Anisotropic Exchange Interaction between Non-magnetic Europium Cations in Eu$_2$O$_3$

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Abstract

The electronic structure of the cubic and (high pressure) hexagonal phases of Eu$_2$O$_3$ have been investigated by mean of full potential linearized augmented plane wave calculations, within the LDA+$U$ method. For the cubic phase, the comparison between ferromagnetic and antiferromagnetic calculations shows that the exchange interaction is very weak and is therefore expected to have a negligible effect on the magnetic susceptibility. This is consistent with the experimental behavior of the susceptibility of solid solutions of Eu$_2$O$_3$ into A$_2$O$_3$ (A=Y, Lu, Sc). The calculations performed for the high pressure hexagonal phase, on the other hand, show that there is an antiferromagnetic exchange interaction between nearest neighbor Eu ions, which should have a sizeable effect on the susceptibility. Our results allow us to discuss the existing theories.
I. INTRODUCTION

Rare earth compounds present a large variety of interesting magnetic behaviors, due to their partially filled $f-$shells. Trivalent europium compounds, in particular, offer an unique chance of observing exchange coupling between ”non-magnetic” ions. The ground state of Eu$^{3+}$ ($4f^6$) ions is $^7F_0$, with a total angular moment $J = 0$ resulting from both $L = S = 3$ (in atomic units), however, spin-dependent exchange effects are present. Furthermore, Eu ions show a substantial admixture of higher energy $J = 1$ states, which contributes significantly to their susceptibility ($\chi$).

Eu$_2$O$_3$ is the prototypical compound of this family, its magnetic susceptibility has been experimentally investigated in detail$^{1-3}$. The first attempt to explain its magnetic behaviour was made by Huang and Van Vleck$^4$, who showed that the susceptibility of Eu$_2$O$_3$ is larger than the corresponding susceptibility of the free Eu$^{3+}$ ion, because the energy levels of the excited $^7F_1$ states are modified by the crystal field, and pointed out the dominant contribution of the Van Vleck component of the susceptibility, $\chi_{VV}$. An explicit calculation of the susceptibility from energy levels obtained by optical spectroscopy measurements$^{5,6}$ was performed in this work. However, the resulting $\chi$ turned out to be smaller than the experimental value, and so the remainder was attributed entirely to the exchange coupling among Eu$^{3+}$ ions$^4$.

This viewpoint has been challenged on the basis of measurements of $\chi$ in solid solutions of Eu$_2$O$_3$ into A$_2$O$_3$ (A=Y, Lu, Sc)$^{2,3,7,8}$, where Eu atoms are diluted. As the number of Eu nearest neighbors is reduced, the total interatomic exchange interaction should decrease and become negligible at small concentration of Eu, and the total susceptibility should decrease along with it. The experimental susceptibility (per mole of Eu), however, does not decrease in the full range of investigation (i.e. up to 10 % of Eu$_2$O$_3$ into A$_2$O$_3$)$^{2,3,7,8}$, suggesting a negligible role of the exchange interaction. This decrease of the exchange component on dilution might be due to compensation caused by change in the crystal field splitting of Eu sites in A$_2$O$_3$ in comparison with Eu$_2$O$_3$; this explanation, however, is not supported by optical measurements of the energy levels$^{6,9,10}$. Yet another explanation has been proposed based on the distribution of Eu atoms in the two available sites (symmetry $S_6$ and $C_2$) of the cubic bixbyite structure of these oxides$^{11}$. The decrease of the exchange component on dilution might be compensated by a preferential occupation of the $S_6$ site in the solid
solution; the Van Vleck susceptibility of this site is larger because the $^7F_1$ levels are lower in energy in comparison with the $C_2$ site. This preferential occupation, however, was not found in X-ray diffraction$^2$, and Mössbauer spectroscopic studies$^{3,12}$.

