Magnetic groundstate and Fermi surface of bcc Eu

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Using spin-spiral technique within the full potential linearized augmented-plane-waves (LAPW) electronic structure method we investigate the magnon spectrum and Néel temperature of bcc Eu. Ground state corresponding to an incommensurate spin-spiral is obtained in agreement with experiment and previous calculations. We demonstrate that the magnetic coupling is primarily through the intra-atomic $f-s$ and $f-d$ exchange and Ruderman-Kittel-Kasuya-Yosida mechanism. We show that the existence of this spin-spiral is closely connected to a nesting feature of the Fermi surface which was not noticed before.

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I. INTRODUCTION

The magnetic behavior of most rare-earth (RE) materials is governed by localized magnetic moments interacting indirectly through the sea of delocalized valence electrons. A typical feature of RE systems is existence of two electron species, localized $4f$’s exhibiting atomic like behavior with strong Coulomb interaction and delocalized $5d$ and $6s$ electrons with interaction merely renormalizing the band dispersion. Yet, a typically weak interaction between these two species, either due to intra-atomic exchange or band mixing (hybridization), gives rise to a variety of magnetic behaviors. On the model level this behavior is captured by periodic Anderson model or Kondo lattice model. The ab initio electronic structure methods based on density functional theory (DFT) and the standard semi-local approximations have noto-rious problems in dealing with the strong correlations within the $4f$ shell. In particular the splitting between occupied and unoccupied $4f$ bands, which is the way a single-particle band structure can capture the effect of Coulomb interaction, is missing. Consequently, the $f$ bands appear at the Fermi level resulting in unrealistic filling of both $f$ and valence orbitals. Two remedies can be used: (i) open-core treatment or (ii) additional Coulomb term with the simplest example being the LDA+U method. In the open-core treatment the $4f$ orbitals are kept separate from the rest of the valence Hamiltonian and the interaction with the valence states is only through the self-consistent potential. Obviously the proper filling of both $f$ and valence bands is easy to achieve if integer, however all kinematic exchange effects (e.g. superexchange) based on band mixing are missing. In the LDA+U approach the splitting between the occupied and unoccupied $f$ band is obtained due to an additional orbital-dependent term. All possible exchange processes are in principle accounted for in this approach.

Compounds containing Eu in 2+ formal valency are particularly well suited for LDA+U treatment, since the orbital degrees of freedom are quenched in the half filled $f$ shell. Examples involve ferromagnetic insulators EuO and EuS, semimetal EuB$_6$ and metallic elemental Eu. Presumably the exchange mechanisms in these materials are quite different.

In this paper we investigate the magnetic ground state and magnon spectrum of elemental Eu. Europium crystallizes in body-centered cubic (bcc) structure with a lattice constant of 4.555 Å at 100 K. The magnetic groundstate was found to be a spin spiral and the Néel temperature of 91 K. The electronic structure was previously investigated by Freeman and Dimmock using the Xα potential. Recently Turek et al. used a real-space perturbation approach based on tight-binding linear muffin-tin orbital (TB-LMTO) method to calculate the exchange parameters and corresponding magnon spectrum and Néel temperature. Here we use a reciprocal space based spin spiral approach which can be viewed as complementary to the real space calculations. Unlike the above authors who used the open core treatment of the $4f$ orbitals we employ the LDA+U method. We use the linearized augmented-plane-waves (LAPW) method and its extension to non-collinear magnetic structures utilizing the generalized Bloch theorem for calculation of the spin spiral states. We interpret our results in terms of Ruderman-Kittel-Kasuya-Yosida (RKKY) exchange mechanism and the Fermi surface property. For this purpose we evaluate the low frequency limit of the generalized susceptibility and identify the nesting features of the Fermi surface.

II. COMPUTATIONAL METHOD

We have used the Wien2k implementation of the full potential LAPW method and its extension for non-collinear spin structures. The effective single-particle...
potential with constructed from LDA+U functional, with the exchange-correlation potential of Perdew and Wang\cite{Perdew1992} and the double-counting scheme of Anisimov et al.\cite{Anisimov1991}. The Coulomb term parametrized with $U$ (7 eV unless stated otherwise) and $J$ (0.75 eV) was applied to the $4f$ orbitals. The spin-spirals were treated using the generalized Bloch theorem\cite{Bloch1929} which prohibits inclusion of the spin-orbit coupling. The atomic sphere approximation was employed, in which the direction of the exchange field is constrained inside atomic spheres and allowed to vary continuously in the interstitial space.

