Research Article

The Jahn-Teller theorem for the 3d magnetic ions

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We argue that the Jahn-Teller theorem, if applied to 3d-ion compounds, has to be considered in the orbital+spin space. It is despite of the weakness of the intraatomic spin-orbit coupling.

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There is ongoing strong discussion [1–3] in Phys. Rev. Lett. and Phys. Rev. B about a relationship between the electronic structure, magnetism, the local 3d-ion surrounding and a (off-cubic) lattice distortion in 3d ionic compounds like $La_{1-x}Ca_xMnO_3$ and $LaCoO_3$. In this discussion, terms like the Jahn-Teller (J-T) effect and the J-T distortions appear that obviously are related with the J-T theorem. This long-time discussion reveals that the physical picture for 3d-ion compounds is far from a consensus. On other side, the x-ray-absorption fine structure (XAFS) experiments provide more and more accurate data on the local surrounding in the atomic scale that are generally discussed in connection to the J-T effect.

The aim of this short Letter is to put the attention that the degeneracy space for the consideration of the J-T theorem for the 3d ions is the orbital+spin space. It is in contrast to the current-literature that considers the J-T theorem, if applied to 3d ions, in the orbital space only.

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In 1937 Jahn and Teller had pointed out [4, 5] that no non-linear molecule could be stable in a degenerate state. It means that one would expect a spontaneous distortion to undergo in order to remove this degeneracy. In the current-literature the J-T theorem and related with it the degeneracy, if applied to $3d$ ions, is considered in the orbital space [6]. It likely repeats the text-book knowledge (Ref. [5] p.193 line 4 bottom, Ref. [8] p. 212. line 12 top, Ref. [9] p. 40 line 8 bottom). This way of thinking is commonly used for the description of the $3d$ ions and $3d$-ion compounds basing on the weakness of the spin-orbit coupling for these ions.

We argue that the J-T theorem has to be considered in the orbital+spin space. It is the consequence of the spin-orbit coupling that, though weak in the $3d$ ions, always exists.

A consequence of it is that practically all $3d$ ions are J-T ions, i.e. their electronic atomic-like structure in the octahedral surrounding is very sensitive to the local symmetry. The electronic atomic-like structure of all 3d ions in the octahedral surrounding in the presence of the spin-orbit coupling has been calculated in Ref. [10]. This prediction is in perfect agreement with experimental observations - everywhere where exact experimental studies are performed the octahedral surroundings is found to be distorted. A nice example presents the Ni^{2+} ion. In the octahedral surrounding having the orbital singlet ground state is not expected to force the lattice distortion - in the orbital+spin space this orbital singlet ground state is the triply degenerated and its degeneracy can be removed by lattice distortions. It can go spontaneously as then the system can decrease the energy [7].

The demanded orbital+spin space for the consideration of the J-T theorem is consistent with the standard treatment of rare-earth-ions.

In conclusion, we argue that the J-T theorem, if applied to $3d$-ion compounds, has to be considered in the orbital+spin space.

[1] C. H. Booth, F. Bridges, G. K. Kwei, J. M. Lawrence, A. L. Cornelius, and J. J. Neumeier, Phys. Rev. Lett. **80**, 853 (1998).
[2] I. Solovyev, N. Hamada, and K. Terakura, Phys. Rev. Lett. **76**, 4825 (1996).
[3] Phys. Rev. Lett. **77**, 5296 (1996).
[4] H. A. Jahn and E. Teller, Proc. Roy. Soc. (London) A161, 220 (1937)(after Ref. 2, p.4 line 15 bottom).
[5] C. Ballhausen, in: *Ligand Field Theory* (McGraw-Hill, 1962).

[6] The present paper has been submitted 16.02.1999 to Phys. Rev. Lett. as a consequence of an erroneous report of the referee of Phys. Rev. Lett. on our paper [7] that "the Jahn-Teller theorem only applies to orbitally degenerate levels and therefore does not apply to the system considered in the paper" [LL6530, report A from 4.12.1997], i.e. the d^8 system in the octahedral crystal field. This report was taken by The Editor of Phys. Rev. Lett. Dr G. Wells as the base for the rejection of the a/m paper. In the paper [LL6530, Ref.7] we have shown that the d^8 system (the Ni^{2+} ion) in the octahedral surrounding is the Jahn-Teller ion, despite of the orbital singlet ground state.
[7] Z. Ropka and R. J. Radwanski, cond-mat/0006196 (2000); PRL submission 14.11.1997.
[8] B. N. Figgis, in: *Introduction to Ligand Fields* (Interscience, 1966).
[9] P. A. Cox, in: *Transition Metal Oxides* (Clarendon, Oxford) 1992.
[10] R. J. Radwanski and Z. Ropka, cond-mat/9907140 (1999).