A further criticism to viewpoint that the exchange coupling guides the physics of susceptibility also comes from the calculations of the Van Vleck susceptibility performed by Caro et al.$^{13}$ These authors determine the crystalline field parameters starting from the experimental values of the energies of the excited states, and the matrix elements of the Van Vleck susceptibility were calculated using this potential and the atomic functions. The susceptibility calculated accordingly agrees well with the experimental one$^1$, validating a picture in which the exchange coupling should be negligible. We should mention here, however, that the optical data used by Caro et al. have been subsequently corrected by more recent measurements$^6$.

Therefore, the question of whether the excess of susceptibility may be entirely attributed to the exchange coupling is still open. Absence of long range magnetic order does not allow direct evaluation of the exchange coupling constants starting from experimental data and so a theoretical determination of these parameters by means of *ab-initio* calculations is highly desirable for understanding the behaviour of susceptibility in the material. Remarkably, to the best of our knowledge, there is no experimental evidence in the literature of exchange coupling between $J = 0$ ions making the "excess" of susceptibility of Eu$_2$O$_3$ a novel puzzle where *ab-initio* calculations have the potential of providing interesting evidence towards the solution of this puzzle.

From the theoretical point of view, rare earth compounds represent a challenge for modern electronic structure calculations. Their multiplet structure cannot be explained on the basis of a single Slater determinant. The traditional density functional theory (DFT) methods with local/semi-local approximations to the exchange correlation functionals fail to describe their correlated nature and result into a qualitatively wrong picture with flat $f$ bands accumulated around the Fermi level ($E_F$). To overcome these problems the LDA+$U$, and the self-interaction corrected local density approximation (SIC-LDA) methods have been widely used in the past. Focusing entirely Eu$^{3+}$ compounds, LDA+$U$ calculations were performed by Johannes and Picket$^{14}$ on EuN and EuP, and by Deniszczyyk et al.$^{15}$ on EuF$_3$ and EuCo$_2$X$_2$ ($X=$Si,Ge). SIC-LDA calculations were performed on several rare earth oxides by Petit *et al.*$^{16,17}$. All these works show that the correct physics in these materials can be
treated within the LDA+U (SIC-LDA) method. Hence in the present work we compute the
electronic and magnetic structure of Eu$_2$O$_3$ using the LDA+U approach. Eu being one of
the heavy rare earths, the use of an all-electron method is almost essential— in the present
work we employ full-potential linearized augmented plane wave (FLAPW) method$^{18}$ imple-
mented within the Elk code$^{19}$. From the corresponding results we obtain very small values
for the exchange coupling constants in cubic Eu$_2$O$_3$, which imply a negligible contribution
of exchange to the magnetic susceptibility.

II. COMPUTATIONAL DETAILS

For the cubic structure a \textbf{k}-point mesh of $2 \times 2 \times 2$ is used for the Brillouin zone (BZ)
integration; given the large dimension of this system (40 atoms per unit cell) and the insu-
lating character of the compound, this choice is a reasonable compromise between accuracy
and computational load. For the (smaller unit cell) hexagonal structure, a mesh of $4 \times 4 \times 4$
is used. Spin-orbit coupling has been included in all self-consistent calculations. We have
used the fully-localised-limit of the LDA+U method$^{20}$. The values of $U$ for Eu $f$-states and
$J$ are chosen to be 7 eV and 0.75 eV respectively$^{21}$.

III. CRYSTAL AND MAGNETIC STRUCTURE

Eu$_2$O$_3$ crystallizes in the cubic bixbyite structure (shown in Fig. 1) with space group $T'_h$
($Ia\overline{3}$); it corresponds to a bcc lattice with a primitive cell of 40 atoms$^{22}$. Eu atoms occupy
the two inequivalent Wyckoff sites 8a (site symmetry $S_6$) and 24d (site symmetry $C_2$), with
a distorted octahedral coordination of O atoms (in the 48e sites). The experimental lattice
constant for Eu$_2$O$_3$ is $a = 10.859$ Å$^{11}$. The bixbyite structure is derived from a defective
cubic fluorite structure, which corresponds to a simple cubic lattice with 10 atoms and half
value of the lattice constant. Eu atoms occupy the positions of a $fcc$ lattice; the defective
structure is obtained by removing two O atoms at 1/4 and 3/4 of the body diagonal. Due
to the large number of atoms in the unit cell in the bixbyite structure, Ref. 16 used this
smaller, defective fluorite unit cell. In order to compare our results with this work, we have
also performed calculations within the defective fluorite unit cell.