A spin spiral is defined by a propagation vector $\mathbf{q}$ and angle $\theta$ between the local moment and the precession axis. The orientation of the precession axis itself is arbitrary unless the spin-orbit coupling is taken into account. Each spin spiral was calculated selfconsistently. This approach has two deficiencies compared the perturbative approach employing the force theorem\cite{Kavokin2004}(i) it costs much more computational effort, (ii) more importantly one has to work with total energies instead of the sums of eigenvalues, i.e. looking at small differences of large numbers which requires high accuracy. As for (i), when performing calculations for $q$-vectors along a certain path in the reciprocal space converged spin density from a nearby $q$ can be used as starting point, which reduces the number of iterations needs significantly compared to starting from scratch for each $q$. As for (ii), $\theta$ dependence of spin spiral energies can be studied without being limited to small angles.

FIG. 1: (color online) The band structure as obtained with LDA+U method. The brighter (red) lines correspond to majority spin. In the side panels the corresponding densities of state for the minority (left) and majority (right) spin projections are shown.

FIG. 2: The $q$-dependent exchange parameter calculated using the spin-spiral approach. Comparison of the results for different k-point samplings indicates that the 15x15x15 mesh is reasonably well converged.

III. RESULTS AND DISCUSSION

A. Bandstructure

In Fig. 1 we show the spin-projected bandstructure obtained with U of 7 eV and J of 0.75 eV. The lowest valence band around the $\Gamma$ point with a predominant $6s$ character corresponds to a strongly dispersive $s$-band. Moving toward the zone boundary mixing with $d$-band takes place and the doublets at $H$ and $P$ points have a pure $d$ symmetry. The states in the vicinity of the Fermi level have mostly $d$ character.

The occupied $4f$ levels are localized about 3 eV below the Fermi level and cross the lowest valence band, with negligible hybridization, which is reflected by completely flat dispersion. The unoccupied $4f$ bands are approximately 7 eV above the Fermi level. A bandwidth of about 2 eV originates from mixing with the $6p$ and $5d$ bands. Lack of mixing with valence states in the occupied $f$ bands indicates that the kinematic exchange, involving hopping from localized $f$ orbitals into the delocalized band states, is not important here. The interaction between the localized $f$ states and the rest of the electronic system, is dominated by intra-atomic $f - s$ and $f - d$ exchange. Consequently the spin polarized bands and density of states below 2 eV exhibit almost a perfect rigid shift. The deviations from this pattern are mostly due to the splitting of the $s$-like bands being less than that of $d$-like bands, because the more extended $s$ orbital has smaller overlap with the polarized $f$ density.
FIG. 3: The q-dependent exchange parameter renormalized to satisfy the sum rule (5) along the high symmetry lines; \textit{ab initio} data (symbols), Fourier interpolation (line). The right panel shows the corresponding density of states.

B. Magnon spectrum

The magnetic excitations are discussed in terms of a classical Heisenberg Hamiltonian

\[ H = - \sum_{RR'} J_{RR'} \mathbf{e}_R \cdot \mathbf{e}_{R'}. \]  

(1)

A spin spiral characterized by the propagation vector \( \mathbf{q} \) and angle \( \theta \) has the form

\[ \mathbf{e}_R = (\sin(\theta) \cos(\mathbf{q} \cdot \mathbf{R}), \sin(\theta) \sin(\mathbf{q} \cdot \mathbf{R}), \cos(\theta)), \]  

(2)

The corresponding energy per lattice site obtained from

\[ E(q) = \sin^2(\theta)(J(q) - J(0)) + J(0) + E_0 \]  

(3)

\[ J(q) = \sum_R J_{0R} \exp(i\mathbf{q} \cdot \mathbf{R}). \]  

(4)

is to be compared to the \textit{ab initio} results. \( E_0 \) is the non-magnetic part of the total energy. Note that only the difference \( J(q) - J(0) \) can be obtained from the knowledge of \( E(q) \). In order to fix the value of \( J(q) \) the sum rule

\[ \int dq J(q) = 0, \]  

(5)

where the integration is over the Brillouin zone, is to be employed. The \( J(q) \) normalized this way contains only information about the inter-site \( J_{RR'} \) and can be related to the ordering temperature, which we discuss below.

