Mechanism of magnetic exchange interactions in europium monochalcogenides

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Using a combination of local-spin-density and Hubbard 1 approximations, we study the mechanism of exchange interaction in EuX (X = O, S, Se and Te). We reproduce known experimental results with regard to bulk modulus, critical pressure for structural phase transition, magnetic ordering temperature, spin-wave dispersions, as well as momentum- and temperature-dependent band shift. Our numerical results show a pressure-induced competition between the hybridization-enhanced exchange interaction and Kondo-like coupling in EuO. Possible ways to enhance Tc are discussed.

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Europium monochalcogenides EuX (X = O, S, Se, and Te) have been studied extensively since 1961. As the only known examples of Heisenberg ferromagnetism in nature, EuO and EuS have Curie temperatures (Tc) of 69.15 and 16.57 K, respectively. On the other hand, EuSe has a complex magnetic structure at low temperatures, and EuTe is antiferromagnetic. It was found that doping of EuO by electrons results in 100% spin polarization of the conduction electrons, and the material has a colossal magnetoresistance effect stronger than famous manganites. Moreover, EuO has been integrated with Si and GaN, making it very attractive for spintronic applications. Very recently, strain-induced ferroelectricity had been predicted, thus strained EuO films may provide a new route toward high-temperature multiferroicity. Therefore, there has recently been renewed interest in these systems.

Finding ways to raise the Tc up to room temperatures in EuX is of both fundamental and technological importance, therefore many previous studies of their magnetic exchange mechanism have appeared in the literature. However, despite the tremendous efforts that have been devoted to these “textbook” FM’s, there still exist several controversies with regard to their magnetic properties: (i) It is widely accepted that the 5d band is important for exchange interaction (El), but the role of the 6s band of Eu and the 6p band of anions is not clear. It had been suggested that the superexchange via the 6p orbital of anions is negligible due to its small hybridization with the localized 4f orbital. But, the importance of p-f hybridization has been demonstrated by a theoretical Wannier function analysis, and has also been confirmed by a very recent experimental observation of the momentum-dependent temperature-induced band shift. Noticing the considerable p-f hybridization, one naturally would conclude that the f-p-f superexchange interaction should be important. It has even been suggested that the f-p superexchange is the leading factor that induces the change of sign in the next-nearest-neighbor El when moving from EuO to EuTe. However, contrary to these viewpoints, a recent x-ray-absorption spectroscopy analysis indicates that the anion p states play only a minor role. There are also works suggesting that the 6s band of Eu plays a dominant role.

(ii) Pressure and epitaxial strain can vary the Tc of EuX significantly. The Tc of EuO will increase with pressure and reach a maximum at about 21 GPa. It is well known that high pressure can induce an electronic collapse for rare-earth compounds, thus originally it had been suggested that the abnormal behavior of Tc is due to a valence instability (i.e., 4f7→5d1 to 4f5→5d3 transition). However, this viewpoint was challenged by subsequent experiments. There are also several ab initio works discussing the effect of pressure or strain, however their scheme [local-spin-density approximation (LSDA) or LSDA+U] limits them to discussing the possible valence instability at high pressure. (iii) Tc can be significantly enhanced by electronic doping, but the exact reason is still unknown.

In this work, we address the controversial issue of the magnetic exchange mechanism in EuX using a recently developed linear-response approximation as well as the constrained orbital hybridization approach. We reproduce the major experimental results including the bulk modulus, critical pressure for the structural phase transition, the magnetic ordering temperature, spin-wave dispersions, as well as the temperature- and moment-dependent band structures. Our constrained orbital calculation allows us to provide conclusive theoretical insights into various contributions to magnetic exchange interactions, while the LSDA+Dynamical Mean Field Theory (DMFT) scheme allows us to study the effect of pressure and possible electronic collapse.

Our electronic structure calculations with the full-potential linearized-muffin-tin-orbital (LMTO) method are done using the LSDA for the conduction electrons and atomic Hubbard 1 (Hub1) self-energy to approximate the localized nature of the Eu f electrons with the on-site Coulomb interaction parameters U = 7 eV and J = 1.2 eV, which have been used well. We also check that our results are robust within the reasonable range of U’s from 6 to 9 eV. We use the standard double-counting correlation suggested by Anisimov et al., which works very well for the El of several systems. With the electronic structure information, one can evaluate the EI in the Heisenberg Hamiltonian Hij = JijSi·Sj based on a magnetic force theorem that evaluates linear response due to rotations of magnetic moments.

