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Exchange Coupling in Eu Monochalcogenides from First Principles

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Using a density functional method with explicit account for strong Coulomb repulsion within the $4f$ shell, we calculate effective exchange parameters and the corresponding ordering temperatures of the (ferro)magnetic insulating Eu monochalcogenides (EuX; X = O, S, Se, Te) at ambient and elevated pressure conditions. Our results provide quantitative account of the many-fold increase of the Curie temperatures with applied pressure and reproduce well the decrease of ferromagnetic coupling across the EuO–EuTe series. The first J_1 and second J_2 neighbor effective exchange are found to follow different pressure dependencies. Finally, our calculations show explicitly that the mixing of Eu $4f$ orbitals with the ligand states is necessary for the ferromagnetic ordering to take place at any pressure.

KEYWORDS: ferromagnetic semiconductor, electronic structure, exchange coupling
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Ferromagnetic (FM) semiconductors have become an object of great technological interest with the appearance of spintronics because they can provide a spin-dependent tunneling barrier. Especially challenging is to achieve a sizable ordered moment at room temperature, which is crucial for a large scale application of the technology. There is currently an intense effort to locate such materials within the dilute magnetic semiconductors, where the magnetic moment is carried by impurities in an otherwise non-magnetic system, but few candidates have been found. An attractive alternative is FM insulators. Ferromagnetism is rare in stoichiometric materials without charge carriers. Europium monochalcogenides (EuO, EuS, EuSe, EuTe) belong to this small group of FM insulators.[1)] The ability to calculate the ordering temperature and understand the exchange mechanisms on the material specific level is of particular importance.

Crystallizing in the rock-salt structure, the first two members of the group order ferromagnetically at 69.2 and 16.6 K respectively,[2)] while EuTe, a type II antiferromagnet, becomes ferromagnetic only at elevated pressure.[3)] EuSe is at the borderline between ferromagnetic and antiferromagnetic order with ferromagnetism stabilized by a moderate pressure of 0.5 GPa.[4)] Application of pressure strongly enhances Curie temperatures of all these materials. The Eu^{2+} valency results in half filling of the Eu $4f$ shell with ^8S configuration of the groundstate multiplet. Due to the localized nature of the moment-carrying f orbitals, direct exchange between f orbitals on different sites is negligible and other states are necessary to provide an inter-site coupling of the magnetic moments. The intra-atomic f–d exchange, which is the leading f-valence interaction, gives rise to temperature dependent features (red shift effect) in the valence electron spectrum which are well captured by the ferromagnetic Kondo lattice model.[5,6)] In an insulator, however, this interaction alone cannot lead to an effective inter-site coupling of the local moments. To do so excitations across the gap, the origin of so called Bloembergen–Rowland (BR) coupling,[7,8)] have to be taken into account. Another possible source of an inter-site coupling is mixing of the Eu $4f$ and ligand p states resulting in processes described on a qualitative level in refs. 9 and 10. While a significant amount of *ab initio* calculations of the Curie temperature in metallic systems has been done (*e.g.*, ref. 11 and references therein) attempts to address the Curie temperature and coupling mechanisms of FM insulators on a material specific level are rare and become quite involved.[12,13)] In particular the question of the importance of f hybridization has not been addressed in detail (except for Ce).

The electronic structure methods based on semi-local approximations[14,15)] to the density functional theory (DFT)[16)] have notorious problems in dealing with strong correlations within the $4f$ shell, in particular the splitting into Hubbard sub-bands is missing, which often results in an incorrect filling of the $4f$ states. Two remedies are possible: (i) open-core method, in which the hybridization and charge transfer between the f orbitals and the rest of the system are forbidden (ii) LDA+U method,[17)] which can be viewed as a static approximation to the LDA+DMFT method,[18)] which is well justified in the parameter range of EuX compounds. While the latter method is more complete and thus superior, comparison of the two approaches allows for assessment of the role of f hybridization. The half filling of the $4f$ shell in Eu^{2+} removes additional problems associated with orbital degrees of freedom.

