

Exploring Structural Oddities in Tin Cluster Compounds RuMSn_6O_8 ($M = \text{Mn, Fe, Co}$) with Quantum Mechanical Methods

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$\text{RuFeSn}_6\text{O}_8$ is among the very few known substances where Fe^{2+} is explicitly located in a tetrahedral surrounding. This causes the iron d_{eg} valence band to be filled with three electrons, which should result in strong lattice distortions. Surprisingly, all phases RuMSn_6O_8 ($M = \text{Mn, Fe, Co}$) are stable paramagnetic semiconductors. However, results from ^{57}Fe Mössbauer spectroscopy and scattering experiments do not allow a final answer about the crystal structure. By using DFT calculations within the GGA+U approach the electronic and magnetic properties have been described and a possible reason for the inconsistencies in the experimental structure data found in an underlying local monoclinic distortion.

1. Introduction

Data obtained from single crystal, X-ray powder and neutron diffraction experiments suggest that all RuMSn_6O_8 ($M = \text{Mn, Fe, Co}$) form cubic face-centered arrangements of RuSn_6 octahedra with MO_4 tetrahedra filling up half of the tetrahedral vacancies analogously to the zinc blende structure type (Fig. 1) [1]. However, these results suggest that there is no structural distortion in face of the strong electronic driving force even at very low temperatures, which seems unlikely.

In contrast to X-ray and neutron diffraction experiments, ^{57}Fe -Mössbauer spectra for $\text{RuFeSn}_6\text{O}_8$ indicate a distortion of the local coordination sphere in case of the Fe compound. At temperatures above 56 K a sharp singlet can be observed, which is consistent with the cubic lattice at room temperature. However, below this temperature the signal splits up into a doublet. The quadrupole splitting increases as the temperature decreases. This process is reversible without any hysteresis and indicates a distortion of the local Fe coordination sphere which, on the other hand, is invisible in scattering experiments.

One possible explanation for this situation could be the so-called dynamical Peierl's distortion where, at sufficient temperatures, the system can switch between two locally distorted states with approximately the same energy. Under these conditions the differently distorted surroundings do not become visible until the temperature is decreased. As soon as the thermal energy is too small to allow rapid transitions more and more FeO_4 tetrahedra become statistically and independently trapped in either the one or the other state, which results in a splitting of the signal into a doublet. However, scattering experiments cannot resolve the

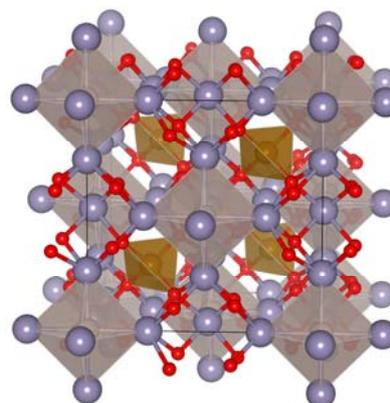


Fig 1. Crystal structure of RuMSn_6O_8 with octahedra: RuSn_6 , and tetrahedra: MO_4 ($M = \text{Mn, Fe, Co}$).



proposed statistical symmetry lowering as the measured signal is always averaged across the whole crystal lattice.

This research is the first attempt to describe the electronic structure of RuMSn_6O_8 ($M = \text{Mn, Fe, Co}$) compounds correctly. Spin-polarized GGA+U calculations within the LAPW approach have been tested for their impact on the compounds' DOS. The symmetry of the lattice has been lowered from the original cubic structure to a monoclinic sub-structure to explore the relations between crystallographic ordering and electronic structure.

It is also notable that $\text{RuFeSn}_6\text{O}_8$ can be counted among the number of Fe^{2+} -containing materials where a +U extension has been used to describe the strongly correlated Fe-d bands correctly [2-4]. Calculations without this method always resulted in DOS where the corresponding d-states appeared in the middle of what ought to become the band-gap and had to be shifted to more reasonable energies.

2. Computational Details

All calculations were performed with the LAPW method implemented into the Wien2k program package [5]. The PBE functional with the +U extension was used and some calculations were performed with magnetic ordering. The parameter U_{eff} was found to lie between 0.5 Ry and 1.00 Ry (6.80 eV and 13.60 eV) to produce reasonable DOS. The parameters R-MT, K-MAX and G-MAX were 7.00 and 12.00 for all calculations and the number of k-points was set to be 200. All calculations were performed in the cubic structure (SG $F4-3m$) and a monoclinic sub-structure (space group Cm). The original experimental atomic positions and lattice constants obtained for the cubic structures were used in the calculations without further optimization and were transformed into the monoclinic lattice.