In order to evaluate the magnetic exchange coupling constant, the band calculations
FIG. 1: (Color online) (a): Spin structure of the Er$_2$O$_3$ determined using neutron diffraction method. (b): Full structure of cubic Eu$_2$O$_3$. (c) O coordination around Eu $S_6$ and (d) O coordination around Eu $C_2$ sites.

need to be performed with different configurations of the Eu spins. Experimentally, Eu$_2$O$_3$ does not have a long range magnetic order; thus as a starting point we have used the spin configuration of isostructural Er$_2$O$_3$ compound (see Fig. 1). This spin configuration also turns out to be a stable for Eu$_2$O$_3$ in our calculations. However, in this Er$_2$O$_3$-like configuration the sum of the scalar products of the spin of one ion with its nearest neighbors (NN) spins is always zero, which does not allow for a determination of the NN coupling within a Heisenberg model. In order to obtain a positive sum of scalar products one half
of the spins of the C$_2$ sites have been reversed relative to the Er$_2$O$_3$-like configuration such that all the spins point along the positive direction of the cartesian $x$, $y$ or $z$ axes. In order to compute the exchange couplings we have also studied other ordered phases— to obtain a ferromagnetic (FM) like state where the direction of the S$_6$ sites is chosen to maximize the number of positive components, which may be written as (1,1,1), (1,1,-1), (-1,1,1) and (1,-1,1) in the appropriate units; we obtain in this way a positive sum of scalar products for a S$_6$ or C$_2$ europium with its twelve NN. In order to obtain an antiferromagnetic (AFM) like state, the S$_6$ spin direction is reversed; the sum of products is then negative.

Eu$_2$O$_3$ undergoes a structural transition under pressure from the cubic to the hexagonal phase (space group $P\bar{3}m1$)\textsuperscript{21} (see Fig. 2), which has 5 atoms per primitive cell (Eu atoms on the Wyckoff positions 2$d$ and O atoms on the 2$d$ and 1$a$ positions)\textsuperscript{22}. The transition begins at 5 GPa and completes at 13 GPa. At this pressure, the lattice parameters are $a = 3.738$ Å and $c = 5.632$ Å\textsuperscript{24}. For this structure, the band calculations are performed with FM as well as AFM spin configuration; in the AFM configuration (shown in Fig. 2), the two cations of the primitive cell have antiparallel spin orientation.
IV. RESULTS AND DISCUSSION

Before calculating the electronic structure a full structural relaxation is performed and the results are compared with the available experimental data. Due to the large size of the bixbyte unit cell, these calculations for the cubic phase have been performed using the defective fluorite cell with a FM configuration. The volume dependence of the energy was fitted to the third order Birch-Murnaghan equation of state\textsuperscript{25}. We obtain an equilibrium lattice constant $a_0 = 5.311$ Å, 2% smaller than the experimental value (consistent with the typical error in LDA or LDA$+U$ calculations). The calculated bulk modulus $B_0 = 140$ GPa, is also in good agreement with the experimental value of $B_{0,\text{exp}} = 145 \pm 2$ GPa\textsuperscript{24} (measured in the bixbyte phase).

As mentioned earlier, the first problem in the study of this system is the choice of spin configuration, since experiments do not report any magnetic order in this $J = 0$ system. We therefore assume as a starting (reference) configuration the experimental magnetic structure of isostructural Er$\textsubscript{2}$O$_3$. In this configuration, spin moments are not collinear, and the two crystallographic sites have totally different directions\textsuperscript{23}: while the $S_6$ moments are directed along the diagonal axes, $C_2$ sites direct their spin along the Cartesian axes (see Fig. 1).

