfunctions and energies determine the detailed properties at room and lower temperatures. The properties at zero temperature are determined by the properties of the ground state. The detailed splitting depends on value of the spin-orbit coupling and on the distortions.

The ground state is an accidental non-magnetic doublet. This doublet structure is easily split by means of lattice distortions and/or spin-dependent interactions. They yield a singlet ground state of the V^{3+} ion in the atomic scale. Despite of the single-ion singlet ground state the magnetism can easily develop as the closely lying states work as a pseudo-doublet. The similar moment-induced mechanism is well known in praseodymium compounds [9]. As the result of local distortions the local V moment can be modelled, both its value and the direction. We get a value of 1.2 μ_B for the V^{3+}-ion magnetic moment in the ordered state at 0 K - this value well reproduces the experimental value. We use the octahedral CEF parameter $B_4^0 = -40$ K and the spin-orbit coupling $\lambda_{s-o} = +150$ K. The sign of B_4 comes out directly from the calculations of the octupolar potential for the octahedral oxygen-anion surroundings.

Our approach yields in the very natural way the insulating ground state. Due to strong correlations all electrons after the charge transfer, from the metal atoms to oxygens, during the formation of the compound, are localized at the oxygens. Within our approach we can understand why the cubic perovskite structure distorts. By the distortion the system gains energy. From 1937, after Jahn and Teller's work we know that system will spontaneously distort to remove the accidental double degeneracy of the ground state. Our understanding of $3d$-ion compounds is close to an original idea of Van Vleck from 1932, that electronic and magnetic properties are largely determined by the atomic-like electronic structure.

IV.   CONCLUSIONS

We have attributed magnetism and electronic structure of V_2O_3 to the V^{3+} ions. We claim that the V^{3+} ion in V_2O_3 should be considered as described by the quantum numbers $S=1$ and $L=3$. Such quantum numbers result from two Hund's rules. We are convinced that the or-

bital degree of freedom, related to the orbital quantum number L and the intra-atomic spin-orbit coupling are indispensable for the physically adequate description of electronic and magnetic properties of V_2O_3. Most up-to-now approaches employ the one-electron t_{2g} (ground state) and excited e_g orbitals and next consider a molecular V-V unit. Within the Quantum Atomistic Solid-State theory we have shown that the value and the direction of the local magnetic moment is predominantly governed by the local lattice symmetry, e.g. Ref. [6]. We get a value of 1.2 μ_B for the V^{3+} ion magnetic moment - this value is very sensitive to the local distortions and contains the substantial orbital moment. We are convinced that our description is also useful for the description of the V^{3+} ions in orthovanades $LaVO_3$ and YVO_3 [10].

[Added 11.03.2003] This paper has been at first rejected at SCES-02 (Prof. J. Spalek, A. M. Oles) due to "an unusual theoretical concept" in the situation where virtually all other workers in the field over the last twenty years have adopted the V-V molecular unit in the unit cell as a basis for their discussion." For us, the atomic approach as the start for the analysis of a compound is obvious owing to a presently well-established, but originally very doubtful, an idea of Dalton and Davy that all solids are built from atoms. So different approaches assure the useful discussion and we believe that the publishing of our paper enables the open scientific discussion and allows to solve the problem in the future. As far as correlations are regarding our approach to V_2O_3 is in the very strongly-correlated limit, though these correlations are primarily on-site and atomic-like. Developing of very different theories, despite of 20 years of studies and in the very last time [10–12], we take as indication that there is very urging need for novel theoretical approaches even such "unusual" as the one presented in this paper. However, we can add that our model provides both the orbital and spin moment [8, 13]. We came out with our approach to $3d$-atom containing compounds in 1996 [14] when the orbital moment was not yet revealed experimentally. Thus, we take the possibility of accounting for the experimentally-revealed orbital moment as the great plus for our theoretical approach. But surely there is still a lot to do in order to describe details of experimental details, but we feel that the atomic-scale properties are essentially important for description of magnetic and electronic properties of $3d$-atom compounds.

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♠ This paper has been submitted 31.05.2002 to Strongly Correlated Electron Conference in Krakow, SCES-02 getting a code MOT026. It has been presented at the Conference but has been rejected with

referee's arguments that "The authors should make a convincing case for their adoption of a strictly atomic model in the discussion of the physical properties of the V^{3+} ion in V_2O_3 when virtually all other workers in the field over the last twenty years have adopted the V-V molecular unit in the unit cell as a basis for their discussion. .... The statements that the V cation is "in the almost perfect oxygen octahedron with some further distortions" and "The symmetry of the crystal field interaction ... is predominantly octahedral" and the caption to Fig. 1 are misleading. The oxygen environment is severely distorted, which renders suspect any scheme based on the disposition of atomic states in a perfect octahedral environment." Our answer of 10.09.2002 " for us your general objection "why we use the atomic picture" as the start is curious as from two hundred years after Davy, Dalton and others chemists all we know is that a solid is built from atoms. Thus atomic starting point is simply obvious. It is not our problem why other people in the field start in the very different way. Your objection that we imply "a strictly atomic scheme" is not true. Also, that we "take no account of the milieu in which the V^{3+} ions find themselves in a V_2O_3 lattice" – is completely misunderstanding of our job. We say just opposite – the milieu, we use a more physical word surroundings (both the charge and spin), is fundamentally important for the realization in a solid of the given atomic-scale ground state and consequently of the whole compound. It is a role of lattice distortions widely discussed by us. In connection to distortions we fully agree that "The oxygen environment is severely distorted" but each consideration in literature starts from the octahedron. Very important is that our electronic structure, shown in Fig. 1c, will be only modified by distortions – the number of states will be preserved. Modification means the removal of degeneracies shown, the change of the energy separations and shape of eigenfunctions. Next, our model provides both orbital and spin moment, Refs [8, 13]. We came out with our approach to 3d-atom containing compounds in 1996 when the orbital moment was not yet derived experimentally. Thus, we take the possibility of accounting for the orbital moment as the great plus for our theoretical approach." did not find the understanding of the SCES-02 Committee. Surely, our many-electron CEF electronic structure is completely different from the one-electron crystal-field electronic structure with two electrons put on the t_{2g} orbitals generally discussed in the presently-in-fashion theories of 3d-atom containing compounds.

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