3. Results

Non-spinpolarised LAPW calculations of the cubic phases within the GGA/PBE and GGA/PBE+U approaches always resulted in densities of states that predicted conducting behavior of the materials, which is not in agreement with the experimental results (Fig. 2). In an attempt to account for the hints given by ^{57}Fe -Mössbauer experiments that at least a local distortion seems to occur at temperatures below 57 K in case of $\text{RuFeSn}_6\text{O}_8$, self-consistent spin-polarized calculations simulating a ferromagnetic state of the compounds in the cubic lattice were performed.

Fig 2. DOS of $\text{RuFeSn}_6\text{O}_8$ in cubic structure obtained from non-spin-polarised GGA+U calculations ($U = 0.5 \text{ Ry}$; $J = 0 \text{ Ry}$).

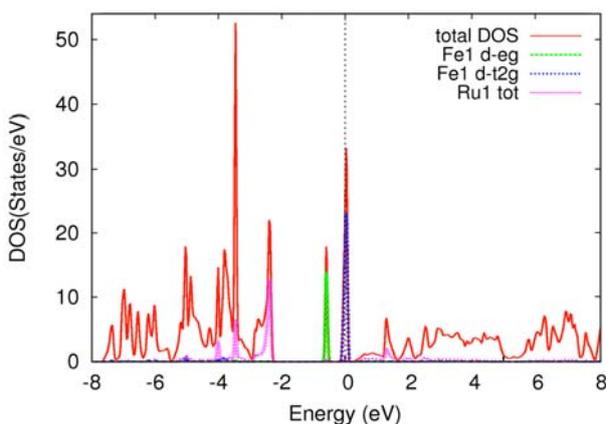


Fig. 3 shows the DOS obtained from spin-polarized GGA+U calculations with $U_{\text{eff}} = 1 \text{ Ry}$ (Mn phase) and 0.5 Ry (Co phase), respectively. These densities of states describe the experimentally observed semi-conducting behaviour of the solid phases. One can see that the metal d-bands are gradually filled in a high-spin fashion according to d^5/Mn^{2+} (filled e_g and t_{2g} majority spin bands) and d^7/Co^{2+} (filled e_g and t_{2g} majority spin bands and filled e_g minority spin bands) ions. This clearly predicts semi-conducting behaviour with band gaps of around