The band structure of cubic Eu$\textsubscript{2}$O$_3$ with the Er$\textsubscript{2}$O$_3$-like spin configuration is shown in Fig. 3. The red squares and blue circles in Fig. 3 represent the importance of the contribution from Eu 4$f$ states, for sites $S_6$ and $C_2$ respectively. The general features of Eu$\textsubscript{2}$O$_3$ bands can be readily explained as follows: the O $p$ states are responsible for the bands located in the energy region between $\approx -3$ eV and the Fermi level (which is the zero of energy in all our plots). The Eu$^{3+}$ ions are in a 4$f^6$ configuration, which leaves an empty 4$f$ orbital per atom in the majority spin channel. Minority 4$f$ states, on the other hand, are completely empty and form the group of bands from +4 to +8 eV. Occupied majority spin 4$f$ states form the group of 24 bands sitting from -5.5 to -3 eV and their splitting into four separated groups is similar to the situation in Eu pnictides\textsuperscript{14}. This splitting in the case of Eu pnictides was interpreted as an effect of the intra-atomic anisotropic exchange–a test calculations based on LDA resulted into a single narrow f-manifold indicating that splitting cannot originate from crystal field effects, making the complex exchange effect in this open shell system the most likely explanation. The large distance between (equal spin) filled and empty counterparts derives from the large $U$ value for localized 4$f$ states. The empty
FIG. 3: (Color online) Band structures of cubic Eu$_2$O$_3$ along the symmetry directions of the Brillouin zone. Eu 4$f$ character is denoted by red squares and blue circles for the $S_6$ and $C_2$ sites respectively.

majority spin states lie around 2.3 eV above $E_F$. This electronic structure therefore reflects the electronic configuration of the Eu$^{3+}$ ions. All the 4$f$ bands have a negligible dispersion ($\approx 0.2$ eV), consistent with the localized nature of these orbitals.

For better understanding of the electronic states presented in Figs. 4 are the densities of states (DOS) of cubic Eu$_2$O$_3$ in the Er$_2$O$_3$-like spin configuration. Figs. 4 confirms the picture given above. In particular, the states from -3 eV to $E_F$ derive from O states, and hybridize only weakly with Eu states. Besides 4$f$ states, Eu’s most prominent contribution to the electronic structure is the 5$d$ states, mostly located in the conduction bands region above 4 eV. The narrow peaks from -5.5 to -3 eV and the structures above 4 eV are derived from filled majority and empty minority Eu 4$f$ states respectively. The peaks in the region $\approx 2 − 2.5$ eV above $E_F$ are predominantly Eu states (in particular, empty majority spin 4$f$ states), with a very small contribution from oxygen orbitals. The marginal Eu 4$f$- O 2$p$ hybridization indicates towards a small value of the NN exchange coupling.

Importance of the crystal field (CF) effects in this compound has been a subject of discussion in past. Optical measurements have been interpreted assuming that the $S_6$ and $C_2$ sites have a very different CF splitting. Our results support this interpretation (see Fig. 4) and show that the f states behave differently for the two sites– the lower symmetry of the $C_2$ site results in a larger subdivision of the 4$f$ peaks with occupied f states shifted 0.5 eV lower in energy compared to the occupied f-states with $S_6$ site symmetry. The unoccupied
f-states show a similar behaviour with $C_2$ site symmetry states moved higher in energy with respect to $S_6$ site projected $f$-states. This leads to $C_2$ site having a much larger energy gap between occupied and empty majority spin states as compared to $S_6$ site, which in turn implies different density matrices for the two sites. This difference can be related to the different expectation values of orbital momentum (to be discussed later).

In order to understand the exchange interaction in Eu$_2$O$_3$ we studied two further spin arrangements, refered to as FM and AFM configurations (we refer to Sect. III for their description). In Fig. 5 we compare the DOS for Eu$_2$O$_3$ in the FM and AFM configurations. It is clear that spin ordering affects the Eu states marginally and the corresponding DOS are almost identical. These results have consequences on the exchange parameters as the total energy difference between these two configurations is very small.