The calculations reported here were performed using the Wien2k[19)] implementation of the full-potential linearized augmented-plane-wave (FLAPW) method with the rotationally invariant LDA+U functional and double-counting scheme of ref. 17. The size of APW+lo basis was determined by the cut-off $R_{\mathrm{mt}}K_{\max} = 8$ corresponding to approximately 100 basis functions per atom. Approximately 30 irreducible k-points (depending on the magnetic structure) out of the 250-k-point regular grid were used in the Brillouin zone integrations. The calculations were performed for lattice constants spanning the experimental range of stability of the rock salt crystal structure. The groundstate energies of three different magnetic structures: (i) ferromagnetic (F), (ii) type II antiferromagnetic and (iii) antiferromagnetic with propagation vector $(0, 0, 2\pi/a)$, were calculated self-consistently and mapped onto the $J_1 - J_2$ Heisenberg Hamiltonian

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$$H = -\sum_{i,j} J_{ij} \boldsymbol{S}_i \cdot \boldsymbol{S}_j \qquad (1)$$

with the corresponding classical energies: (i) $-(12J_1 + 6J_2)S^2$, (ii) $6J_2S^2$, and (iii) $(4J_1 - 6J_2)S^2$. The groundstate magnetic ordering is determined by the difference of (i) and (ii), i.e., by the sign of $J_1 + J_2$. The real space cut-off at the second-nearest-neighbor, which is well established experimentally, was confirmed for EuS at ambient pressure by the spin-spiral calculation similar to those of ref. 20. The calculated exchange constants as a function of the lattice parameter are shown in Figs. 1 and 2. In order to assess the role of U, which is an external parameter in our approach, we have used U in the range 6–9 eV. We also show the results obtained with the open-core treatment. In this case the f orbitals enter only through their spin-polarized density and the inter-site exchange is determined primarily by the BR mechanism. Notably, the open-core exchange parameters do not favor ferromagnetism for any of the compounds at any volume.

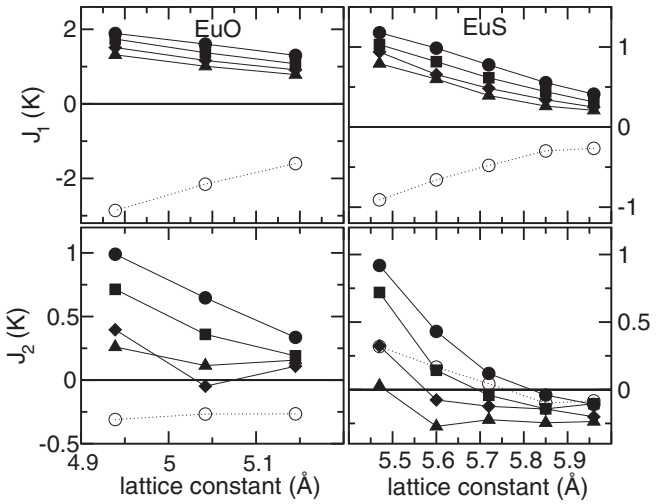

Fig. 1. The nearest-neighbor J_1 and next-nearest-neighbor J_2 effective exchange parameters in EuO and EuS as functions of the lattice constant calculated for different values of U (circle—6 eV, square—7 eV, diamond—8 eV, triangle—9 eV, the lines serve as guides for eye). The open symbols mark the results obtained with the open-core treatment.

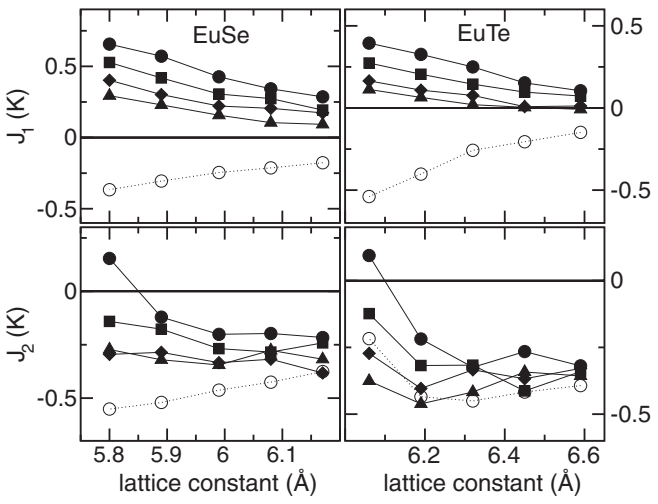

Fig. 2. The same as in Fig. 1 for EuSe and EuTe.

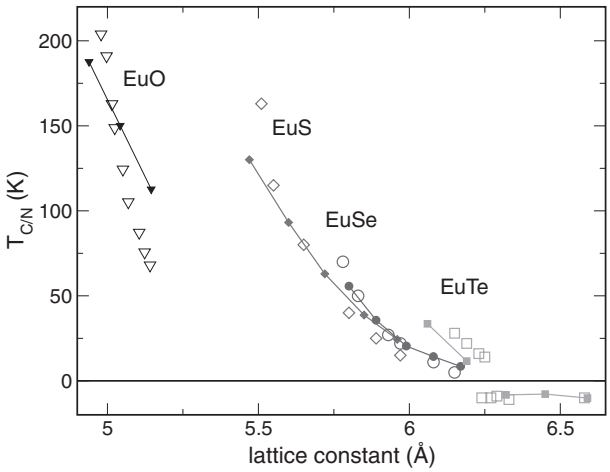

Fig. 3. The magnetic ordering temperatures calculated for $U = 6$ eV (lines+symbols) compared to the experimental values for EuO and EuS, EuSe, and EuTe.[24–26] (open symbols) The negative values indicate Néel temperature.

