Electric field gradient analysis of RIn₃ and RSn₃ compounds (R = La, Ce, Pr and Nd)

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A B S T R A C T

In this paper we explore the electronic charge distribution at different atomic sites in the rare-earth intermetallics RIn₃ and RSn₃ (R = La, Ce, Pr and Nd) using the analysis of the electric field gradients (EFGs) calculated by the FP-LAPW + lo method. The f-state in these compounds makes them strongly correlated systems, therefore the exchange and correlations are treated with GGA + U along with the GGA whereas GGA + SOC is also used to treat the relativistic effects. The calculated EFG values are consistent with the experimental results of the Mössbauer spectroscopy for LaSn₃, CeSn₃, CeIn₃, PrSn₃ and NdSn₃ and therefore we expect that our calculated values for the remaining compounds will be also consistent with the experimental results. The anisotropy of the charge distribution in the vicinity of a nucleus causes EFG and therefore the orbitals contribution of EFG i.e., $V_{zz}^{(1)}$, $V_{zz}^{(2)}$, $V_{zz}^{(3)}$, $V_{zz}^{(4)}$ and $V_{zz}^{(5)}$ are evaluated for nonmagnetic and AMF phases using GGA, GGA + U and GGA + SOC.

1. Introduction

The analyses of the nucleus-electron interactions beyond the nuclear point charge approximation provides useful information in condensed matter physics. Electric field gradient (EFG) is one of those physical quantities, which is obtained from this analysis. The EFG serves as a powerful tool to measure the interaction between atomic nucleus and electronic charge density around the nucleus [1]. The EFG takes place due to the rate of Coulomb potential change at the nucleus and the nature of EFG is very sensitive to a slight change in bonding, structure and dynamics of an atom [2,3]. These properties are highly dependent upon the symmetry of the electronic charge density of core electrons [4] and valence electrons [5]. EFG can be used as a measure of the degree of electron’s localization in the solids [6]. Experimentally EFG cannot be measured directly, but it can be obtained by different techniques such as Mössbauer spectroscopy (MS), perturbed angular correlation (PAC) spectroscopy, nuclear magnetic resonance (NMR), and nuclear quadrupole resonance (NQR) [7]. However, theoretically EFG can be accurately predicted by ab-initio method using density functional theory (DFT) [8]. Various theoretical studies are reported in the literature on the EFG in a variety of materials, for example, intermetallics [9], metal complexes [10], magnetic [11] or multiferroic compounds [12].

Rare-earth (RE) intermetallic compounds RIn₃ and RSn₃ (R = La, Ce, Pr and Nd) have cubic AuCu₃-type structure. The corner site is occupied by R atom having cubic symmetry m-3m and the face centered sites are occupied by X atoms having tetragonal symmetry 4/mmm [6].

The strongly correlated rare-earth (RE) intermetallic compounds RX₃ (R = rare-earth and X = In, Sn) have attracted special attention because of their interesting physical, electronic, and mechanical properties, which make them significant materials for technological and industrial applications [13–15]. Some of the attractive features of these compounds are their low superconducting transition temperature, magnetic susceptibility and thermoelectric power as a function of their electron concentration [16,17]. The RX₃ compounds are also significant due to their simple crystal structure, stability in the cubic structure over a wide range of pressures [18] and more favorable structure for superconductivity than lower symmetry [19].

The rare-earth elements have different occupation numbers for the shallow inner 4f shell, ranging from 0 to 14 through the series. This changing of 4f occupation determines a wide range of different physical properties of rare-earth elements and compounds. Due to the unfilled 4f shells of rare-earth atoms, it is a challenging problem to obtain an accurate theoretical description of the lanthanide based compounds [15,20]. The rare earth intermetallic compounds RX₃ show certain trends in the lattice constant value across the lanthanide series and...
exhibit the characteristic lanthanide contraction. In RX₃ compounds from La to Lu, the rare-earth element form trivalent ions except Eu and Yb, which form divalent oxidation. The lattice constant of divalent ion (Eu and Yb) is larger than trivalent ion by almost 10% [19,21]. The structural and magnetic properties of RIn₃ (R = Ce, Pr, Nd, Gd, Tb, Dy, Ho, Er, and Tm) compounds have been reported by Buschow et al. [22] and the magnetic behavior of RSn₃ (R = Ce, Pr, Nd, Sm, and Gd) have been investigated by Tsuchida and Wallace [23]. From the magnetic measurement it was observed that most of RIn₃ and RSn₃ compounds have antiferromagnetic (AFM) ordering with the exception of Pauli paramagnetic material LaIn₃, and paramagnetic materials LaSn₃, CeSn₃ and PrIn₃ [24–26]. The structural, electronic and magnetic properties of RSn₃ compounds (R = La, Ce, Pr, Nd, Sm, Eu, Gd, Yb) have been investigated using the 23.8 keV Mössbauer resonance of ¹¹⁵Sn [27]. The Fermi surface properties and the de Haas–van Alphen (dHvA) effect in RX₃ compounds were reported by Onuki and Settai [26].