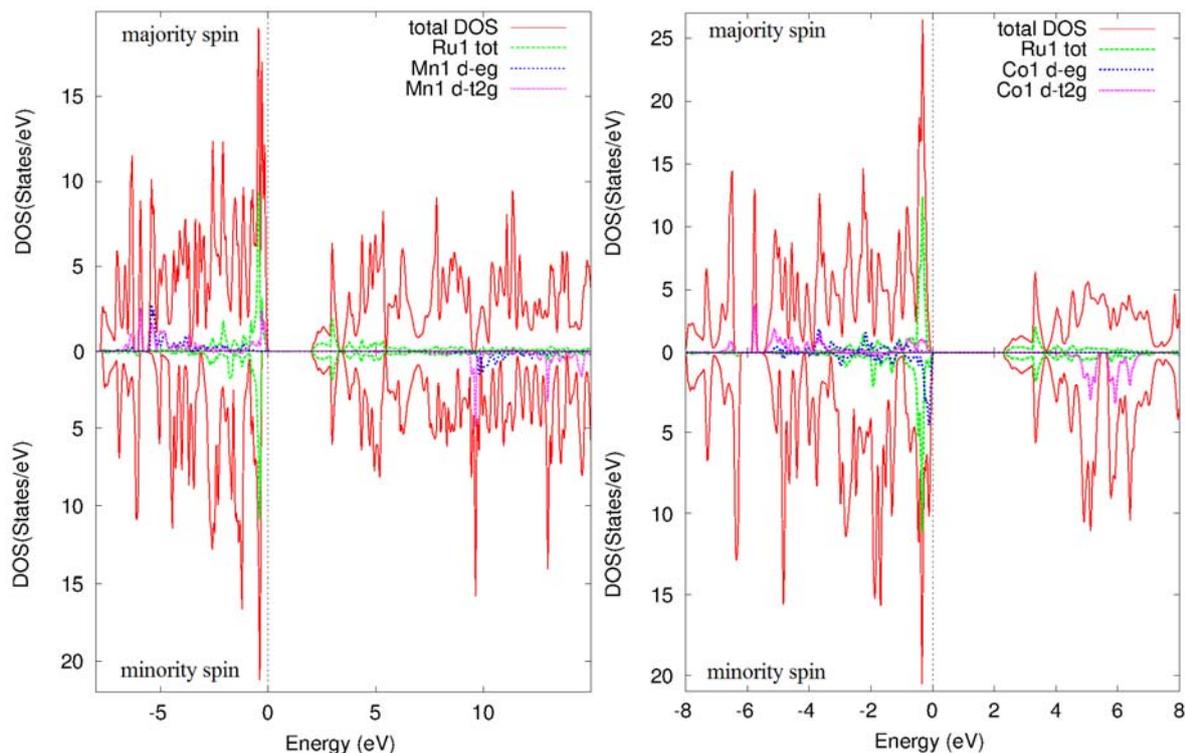


Fig 3. DOS of $\text{RuMnSn}_6\text{O}_8$ in cubic symmetry obtained from spin-polarised GGA+U calculations. Left: $\text{RuMnSn}_6\text{O}_8$, resulting in a ferromagnetic ordering of $5 \mu\text{B}$ magnitude ($U = 2 \text{ Ry}$, $J = 1 \text{ Ry}$ were applied); Right: $\text{RuCoSn}_6\text{O}_8$ resulting in a ferromagnetic ordering of $3 \mu\text{B}$ magnitude ($U = 0.5 \text{ Ry}$, $J = 0 \text{ Ry}$ were applied).

2 eV for the manganese and cobalt phases. The latter is not found for the iron phase as spin-polarized GGA+U calculations in the cubic unit cell turned out to be very unstable. This can be understood, as it is impossible to split up the unevenly filled d- e_g band for the minority spins.

In a second attempt the internal degrees of freedom were further increased by lowering the symmetry of the structure from cubic to monoclinic, resulting in decoupling of all metal d-bands. The DOS shows semi-conducting behavior for the iron phase with a band gap of about 2.2 eV, which finally matches the expectations from experimental evidence. The corresponding parameters used were $U = 0.5 \text{ Ry}$ and $J = 0 \text{ Ry}$.

Fig. 4 shows the DOS of this calculation where the nicely dispersed iron d-bands, in both the valence and the conduction band, can be seen. The magnetic moment of the phase was calculated to be zero, implying a non-magnetically ordered structure. The sums over all

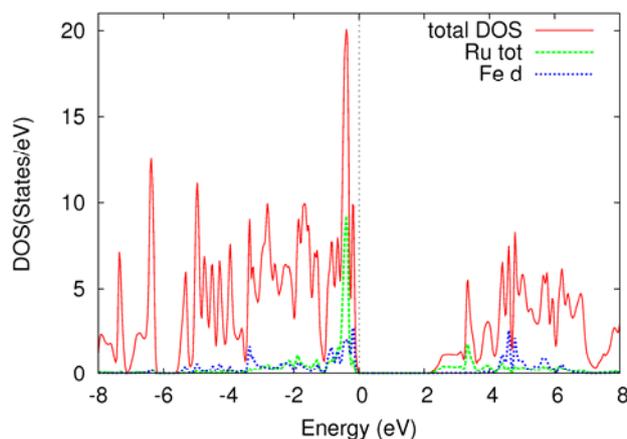


Fig 4. DOS of $\text{RuFeSn}_6\text{O}_8$ in monoclinic symmetry obtained from spin-polarised GGA+U calculations ($U = 0.5 \text{ Ry}$; $J = 0 \text{ Ry}$); overall magnetic moment was calculated to be zero.



contributions to up and down spins are identical, even though the different d bands contribute differently to the two situations. The Mn and Co phases showed the same qualitative behavior of non-magnetically ordered semi-conducting materials.

4. Conclusions

In this work the electronic structures of the compounds $RuMSn_6O_8$ ($M = Mn, Fe, Co$) were explored with different quantum chemical methods. Discrepancies between the results of ^{57}Fe Mössbauer spectroscopy for Fe-containing phase on one hand and X-ray and neutron scattering experiments on the other hand had already indicated a complex relationship between electronic and spatial symmetry. One attempt to explain those findings is postulating a dynamic Peierl's distortion of the FeO_4 tetrahedra, which could be promoted by the unusual d^6 -configuration of the Fe-atoms for the tetrahedral surrounding. The presence of a dynamic Peierl's distortion assumes lowered underlying lattice symmetry than the cubic one that was found in scattering experiments. Therefore one important aim of this work was to verify whether it is possible to find solid evidence for this theory or not. In order to derive or identify certain trends the DOS of the phases $RuMnSn_6O_8$ and $RuCoSn_6O_8$ were also calculated.

In the cubic symmetry, GGA/PBE+U calculations resulted in the prediction of magnetically ordered semi-conductors for $M = Mn$ and Co . The Fe phase was predicted to be a metallic conductor, which does not match the experimental results. Being aware of the experimental hints towards a symmetry lowering, the same calculations were performed for a monoclinic lattice. This resulted in the correct calculation of semi-conducting DOS for all three phases. The calculations also no longer predict magnetically ordered materials. These findings strongly support the idea of an underlying local symmetry of the compound, which may not be cubic.

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