The ground-state properties predicted by LSDA+Hub1 calculation including magnetic moments and energy gaps are found to be in agreement with experiment. Moreover, the obtained exchange splitting of the conduction band is...
about 0.65 eV, which is close to the experimental value 0.60 eV. Since with increasing pressure EuX will change from rock-salt to CsCl-type structure,26,27 we perform calculations for both NaCl- and CsCl-type structures for a number of different volumes. The total energy versus volume, \( E(V) \), curves were fitted by the Murnaghan equation of state (EOS). The crystal phase stability is analyzed by evaluating the enthalpy \( (H = E + PV) \), and the phase-transition pressure \( P_\text{c} \) is evaluated from crossing the \( H(P) \) curves. It is found that the LSDA alone significantly overestimates the values of bulk modulus \( B_0 \) and \( P_\text{c} \). After inclusion of the correlation effects, the LSDA+Hub1 calculation reproduces the experimental values successfully. This is shown in Table I. We also perform the GGA+Hub1 (where GGA denotes generalized gradient approximation) calculation, and we display the numerical data in Table I. Compared with the LSDA+Hub1, the LSDA+Hub1 gives a large bulk modulus, but the difference is quite small. We also confirm that the parameters of the EOS and \( P_\text{c} \) are not sensitive to \( U \)’s in the range 6–9 eV.

We subsequently evaluate the EI as the integral over the \( q \) space using an \((8,8,8)\) grid.33 Our linear-response approach allows us to evaluate \( J \)’s in real space, and the numerical results confirm that they are short-ranged with the magnetic coupling further than the second nearest neighbor to be almost equal to zero. As shown in Table II, our \( J_1 \) (nearest-neighbor EI) and \( J_2 \) (second-nearest-neighbor EI) are smaller than the values extracted from neutron-scattering experiment,40 while they are quite close to the thermodynamic data.41 Consistent with the experiment, we obtain that moving from EuO to EuTe, the strength of \( J_1 \) decreases while \( J_2 \) changes from ferromagnetic (FM)- to antiferromagnetic (AFM)- like. For EuSe, the magnitude of \( J_1 \) is smaller than \( J_2 \), but notice that for the rock-salt structure, the number of nearest neighbors and second nearest neighbors is 12 and 6, respectively, so there is a competition resulting in a complex magnetic structure at low temperatures.2 For EuTe, both \( J_1 \) and \( J_2 \) become AFM-like and the ground state changes to AFM.2 Using the mean-field approximation, we also estimate the magnetic ordering temperature. The agreement between the experimental and calculated \( T_\text{c} \) is good, with the expected overestimate of the mean-field value.

![FIG. 1. (Color online) Calculated spin-wave dispersions of EuO along major high-symmetry directions. As shown in Fig. 1, our numerical data are found to be in good agreement with the neutron-scattering measurements,40 which are done on polycrystalline samples, thus accessing direction-averaged spin-wave excitations.](image-url)
the \( \text{p} \) band can only come from the hybridization with the \( \text{4f} \) band of Eu. Thus, we confirm that the \( \text{f-p} \) hybridization is not negligible.\(^{18,22}\)

To further understand the effect of the \( \text{f-p} \) hybridization and to make comparisons with recent angle-resolved photoemission spectroscopy (ARPES) data\(^{13}\) regarding the temperature- and moment-dependent Eu-4\(f\) and O-2\(p\) band shifts, we perform the LSDA+Hub1 calculation at temperatures below and above \( T_c \). In agreement with the experiment,\(^{13}\) our calculation shows that at low temperature (5 K), the O 2\(p\) state has considerable spin splitting, as shown in Fig. 2(a). With increasing temperature, the spin splitting decreases and eventually becomes zero when temperature becomes above \( T_c \), as shown in Fig. 2(b). We also reproduce the temperature- and moment-dependent Eu 4\(f\) band shift. As shown in Fig. 2, our calculation predicts that from low temperature to high temperature, the top of the Eu 4\(f\) band at the \( \Gamma \) point and the \( X \) point have a shift of 0.35 and 0.18 eV, respectively. These values are in good agreement with the experimental values of 0.32 and 0.07 eV.\(^{13}\)