In this paper we explore the electric field gradients of RX₃ series (X = In and Sn, X = La, Ce, Pr and Nd) using ab-initio density functional theory calculations to better understand the physics and chemistry of these compounds due to the distribution of the electronic charge around the nucleus and nuclei-electrons interaction. The calculations are carried out with the all electron full potential linearized augmented plane waves plus local orbital (FP-LAPW + lo) method within the framework of the density functional theory (DFT), where the correlation effects are treated with the Hubbard potential and the relativistic effects are considered by the spin-orbit coupling.

2. Method of calculations

In the present work, the calculations have been performed by using the density functional theory (DFT) as implemented in the WIEN2k code [28] employing the full potential linearized augmented plane waves plus local orbitals (FP-LAPW + lo) method [29]. The exchange correlation effects are treated by the generalized gradient approximation (GGA) [30] with and without including spin effects.

The most popular approximations for the treatment of exchange correlation functional are LDA and the GGA. However, in most cases the results of these schemes are not consistent with the experimental values. As lanthanides are strongly correlated systems with localized ⁴f electrons [11,31], to obtain the exact electronic nature of the compounds under consideration, we used GGA + U methods [32]. The DFT + U method is based on the Hubbard model, which treats the strongly correlated electron systems with an orbital dependent potential of Coulomb and exchange interactions [41]. The optimized values of the U parameter are obtained by varying U, step by step.

Fig. 1 shows the effect of U on the EFG value of CeIn₃. It is clear from the figure that the value of EFG decreases with increase in U, consequently the difference of the calculated value decreases from the experimental results. The value of EFG at 6.5 eV is closer than the other values of U, beyond 6.5 eV the value of EFG again increases. Therefore, we select U = 6.5 eV for our calculation. Furthermore, spin-orbit coupling (SOC) is included to treat the relativistic effects. The SOC are included by a second variational method [33]. The second variational method, which makes use of the scalar-relativistic basis, based on the reduction of the original basis. In the first step of this approach, the scalar-relativistic part of the Hamiltonian is diagonalized in the scalar-relativistic basis. In the second step the full Hamiltonian matrix including SOC is constructed using the eigen functions of the first step Hamiltonian. Once the effects of spin-orbit coupling included, the full Hamiltonian can be written as:

\[ H_{\text{so}} = \psi \hat{V} \psi + H_0 \psi \]  

where \( H_{\text{so}} \) is spin-orbit Hamiltonian and given by Ref. [34]:

\[ H_{\text{so}} = \frac{\hbar}{2m_e} \int V(\mathbf{r}) J_z(r)(K\delta(r))Y_3(\hat{k}) \]  

where \( J_z \) is the spherical Bessel function, \( Y_3(\hat{k}) \) is the spherical harmonic for \( l = 2, m = 0 \) and \( \rho_{LM} \) is the component of charge density, \( \rho_{LM} \) for \( L = 2, M = 0 \) when it is expressed by lattice harmonics, i.e., LM form.
The first term in Eq. (2) is known as valence contribution of EFG \((V_{zz}^{\text{val}})\). \(V_{zz}^{\text{val}}\) comes from the non-spherical electron density of the valence and semicore electrons in Muffin-tin spheres. The sum of the second and third terms represents the lattice contribution of EFG and \(V_{zz}^{\text{latt}}\) arises from the outside of the Muffin-tin spheres and interstitial region.

The calculated values of the largest component of the EFGs \((V_{zz}^{\text{tot}})\) and their valence \((V_{zz}^{\text{val}})\) and lattice \((V_{zz}^{\text{latt}})\) contributions for LaIn\(_3\), PrIn\(_3\), LaSn\(_3\) and CeSn\(_3\) compounds using GGA and GGA + SOC are presented in Table 1. The calculated values of EFGs are also compared with the experimental values obtained from Mössbauer spectroscopy [27]. As LaIn\(_3\), PrIn\(_3\), LaSn\(_3\) and CeSn\(_3\) compounds exist in paramagnetic phase [24–26], therefore as a first approximation the calculations for these compounds are performed in nonmagnetic phase. It is clear from Table 1 that in nonmagnetic phase, the GGA functional provides good results, consistent with the experimental values for these compounds. In these compounds only the In and Sn with nuclei of non-cubic symmetry, exhibit the electric quadrupole interaction, and have nonzero EFG. At rare-earth elements La, Ce and Pr sites Table 1 the EFGs are zero due to the cubic symmetry for all the nonmagnetic phase with and without SOC effects. The results show that, the magnitude of the EFGs for LaIn\(_3\) and PrIn\(_3\) are closer to each other, hence the electron density distributions near the In nuclei are similar. The same also holds for Sn nuclei in LaSn\(_3\) and CeSn\(_3\). The total EFG \((V_{zz}^{\text{tot}})\) of In and Sn sites in LaIn\(_3\), PrIn\(_3\), LaSn\(_3\) and CeSn\(_3\) is positive which predict the prolate distribution of electrons.

