P01

The Superexchange Mechanism in Crystalline Compounds: The Case of KMF_3 (M=Mn, Fe, Co, Ni) Perovskites

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ABSTRACT

The ferromagnetic and antiferromagnetic wavefunctions of four KMF_3 (M= Mn, Fe, Co and Ni) perovskites have been obtained quantum-mechanically with the CRYSTAL code, by using the Hartree-Fock (HF) Hamiltonian and three flavours of DFT (PBE, B3LYP and PBE0) andan *all- electron* Gaussian type basis set. In the Fe and Co cases, with d^6 and d^7 occupation, the JahnTeller distortion of the cubic cell is as large as 0.12 $^{\circ}$A. Various features of the superexchange interaction energies (SIE), namely additivity, dependence on the M-M distance, on the $\widehat{MFM}$ angle, and on the adopted functional, are explored. The effect of SIE on the equilibrium geometryand volume of the unit cell is discussed, and it is shown that the key quantity is the spin polarization of the (closed shell) F ions along the M-F-M path. The effect of this *magnetic pressure* is evaluatedquantitatively for the first time.

The superexchange coupling constant J, evaluated at the HF level and through the Ising model, underestimates the experimental values by about 60-70%. The more sophisticated Yamaguchi model (that takes into account the contamination of the FM and AFM spin states) does not reduce the discrepancy. These latters are bracketed by HF and PBE0. For PBE, the overestimation is huge.

Finally, Mulliken population data, charge and spin density maps and density of states are used to illustrate the electronic structure.

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