Using the Hamiltonian (1) involves several approximation. Quenching of the orbital moment in a half filled shell, rigidity of the \( f \) moment and its size \( (S=7/2) \) well justify the use of Heisenberg Hamiltonian in classical approximation. In addition we assume that the exchange parameters are constant. This is not \textit{a priori} guaranteed, since the electronic structure of the band electrons, which carry the exchange interaction between the local \( f \) moments, depends on the arrangement of local moments. This question was discussed in detail by Nolting \textit{et al}\textsuperscript{22} who derived an expression for the effective exchange parameters \( J_{RR'} \) in terms of the conduction electron self-energy. Experimentally this leads to temperature dependence of the effective exchange parameters. If this effect were important a deviation from the \( \theta \) dependence of eq. (3) is expected. The fact that we have not found any significant deviation from (3) in the range from 90° to 30° serves as a justification of use of Hamiltonian (1). This is also agreement with a rather big ratio of the band-width to the exchange splitting in the conduction band.

In Fig. 2 we show the q-dependent exchange parameter obtained with maximum \( \theta \) of 90°. Calculations performed with \( U \) of 6 eV and 8 eV lead to almost identical dispersion supporting our previous conclusion about the \( f-d \) exchange mechanism which does not depend on the position of the \( f \) bands. The calculations yield a minimum energy corresponding to a spiral with propagation vector \( Q \) of about \( 0.3 \times (\frac{\pi}{a}, 0, 0) \) and another two local minima along \( \Gamma N \) and \( \Gamma P \) lines. In order to address the Néel temperature the \( E(q) \) throughout the Brillouin zone is needed. To this end we have calculated the spin-spirals on a \( 10 \times 10 \times 10 \) regular q-grid (44 irreducible q-points) and used a smooth Fourier interpolation\textsuperscript{23,24,25} to obtain \( J(q) \) on a denser grid. In Fig. 3 we compare the inter-
In this section we discuss the paramagnetic Fermi surface and its connection to the spin-spiral ground state. Very fine k-point sampling is required in order to study the fine details of the Fermi surface. We adopted the following approach. Starting with 100 irreducible k-points obtained with LAPW code we have used the procedure for smooth Fourier interpolation\textsuperscript{23} for the bands at the Fermi energy. We have generated the band energies on a finer mesh of approximately $1.5 \times 10^6$ k-points in the whole Brillouin zone, which was used for the calculations reported below. In Fig. 5 we show the paramagnetic bandstructure together with the Fourier interpolation,
which is excellent near $E_F$ (note that the interpolation was performed on different–regular mesh).

The paramagnetic Fermi surface of bcc Eu, Fig. \ref{fig:EuFS} consists of an electron pocket centered at H point, and a hole pocket located at P point. Symmetry related degeneracy of the valence band along the P-H direction results in touching of these pockets. The first numerical investigation of the Fermi surface of bcc Eu was reported by Andersen and Loucks, who called these pockets ‘superegg’ and ‘tetracube’ respectively. While our calculation reproduces the ‘superegg’ shape, contrary to Andersen’s cube with lobes we find rather a rounded tetrahedron with lobes.

In order to make connection between the Fermi surface geometry and calculated spin spiral dispersion we have evaluated the imaginary part of the generalized susceptibility

$$\chi_{ij}(q, \omega) = - \sum_k \frac{f(\epsilon_i(k)) - f(\epsilon_j(k + q))}{\epsilon_i(k) - \epsilon_j(k + q) - \omega + i0^+}, \tag{8}$$

where $\epsilon(k)$ is the band energy, $f(\epsilon)$ is the Fermi-Dirac function and $i$ and $j$ are band indices. In the limit $\omega \to 0$ the imaginary part of $\chi(q, \omega)$ behaves as

$$\text{Im} \chi_{ij}(q, \omega) = \pi \omega \sum_k \delta(\epsilon_i(k) - \epsilon_F) \delta(\epsilon_j(k + q) - \epsilon_F)$$

$$= \pi \omega \nu_{ij}(q), \tag{9}$$

where $\nu(q)$ measures so called nesting, i.e. the extent to which different parts of the Fermi surface weighted by the inverse square of the Fermi velocity are parallel. While the real part of the generalized susceptibility is directly related to the exchange parameters $J(q)$ it is the imaginary part which has a straightforward geometrical interpretation. The real and imaginary parts are bound by the Kramers-Kronig relations, which for $\omega = 0$ limit read

$$\text{Re} \chi(q, \omega = 0) = \frac{1}{\pi} \int_{-\infty}^{+\infty} d\omega' \frac{\text{Im} \chi(q, \omega')}{\omega'}. \tag{11}$$