We have also calculated the expectation values of the quantum operators $L$, $S$ and $J$ for the two different sites. The quantization axes are different for the two sites: in the case of $C_2$ it points along the Cartesian axes, and in the $S_6$ site along the main cube diagonal. In units of $\hbar$ we obtain for the $S_6$ site $S_\alpha = 2.77$, $L_\alpha = -1.56$ and $J_\alpha = 1.21$. Our value of $S_\alpha$ differs from the expected value $S_\alpha = 3$ for the free ion probably because of the use of muffin-tin sphere for computing integrals, and also because of an incomplete spin polarization. In the case of the $C_2$ site, on the other hand, we get very different results: the components along the corresponding local quantization axes $\alpha'$ are $S_{\alpha'} = 2.41$, $L_{\alpha'} = -2.34$ and $J_{\alpha'} = 0.07$. In other words, the $J = 0$ ground state of Eu seems to be reproduced to a much larger extent. Again (consistent with experiments) we find very different behaviors for the two sites. We
should mention that our small value of $L_\alpha$ for the $S_6$ site is similar to the value $L_\alpha = -1.5$ obtained in EuN by Johannes and Pickett\textsuperscript{14}, who ascribed this result to an overquenching of angular momentum caused by an overestimated crystal field effect within DFT.

At this point it is interesting to compare the electronic structures of Eu$_2$O$_3$ and EuN\textsuperscript{14} (which crystallizes in the rocksalt structure and correspond to an Eu$^{3+}$ configuration). The general features of the band structures are quite similar, a part from obvious differences associated with the different ligand (the center of gravity of O 2$p$ states lies slightly deeper in energy). A qualitative difference exists in the properties of Eu$_2$O$_3$ and EuN: EuN is metallic in nature and this metallic character arises from partially occupied dispersed Eu 5$d$ bands, crossing the empty majority 4$f$ bands. On the other hand in case of Eu$_2$O$_3$ similar dispersed bands with Eu 5$d$ contribution exist but they also have a relevant interstitial character and lie above the empty majority 4$f$ bands; as a consequence, Eu$_2$O$_3$ turns out to be an insulator. It is interesting to notice that both in our calculations for the simplified structure suggested by Petit et al.\textsuperscript{16} and in their SIC calculations these bands cross $E_F$ and in contrast with experiments gives a spurious metallic character to Eu$_2$O$_3$. The origin of the difference in character between the bixbyte and the simplified structures lies in the relaxation around the vacancies, which is not allowed by symmetry in the latter. In fact, an inspection of the charge corresponding to these dispersed bands in the model structure shows that these bands derive from quantum states localized in the O vacancy sites.

Under pressure Eu$_2$O$_3$ undergoes a structural phase transition to a hexagonal phase (see
FIG. 6: (Color online) Band structures of hexagonal Eu$_2$O$_3$ in the primitive cell. Left panel: ferromagnetic (FM) state. Right panel: antiferromagnetic (AFM) state. Eu 4f character is denoted by red circles.

Fig. 2). Due to the very large computational load involved, the calculation of the transition pressure is out of the scope of the present investigation. However, we minimized the total energy of Eu$_2$O$_3$ in the hexagonal phase. The fitted energy minimum is at $V_0 = 67.62$ Å$^3$, and $B_0 = 180$ GPa. The calculated bulk modulus compares well with the experimental value $B_{0,exp} = 151 \pm 6$ GPa$^{24}$. As for the equilibrium volume, the experimental hexagonal volume is $V_{exp} = 68.15$ Å$^3$ when the transition is completed (at 13.1 GPa)$^{24}$. Using the theoretical bulk modulus, we arrive at an equilibrium volume at 13.1 GPa equal to 62.7 Å$^3$, which underestimates the experimental lattice constant by about 2.8% (which is typical of LDA based functionals).

In order to understand how pressure modifies the electronic structure of this compound, we have studied its properties in the hexagonal phase, at the lattice parameters corresponding to $P = 13.1$ GPa. The band structure of the hexagonal Eu$_2$O$_3$ is shown in Fig. 6 for both FM and AFM configurations. The general features of the bands are similar to the cubic phase; hexagonal Eu$_2$O$_3$ is a semiconductor, with a gap of 2.3 eV between valence and unoccupied 4f band, and a gap of 4.1 eV between valence and conduction band. This semiconducting behaviour is in agreement with the experimental optical and transport properties of Eu$_2$O$_3$. In contrast to the cubic phase, in the hexagonal phase the dispersed band with the minimum around 3.5 eV at the Γ point are not present. This difference may be related to the fact that the hexagonal structure has no vacancies in the atomic O positions ruling out the possibility of having bands with a large interstitial character.