From the parameters of the Heisenberg Hamiltonian ordering temperatures were calculated using the result of the Tyablikov decoupling method[21,22]

$$(k_B T_C)^{-1} = \frac{3}{2S(S+1)} \frac{1}{N} \sum_{\boldsymbol{q}} [J(\boldsymbol{0}) - J(\boldsymbol{q})]^{-1}, \qquad (2)$$

where $J(\boldsymbol{q})$ stands for the lattice Fourier transform of the effective exchange parameter. For EuTe we have calculated the Néel temperature using a generalized equation (2).[23] The ordering temperatures as functions of lattice constant are shown in Fig. 3 and compared to the experimental data of Goncharenko and Mirebeau[24,25] (see also refs. 3, 4, 27). The trend of weakening ferromagnetism in favor of antiferromagnetism when going from oxide to telluride is well reproduced as well as the effect of pressure. Both experimental and numerical data indicate that the effect of different ligand substitution cannot be reduced to a volume effect (compare EuS and EuSe at the same lattice constant). While quantitatively the results are rather sensitive to the value of U (the literature value of $U \approx 6$–7 eV[28] gives the best agreement throughout the series) the qualitative features are common to the whole range of U from 6 to 9 eV.

Based on the fact that in the type II antiferromagnetic structure the first neighbor exchange is frustrated and thus the mean-field Néel temperature is proportional to J_2, Goncharenko and Mirebeu concluded that for EuTe J_2 is pressure independent while J_1 exhibits a non-linear increase with the applied pressure. In their scenario the transition from low-pressure antiferromagnetic groundstate to high-pressure ferromagnetic groundstate is solely due to the increase of J_1. Our calculations provide a different picture. In all studied cases, we find more or less linear dependence of J_1 on the lattice parameter. On the other hand J_2 exhibits quite non-linear behavior, which in the case of EuTe translates to being almost constant at low pressures and increasing rapidly at higher pressures and thus significantly contributes to stabilization of the ferromagnetic state.

The success of the LDA+U functional in describing the trend across the EuX series as well as capturing the pressure

dependence of the ordering temperature indicates that the relevant coupling mechanisms are well accounted for. Several observations can be made. Perhaps the most important one is the crucial role of f-ligand hybridization for the ferromagnetism of EuX compounds. In Fig. 4 we show the majority-spin bandstructure (i.e., the f band corresponds to the lower Hubbard band) for EuSe. The f complex consists of four flat bands and three bands with sizable bandwidths of about 1 eV, the origin of which is the Eu $4f$–Se $4p$ mixing. We have used the procedure of Ku[12] to calculate the Wannier functions corresponding to the occupied f bands. In Fig. 5 the Wannier orbital (one of the three symmetry related orbitals) which gives rise to the dispersive f band is shown. The lobes at the Se sites clearly demonstrate the sizable f–p mixing, which leads to a large contribution to the inter-site coupling of the kinematic processes, involving hopping to and from the f states. Sensitivity of the exchange parameters to the value of U is related to the kinematic contribution, which depends on the energy of the f bands relative to the rest of the spectrum (compare to metallic Eu,[20] where the value of U does not matter).

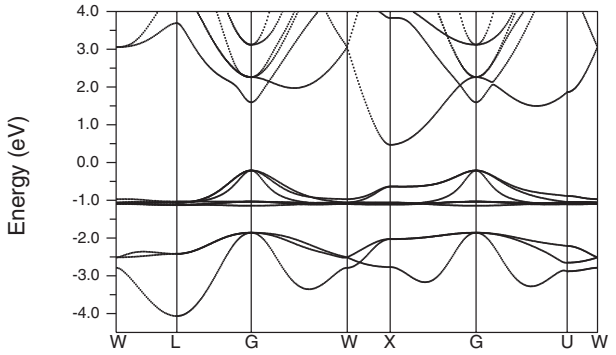

Fig. 4. Majority spin bandstructure of EuSe obtained with $U = 7$ eV at ambient pressure. The valence bands have dominant Se $4p$ character while the conduction bands are mostly Eu d and s states. The occupied f states are located inside the semiconductor gap.