Table 2 represents the calculated values of the EFG’s \((V_{zz}^{\text{tot}})\) and their related valence \((V_{zz}^{\text{val}})\) and lattice \((V_{zz}^{\text{latt}})\) contributions for CeIn\(_3\), NdIn\(_3\), PrSn\(_3\) and NdSn\(_3\) compounds. RIn\(_3\) and RSn\(_3\) compounds with \(R = \text{Ce, Pr and Nd}\) exist in AFM phase [37–39]. The calculations for these compounds are performed in the magnetically split AFM phase by using GGA, GGA + U and GGA + SOC. The results listed in Table 2 are compared with the available experimental results. It is evident from Table 2 that our calculated results by GGA and GGA + SOC approaches overestimate the EFG values with respect to the experimental results. Our theoretical calculations for EFG values performed with GGA + U agree well with the experimental results. As lanthanides are strongly correlated systems due to their 4f electrons, hence the better agreement confirms that we have properly treated correlations among the 4f electrons within GGA + U calculations. Table 2 also indicates nonzero EFG values at rare-earth (Ce, Pr and Nd) site. The nonzero EFG values are due to the fact that AFM ordering can cause a slight deviation from the cubic symmetry around the rare-earth atom. The total EFG \((V_{zz}^{\text{tot}})\) of In and Sn sites in CeIn\(_3\), NdIn\(_3\), PrSn\(_3\) and NdSn\(_3\) compounds is positive which predict the prolate distribution of electrons. The positive value of total EFG \((V_{zz}^{\text{tot}})\) of rare-earth element Ce in CeIn\(_3\) predict the prolate shape of orbital while the negative value of \(V_{zz}^{\text{tot}}\) of rare-earth element Nd in NdIn\(_3\) and NdSn\(_3\) and Pr in PrSn\(_3\) indicate the oblate nuclear charge distribution.

The main contribution of the EFG is due to the anisotropy of the charge distribution in the vicinity of a nucleus. In order to further analyze these contributions, we evaluate the orbital contributions \(V_{zz}^{\text{p-f}}\), \(V_{zz}^{\text{d-d}}\), \(V_{zz}^{\text{p-d}}\), \(V_{zz}^{\text{p-d}}\) and \(V_{zz}^{\text{f-f}}\). Fig. 2 shows the orbital contributions of the nonmagnetic phase and AMF phase of the compounds under consideration using GGA, GGA + U and GGA + SOC. It is clear from the figure that the \(p-p\) contribution is dominant at In and Sn sites in case of all approximations for both nonmagnetic and AFM phases. In RIn\(_3\) and RSn\(_3\) compounds, In and Sn atom which has 4d complete shell, the d orbital is spherical symmetric. The \(5p\) contribution is the consequences of the non spherical distribution of charge as compared to rare-earth element. The dominant value of \(p-p\) contribution indicates that, the electron density of 5p electrons around the indium (in RIn\(_3\)) and tin (in RSn\(_3\)) atoms is identical across the series and independent of rare-earth atom. It is also seen from Fig. 2, that \(s-d, d-d, p-f\) and \(f-f\) contributions are very small as compared to the valance EFGs and are comparable in magnitude.

Fig. 3 represents the orbital contribution of Ce atom in CeIn\(_3\). It is evident from the figure that at rare-earth (Ce in this case) site the \(f-f\) contribution dominates as compared to the \(p\)-states in the compounds under investigation. The valence character of \(f-f\) orbitals of Ce site specifies the non spherical distribution of nuclear charge. This demonstrates that at rare-earth nuclei (Ce, Pr, and Nd), the main contribution to valence EFGs are originated by \(4f\) states.

4. Conclusions

In summary we have calculated the electric field gradients (EFGs) and their valence contributions at rare-earth and In/Sn sites for RIn\(_3\) and RSn\(_3\) \((R = \text{La, Ce, Pr and Nd})\) using FP-LAPW + io method with
various exchange-correlation functionals. Our analysis concludes that the main EFG contributions to In and Sn sites come mainly from 5p state. At rare-earth site the valance EFG is predominantly from 4f states. From the orbital contributions it is evident that the p-p contribution is dominant at In and Sn sites in case of all approximations for both nonmagnetic and AFM phases. Although, EFG is a very sensitive quantity but even then our calculated EFG parameters for LaSn3, CeSn3, CeIn3, PrSn3 and NdSn3 materials are consistent with the experimental results of the Mössbauer spectroscopy. This comparison concludes the effectiveness of the theoretical tools for the accurate EFG calculations. Furthermore, on the basis of this former conclusion we also conclude that the calculated values of EFGs for LaIn3, PrSn3 and NdSn3 compounds will be also consistent with the experimental results.

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