The total DOS of cubic and hexagonal Eu$_2$O$_3$ are presented in Fig. 7. While the structure
of levels is similar, the O 2p states have larger bandwidth and overlap with the occupied Eu 4f manifold. This increase of the O 2p bandwidth is clearly a consequence of the compression O atoms experience under pressure. Also, the exchange-related splitting of the 4f levels is different in the cubic and hexagonal phases.

Some results of our calculations on cubic Eu$_2$O$_3$ may be compared with experimental values. The gap between the valence and the conduction band ($\Delta E_{v\rightarrow c}$) has been obtained by optical measurements; the calculated value $\Delta E_{v\rightarrow c} = 3.50$ eV is close to the experimental one $\Delta E_{opt} = 4.3 \pm 0.3$ eV\textsuperscript{26}. The gap between the valence and the empty majority spin Eu f-band has been determined by the experimental curve of conductivity vs. temperature; the calculated value $\Delta E_{v\rightarrow f} = 2.18$ eV is in reasonable agreement with the experimental value of $\Delta E_{cond} = 1.84$ eV\textsuperscript{27}.

Our calculations allow us to calculate the electron density on the nucleus, which is relevant in the context of the Mössbauer spectroscopy of $^{151}$Eu in cubic Eu$_2$O$_3$. The electron density on the nucleus may be evaluated in terms of the difference relative to tetragonal EuF$_3$, which is the reference compound. Using the experimental isomer shift $\delta = 1.03 \pm 0.01$ mm/s\textsuperscript{12} and the differential nuclear radius of Ref.\textsuperscript{28}, we find an experimental density difference to be $\Delta \rho(0) = 3.18 \pm 0.03$ a$_0^{-3}$; the calculated value for the dominating C$_2$ site is $\Delta \rho(0) = 3.17$ a$_0^{-3}$ which is in very good agreement with the experimental value.

![Graph showing the total DOS of cubic and hexagonal Eu$_2$O$_3$ in the FM state.](image)
V. EXCHANGE INTERACTIONS

The exchange interaction in ions with \( L \neq 0 \) is characterized by the dependence of the exchange integral on orbital orientation. According to Van Vleck and Huang, this effect gives rise to an "anisotropic exchange," resulting from the dependence of orbital charge density on the direction. The coupling between the ions \( i \) and \( j \) may be described by the exchange potential

\[
V_{\text{ex}} = -\sum_{i=1}^{n_i} \sum_{j=1}^{n_j} \sum_{\mu, \mu'}^{\mu, \mu'} a_{\mu \mu', \nu \nu'} Y_{\mu \nu}(l_i) Y_{\mu' \nu'}(l_j) \left( \frac{1}{2} + 2 s_i \cdot s_j \right)
\]

where \( Y_{\mu \nu} \) are the tesseral harmonic operators equivalent to Ref. \(^{29}\); \( n_i \) is the number of electrons in incomplete shell of the ion \( i \), \( s_i \) is the electron spin and \( \mu = \mu' = 6 \) for Eu\(^{3+}\). As demonstrated in Ref. \(^{29}\), the exchange coupling for Eu\(^{3+}\) ions in their ground state and in cubic compounds, may be written in the standard form

\[
V_{\text{ex}} = -2 a_{\text{eff}}^{(ij)} S_i \cdot S_j
\]

where \( S_i \) is the spin of the ion \( i \) and \( a_{\text{eff}}^{(ij)} \) are the effective exchange constants. In other words, we can use the standard form of the isotropic coupling, to deal with an anisotropic exchange. Therefore, it is possible to determine the \( a_{\text{eff}}^{(ij)} \) constants by calculating the energies of different spin configurations. These constants allow to determine the effect of the exchange coupling on the magnetic susceptibility.