Since the \( \text{f-p} \) hybridization is important, and noticing that EuX has a NaCl-type structure with the anion located between two Eu atoms, one would then naturally expect that the \( 4f\)-2\(p\)-4\(f\) superexchange should play an important role. However, our values of \( J_1 \) and \( J_2 \) extracted from the LDA+Hub1 calculation turned out to be very small (e.g., for EuO, both \( J_1 \) and \( J_2 \lesssim 0.001 \) K) as compared to the LSDA+Hub1 result shown in Table II. This emphasizes the fact that the major part of the exchange process is going through virtual excitations to the conduction band. If one does the same test for Mott insulating oxides\(^{33}\) and cuprates,\(^{38}\) where the 3\(d\)-2\(p\)-3\(d\) superexchange dominates, one finds that the results of the calculations with LDA+Hub1 and LSDA+Hub1 are indeed similar to each other. This clearly indicates that the spin polarization in the conduction band is essential to explain the magnetic behavior of EuX. One can thus conclude that despite considerable \( \text{f-p} \) hybridization, the \( \text{f-p} \) superexchange is a second-order effect and can be ignored for those systems.

It is well known that the strength of hybridization between two orbits is strongly dependent on their energy difference. We thus made a calculation of \( J \)’s with an artificially constrained external potential applied to a particular orbital to adjust its energy level and consequently vary the hybridization.\(^{34}\) This constrained orbital-hybridization calculation\(^{34}\) allows us to exactly analyze all possible virtual exchange mechanisms directly. It turns out that a downshift of the \( 5p \) orbital for Eu or \( s \) orbitals for anions does not affect the exchange constants. On the other hand, they are sensitive to the position of 5\(d\) states of Eu: even a small up-shift here decreases the strength of \( J_1 \) and \( J_2 \) due to the increase of band separation between 4\(f\) and 5\(d\) and following 5\(d\)-4\(f\) dehybridization. Shifting the 6\(s\) level of Eu affects the \( J_1 \) and \( J_2 \) as well, although the effect is smaller than for 5\(d\). Since anion atoms are between second-nearest-neighbor Eu ions, it is natural to expect that \( J_2 \) should depend on the position of the 2\(p\) band. Our numerical calculation, on the other hand, shows that both \( J_1 \) and \( J_2 \) are almost insensitive to the shift of the \( p \) band of anions. This result is consistent with our previous conclusion on the smallness of \( 4f\)-2\(p\)-4\(f\) superexchange. For example, we upshift the 2\(p\) level of O in EuO by 1.0 eV, but \( J_1 \) and \( J_2 \) are almost unchanged. We also perform a constrained orbital-hybridization calculation for EuS, EuSe, and EuTe, and the results are almost exactly the same as that of EuO. So, our calculation clearly rules out possible contributions

![FIG. 2. (Color online) Temperature-dependent LSDA+Hub1 band structure of EuO. (a) Temperature is 5 K. The red and black lines denote the majority- and minority-spin state, respectively. (b) Temperature is above \( T_c \). Arrows show the experimental spin splitting in the 2\(p\) O band and the momentum-dependent shift for the top of the 4\(f\) Eu band.](image)

![FIG. 3. (Color online) Pressure dependence of the magnetic transition temperature of EuO experimental (triangle),\(^{28}\) theoretical (circles), as well as pressure dependence of Kondo coupling \( J_K \).](image)
and the only enhances the hybridization between the conduction band important for the ferromagnetism of EuO. This is consistent one can conclude that 4
Since 4
exchanging interaction.18 Excluding the hybridization between the 4
second-nearest-neighbor coupling J
second-nearest-neighbor, J
exchange couplings as well as magnetic transition temperature T
for EuO. The unit is K.