Comparing this to \cite{Landau}, one can readily see that a peak in $\nu(q)$ provides a significant contribution to a peak in $\text{Re} \chi(q, \omega = 0)$. In the special case $q \to 0$ limit $\nu(q)$ diverges as $1/|q|$, however the limit $\lim_{q \to 0} \lim_{\omega \to 0} \text{Re} \chi(q, \omega)$ remains finite, equal to the density of states (or corresponding partial density of states) at the Fermi level $N(\epsilon_F)$. In general peaks in $\nu(q)$ indicate a tendency toward instability of the Fermi surface toward formation of incommensurate structures such as spin or charge density waves.

Andersen and Loucks concluded that the origin of the spin spiral groundstate is the nesting between the opposite faces of their ‘tetracube’. However, our investigation provides a different picture. In Fig. \ref{fig:Nesting} we show the nesting function $\nu(q)$ in the $\Gamma$HPN plane. There is a prominent peak on the $\Gamma$-H line and a weaker feature on the $\Gamma$-N line. In order to identify the origin of these features we have calculated separately the contributions of the different sheets of the Fermi surface. Fig. \ref{fig:Nesting} demonstrates that both peaks originate from transitions between the lobed tetrahedra surfaces. The $q$ parallel to the $\Gamma$-H direction amounts to moving the lobed tetrahedron centered at the P point toward the next P point on the same face. The peak on the $\Gamma$-H line correspond to the overlap of the lobes, which is illustrated explicitly in Fig. \ref{fig:Nesting}. The peak on the $\Gamma$-N line corresponds to the sum of two nesting vectors along adjacent $\Gamma$-H directions. Therefore it originates from an overlap of the tips of the lobes, however, belonging to tetrahedra centered at P points which are not on the same face. In Fig. \ref{fig:Nesting} we show the nesting function in the $\Gamma$HPN plane. Besides the peaks on $\Gamma$-H and $\Gamma$-N lines we find weaker features on the $\Gamma$-P line. Analysis of the contributions from different sheets shows that these features originate from transitions between the two types of Fermi surfaces.

Eventually we can compare the information obtained from the nesting function to the magnon dispersion. We have found a prominent nesting feature on the $\Gamma$-H line and weaker one on the $\Gamma$-N line. These are related to the minima in the spin-spiral energies. The energy minima do not sit exactly at the positions of corresponding the nesting vectors. While the nesting vectors contain information about the states directly at the Fermi energy, all states contribute to the spin-spiral minima, yet with a weight decreasing with the distance from the Fermi level. A discussion of the generalized susceptibility in the context of electron-phonon coupling can be found in Ref. \cite{Kamihara}. The features on the $\Gamma$-P line are rather weak and do not fit well with the position of the $\Gamma$-P peak therefore we do not draw any conclusion about its direct relation to the local energy minimum on the $\Gamma$-P line.
FIG. 8: The lobed tetrahedron translated by \( q = 0.4 \times (\frac{2\pi}{a}, 0, 0) \) corresponding to the \( \Gamma - H \) peak elucidates the origin of the spin-spiral groundstate.

IV. CONCLUSIONS

Using a full-potential method with LDA+U functional and spin-spiral approach we have obtained a magnon spectrum which is in good agreement with that published by Turek et al. using TB-LMTO. The calculations reproduce well the experimentally observed spin-spiral groundstate and provide a reasonable estimate of the Néel temperature. The good agreement of two rather different computational methods indicates a robustness of these physical properties. Moreover we have shown that the values of the exchange parameters are insensitive to the precession angle of the spin spiral as well as the value of \( U \), i.e. exact position of the occupied \( f \) bands. This confirms the picture of bcc Eu as a Kondo-lattice system with ferromagnetic exchange of intra-atomic origin in the RKKY regime. We have identified the origin of the spin-spiral ground state in terms of nesting properties of the Fermi surface. In particular we have shown that the nesting is connected to the lobed tetrahedron hole pockets centered at the \( P \) point of the Brillouin zone.

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