Our results show that there is no significant total energy difference between the FM-like and the AFM-like phases (for their definition see section \[\text{III}\]), with an energy convergence parameter \( \epsilon \sim 3 \times 10^{-4} \) eV and a total energy \( E_t \sim 5 \times 10^6 \) eV. The maximum possible strenght of the exchange coupling consistent with these results corresponds to an energy difference per primitive cell \( \Delta E_t \sim 2 \epsilon \) which leads to a difference per Eu atom of \( \Delta E \sim 0.04 \) meV. In this work we consider only the exchange coupling of the Eu\(^{3+}\) ion with its twelve NN, since it is expected to be the largest. In fact, in the bixbyite structure, NN exchange is mediated by the oxygen atom, which is not the case for next NN Eu atoms. With this assumption, the effective exchange constants refer only to the coupling of NN Eu ions. We also assume that all the NN pairs have the same \( a_{\text{eff}}^{(ij)} = a_{\text{eff}} \). Starting from the energy difference \( \Delta E \sim 0.04 \) meV and the spin values given by our calculations, we obtain that the upper bound of the effective exchange constant to be \( a_{\text{eff}} \sim 0.002 \) meV.
Due to lack of long range magnetic order\textsuperscript{30}, the value of $a_{eff}$ cannot be verified by direct comparison with experimental magnetic data. However, this interaction may give a contribution to the magnetic susceptibility. According to Ref.\textsuperscript{4}, the magnetic susceptibility $\chi$ may be written as

$$\chi = \chi_{dia} + \chi_p = \chi_{dia} + \chi_{VV} + \chi_{ex}$$

(3)

where the paramagnetic susceptibility $\chi_p$, obtained by subtraction of the diamagnetic core component $\chi_{dia}$, is the sum of the Van Vleck contribution $\chi_{VV}$ and of the exchange contribution $\chi_{ex}$\textsuperscript{4}. At $T = 0$ K,

$$\chi_{VV} = \frac{8N\mu_B^2}{3K_B} \sum_{k=1}^{3} \frac{1}{E_{1k}}$$

(4)

$$\chi_{ex} = \frac{128N\mu_B^2 A_{eff}}{E_1(E_1 - 16A_{eff})}$$

(5)

where $N$ is the number of atoms, $\mu_B$ is the Bohr’s magneton, $K_B$ is the Boltzmann’s constant, $E_{1k}$ are the energies of the triplet state $^7F_1$ centered around the energy $E_1$, and

$$A_{eff} = \sum_{j=1}^{12} a_{eff}^{(ij)} = 12a_{eff}$$

(6)

However, the contribution of the $S_6$ and $C_2$ sites must be evaluated separately, because the energies of the $^7F_1$ state are different. Since the multiplet energies are not accessible from our one-particle calculations, we calculate the Van Vleck contribution by using the experimental optical energies for the two sites given by Ref.\textsuperscript{6}; we get $\chi_{VV}^{(exp)} = 7.72 \times 10^{-3}$ cm\textsuperscript{3}/mol of Eu (in CGS units). If we subtract this contribution from the experimental value of the paramagnetic susceptibility $\chi_p^{(exp)} = 9.1 \times 10^{-3}$ cm\textsuperscript{3}/mol of Eu (in CGS units) of Ref.\textsuperscript{3}, we obtain the value of the excess susceptibility $\Delta \chi = \chi_p - \chi_{VV} = 1.38 \times 10^{-3}$ cm\textsuperscript{3}/mol of Eu.

In accordance with Van Vleck and Huang\textsuperscript{4,29}, if we assume that this excess susceptibility is due to the exchange contribution only ($\Delta \chi = \chi_{ex}$) and that $A_{eff}$ is equal for both sites, we can estimate the experimental value of $A_{eff} = 0.41$ meV. By using the maximum value of $a_{eff}$ obtained by our band calculations, we obtain a theoretical upper bound for the constant to be $A_{eff} \sim 0.02$ meV. Our results, therefore, lead to the conclusion that in cubic Eu\textsubscript{2}O\textsubscript{3} the difference between the experimental paramagnetic susceptibility and the Van Vleck contribution cannot be due to the contribution of the exchange interaction, in contrast with conclusions of Van Vleck and Huang\textsuperscript{4,29}. It is consistent, on the other hand, with the fact that the experimental susceptibility (per mole of Eu) does not decrease in
the solid solutions of Eu₂O₃ into A₂O₃. The point of view of Van Vleck and Huang has also been criticized before by Caro et al.¹³, who performed a calculation of the Van Vleck contribution χᵥᵥ including the matrix elements among atomic wavefunctions of the Eu 4f states. They obtained a resulting χᵃ in good agreement with experiment, without invoking any contribution from the exchange interaction. Our calculations are also consistent with these results.