| U   | J_1 | J_2 | T_c |
|-----|-----|-----|-----|
| 6 eV| 0.65| 0.06| 91  |
| 8 eV| 0.57|−0.04| 72  |

illustrated in Fig. 3. Our calculation shows that pressure will enlarge the bandwidth, decrease the band gap, and there is considerable density of states at the Fermi level when pressure is larger than 10 GPa, as shown in Fig. 4. But even for pressures as high as 40 GPa, the calculated exchange coupling is still short-ranged. The LDA+U can give reasonable EI for the Mott insulator,33,38 but our LSDA+Hub1 scheme31 allows us to check the possible pressure-induced electronic collapse in EuO.29,32 The 4f occupation from LSDA+Hub1 does not change significantly up to 40 GPa, thus the abnormal behavior in the T_c-P curve is not due to the valence transition, which may happen at higher pressure. Based on the LSDA+Hub1 scheme, on the other hand, we estimate the on-site Kondo coupling strength J_K using a method described by us earlier.42 As shown in Fig. 3, J_K increases rapidly above 20 GPa, which results in not only Kondo-like screening but also in an AFM-like intersite coupling in the second-order perturbation theory with respect to J_K. Both effects will suppress the T_c, as is seen experimentally.28

We have finally studied the effect of electron doping on T_c for EuO using the virtual crystal approximation. Our calculation shows that there are two competing factors: since the bottom of the conduction band consists mainly of the majority spin, the doped electron will enter the spin-polarized manifold, and this results in the onset of moment in the 5d band, which will enhance T_c slightly. On the other hand, free carriers will induce the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction, which will suppress T_c. We indeed find that our theoretical T_c first increases as a function of doping and then goes through a maximum, in agreement with the experimental trend.23 It is interesting to notice that a previous rigid band calculation also gives similar results.22 So we conclude that a combination of both doping and pressure can be an efficient way to reach higher T_c in those systems.43

We also check the effect of Coulomb U, and show the results of U = 6 and 8 eV for EuO in Table III. It is found that reducing U will enhance not only J_1 but also J_2. But as shown in Table III, the EI and the numerical T_c are not sensitive to the value of U, and our results are robust within the reasonable range of U’s from 6 to 9 eV. We also confirm that replacing LSDA by GGA does not change our conclusion. For example, for EuO, the J_1, J_2 from the GGA+Hub1 calculation (with U = 7 eV) are 0.58 and 0.06 K, respectively, which are close to the LSDA+Hub1 results given in Table II.

In summary, based on the recently developed theoretical scheme, we studied the magnetic EI in EuX and addressed several controversies. We showed that the 5d-4f and 6s-4f

![Figure 4](https://example.com/figure4.png)

**FIG. 4.** (Color online) Pressure dependence of the density of state EuO. (a) P = 0.0 GPa; (b) P = 5.0 GPa; (c) P = 10.0 GPa; (d) P = 40.0 GPa.

from the 4f-p, 5d-p, and 6s-p hybridization, and even the second-nearest-neighbor coupling J_2 is mediated by the 6s and 5d electrons.

Using an open-core scheme, Kunes et al. also estimate exchange interaction.18 Excluding the hybridization between the 4f orbitals of Eu and the rest of the system, open-core calculation fail to reproduce the ferromagnetism of EuO.18 Since 4f-2p-4f superexchange gives antiferromagnetic EI, one can conclude that 4f-5d and 4f-6s hybridization are important for the ferromagnetism of EuO. This is consistent with our conclusion.

We have also studied the effect of pressure, which not only enhances the hybridization between the conduction band and the f states, but also increases the crystal-field splitting between 5d t_2g and e_g states of Eu and reduces the energy gap between the t_2g and the 4f states.24 Consistent with the experiment, our theoretical results show that pressure enhances the exchange constants and T_c of EuS, while it changes the ground state of EuSe and EuTe from AFM to FM. However, for EuO our numerical data agree with the experiment only at the low-pressure region, while for pressures larger than 20 GPa, our calculated Curie temperature still rises but the experimental one decreases.28
indirect exchange is dominant while the p electrons of anions make no contribution to it. We also suggested that the abnormal behavior of pressure-dependent $T_c$ in EuO is due to an increase in Kondo-like coupling in the metallic phase. Our results and conclusions are robust within the reasonable range of $U$’s (6−9 eV).

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