MS20-2-1 Superexchange Mechanism In M(II) Formate Dihydrate Series And Charge-Density Study Of The Co(II) Formate Dihydrate
#MS20-2-1

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Abstract
The Co(II) formate dihydrate (Co-formate) system exhibits a two-dimensional antiferromagnetically ordered structure intercalated by paramagnetic Co ions below [1]. Structurally, the magnetic planes are composed of Co-sites linked by formate ligands, while the paramagnetic Co ions do not exhibit the same two-dimensional structure. However, signs of short-range ferromagnetic order between the magnetic planes and paramagnetic ions have been observed upon further cooling [2].
Following a polarised neutron scattering experiment on the structural congener Mn-formate [3], it has been proposed that the two-dimensional magnetic order can be explained by superexchange facilitated by the formate ligands. Herein, this is further studied by analysing the charge density of Co-formate derived from a single crystal X-ray scattering experiment where it is observed from Laplacian maps that the formate ligands can coordinate into d-orbitals of t_{2g}-symmetry through a π-symmetric interaction. Correlating the possible interactions with extracted d-orbital populations, and interpreting these in terms of relative orbital energies, the interaction can be understood as back-donation.
This opens up the possibility of superexchange facilitated via π-symmetric interactions in addition to σ-symmetric interactions over the delocalised formate electron system. Applying the superexchange symmetry rules of Kanamori [4] together with the observed d-orbital populations allows for a mechanistic description of the antiferromagnetic 2-dimensional order and the short-range ferromagnetic order where the former is facilitated by σ-symmetric interactions and the latter by π-symmetric interactions. Furthermore, the short-range interaction is influenced by competing superexchange mechanisms in agreement with the lower ordering temperature.

References
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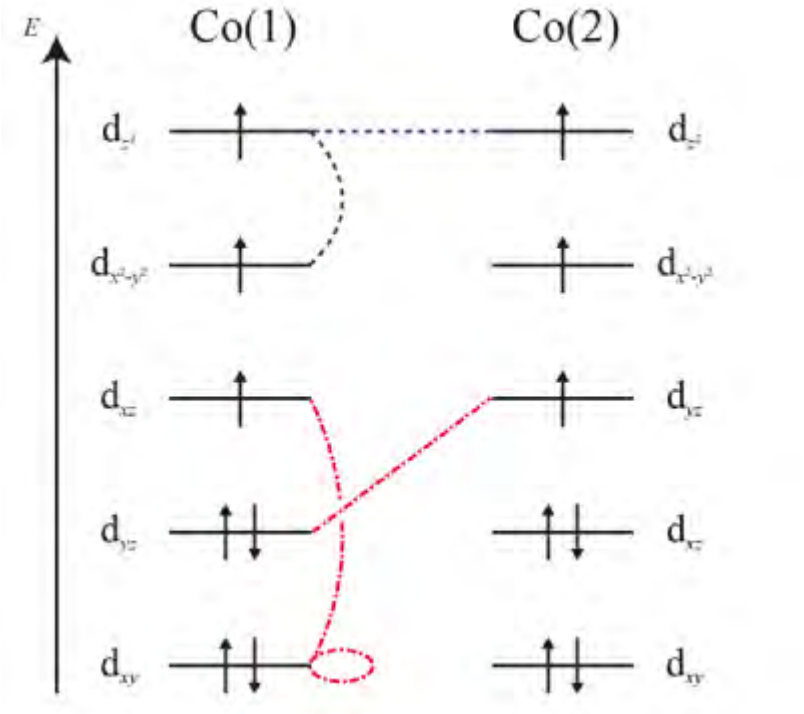
Orbital ordering based on extracted d-populations.



Superexchange mechanism through pi-orbitals.