The investigation of the exchange interaction has also been performed for the hexagonal phase of Eu₂O₃ under pressure. In this case, Eq. 2 is not applicable, because the structure of the compound is not cubic; therefore, it is not possible to determine the exchange constants by total energy differences. In contrast to the cubic phase in the case of the hexagonal structure the application of a weak magnetic field along the c axis gives collinear spins. In the AFM configuration (described in Section III), the cation spins have parallel orientation in planes perpendicular to the magnetic field direction (z axis), with antiparallel orientation between planes. The Eu atom has three neighbors at 3.50 Å in the lower plane, three at 3.59 Å in the upper plane, and four neighbors at a distance of 3.74 Å in the same plane.²²,²⁴ The energy difference per Eu atom is \( E_{AFM} - E_{FM} = -3.63 \) meV. Therefore in the hexagonal structure we obtain a small but sizable AFM exchange interaction between the Eu ion and its six NN. Interestingly the energy difference is of the same order of magnitude as that found by Johannes and Pickett for EuN and EuP.¹⁴

The exchange interaction is about 100 times stronger in the hexagonal phase than in the cubic one. As a first guess, one might attribute this difference to the shorter Eu-Eu distance in the hexagonal phase (\( d_{Eu-Eu} \) is 3.50-3.74 Å in the hexagonal phase and 3.84 Å in the cubic one). To verify this possibility, we performed test calculations in the hexagonal structure, changing the lattice constant so as to match the interatomic Eu-Eu distance of the cubic phase. The corresponding exchange coupling did not decrease sufficiently to support this view. The rational for the different couplings may probably be found in the different local O coordination around Eu ions, as the oxygen orbitals mediate the Eu-Eu interaction: in the hexagonal structure there are two O atoms binding two NN Eu ions, while there is only one intermediate O atom in the cubic one. An analysis of the partial densities of states in the two structures supports this view, with a quite large hybridization of Eu 4f and O orbitals in the hexagonal phase. Interestingly we also observe that the phase with stronger exchange coupling has a collinear spin structure, while the structure with weaker interaction
is characterized by non-collinear spins.

VI. CONCLUSION

In conclusion, we studied the electronic structure of cubic bixbyte Eu$_2$O$_3$ and its high pressure hexagonal phase by mean of full potential linearized augmented plane wave calculations, within the LDA+$U$ method. In both phases the filled O $2p$ and empty majority spin Eu $4f$ states are separated by a $\approx 2.1$ eV gap, while minority Eu $4f$ states start around 4 eV above $E_F$, in agreement with the optical and transport measurements$^{26,27}$.

From the comparison of FM and AFM calculations we infer that the interatomic exchange interaction is negligible in cubic Eu$_2$O$_3$, and so is its effect on the susceptibility. This is consistent with the experimental observation of a constant susceptibility (per mole of Eu) of solid solutions of Eu$_2$O$_3$ into A$_2$O$_3$ (A=Y, Lu, Sc). Our calculations are in contrast with the point of view of Van Vleck and Huang$^{4,29}$, according to which exchange is needed to explain the behavior of the magnetic susceptibility. Our results are consistent with later calculation$^{13}$ which could explain the experimental susceptibility by including matrix element in the Van Vleck contribution. In the hexagonal phase we observe the presence of a small but sizable AFM exchange interaction between the Eu ion and its six nearest neighbors. Therefore, in this phase we could have a non negligible contribution of exchange to the magnetic susceptibility, but for now no experimental measurements are available for comparison.

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