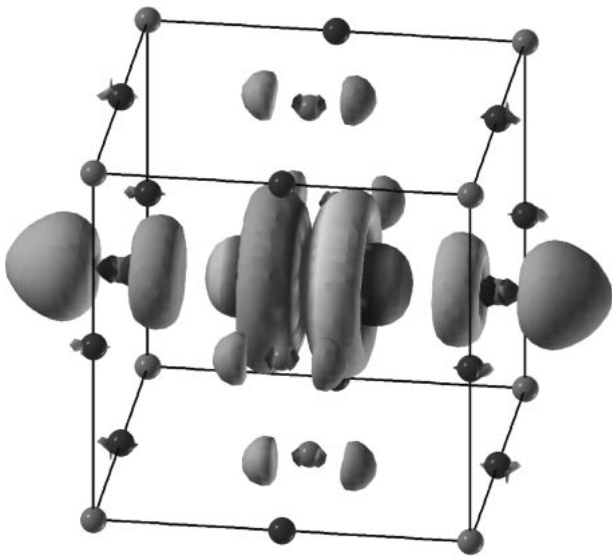

Fig. 5. The Wannier orbital corresponding to the dispersive f band represented by isosurface of $|\phi(r)|$. The large lobes on Se sites on the axis of the orbital as well as smaller lobes on the four remaining nearest-neighbor Se sites indicate a rather strong Eu $4f$–Se $4p$ mixing. There are two other symmetry related orbitals on the same site.

The open core results account only for the effect of spin polarization (intra-atomic f–d exchange). The BR coupling is the leading mechanism of this type. Our calculations show that the BR contribution to J_1 is anti-ferromagnetic with magnitude increasing with pressure. The positive sign of J_1 is due to overcompensation by the kinematic effects. The effect of the kinematic processes on J_2 is smaller that for J_1.

The kinematic processes include direct exchange between the overlapping Wannier orbitals, hopping from f to the valence states (indirect exchange) and hopping from occupied to unoccupied f-Wannier orbitals (superexchange). The role of the latter can be assessed by a simple model calculation. Adding an auxiliary orbital-dependent potential, which acts on the unoccupied f orbitals only, we can control the effective Hubbard splitting without affecting the energy of the occupied f's. Obviously such a term does not enter the groundstate energy directly, but only through the mixing of the minority-spin f bands with the occupied bands. In Fig. 6 we show the energy difference between the ferromagnetic and type II antiferromagnetic groundstates as a function of the energy separation between the occupied and unoccupied f bands. Apparently the auxiliary potential has a sizable effect consistent with $1/U_f$ dependency of the superexchange interaction indicating a non-negligible role of the upper Hubbard band for the inter-site coupling.

Now we summarize. Our calculations show that accounting for inter-atomic repulsion using the LDA+U method provides a reliable description of effective exchange coupling in ferromagnetic insulators with localized moments. The trend favoring ferromagnetism for lighter chalcogenides as well as the pressure induced antiferro-to-ferromagnetic transition in EuTe are well captured. The pressure dependences of the magnetic ordering temperatures, which correspond well to the experimental observations, are connected to distinct under-pressure behavior of the exchange parameters J_1 and J_2. We find the mixing of f

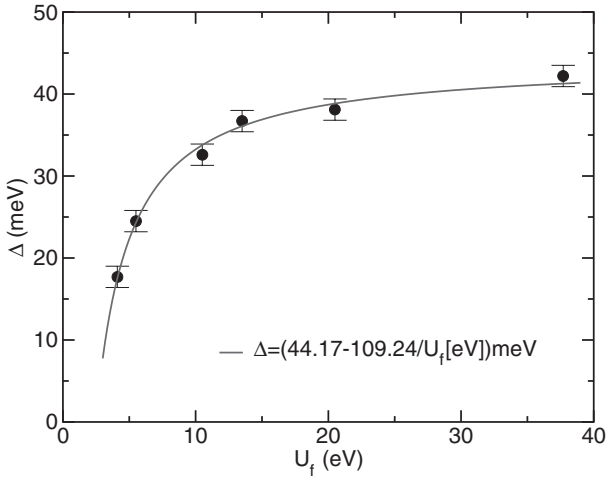

Fig. 6. Difference between the groundstate energies of type II antiferromagnetic and ferromagnetic structures as a function of the splitting U_f between the occupied and unoccupied f bands obtained with auxiliary potential on top of LDA+U with U of 7 eV. U_f of 11 eV corresponds to zero auxiliary potential.

states with the ligand states to be crucial for ferromagnetic ordering in Eu chalcogenides.

Acknowledgements

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