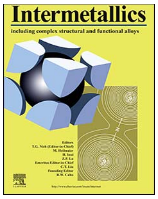
Intermetallics 91 (2017) 95–99

Contents lists available at ScienceDirect

Intermetallics

journal homepage: www.elsevier.com/locate/intermet



Electric field gradient analysis of RIn_3 and RSn_3 compounds (R = La, Ce, Pr and Nd)

M. Shafiq[a,b,*], M. Yazdani-Kachoei[c], S. Jalali-Asadabadi[c], Iftikhar Ahmad[a,b]

[a] Department of Physics, Abbottabad University of Science and Technology, Havelian, Abbottabad, Pakistan
[b] Center for Computational Materials Science, University of Malakand, Pakistan
[c] Department of Physics, Faculty of Sciences, University of Isfahan, HezarGerib Avenue, Isfahan 81744-73441, Iran

ARTICLE INFO

Keywords:
Electric field gradient
Rare-earth intermetallics
Strongly correlated
Spin-orbit coupling

ABSTRACT

In this paper we explore the electronic charge distribution at different atomic sites in the rare-earth intermetallics RIn_3 and RSn_3 (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 $LaSn_3$, $CeSn_3$, $CeIn_3$, $PrSn_3$ and $NdSn_3$ 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}^{p-p}, V_{zz}^{s-d}, V_{zz}^{d-d}, V_{zz}^{p-f} and V_{zz}^{f-f} 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 RIn_3 and RSn_3 (R = La, Ce, Pr and Nd) have cubic $AuCu_3$-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 RX_3 (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 RX_3 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 4*f* shell, ranging from 0 to 14 through the series. This changing of 4*f* occupation determines a wide range of different physical properties of rare-earth elements and compounds. Due to the unfilled 4*f* 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 RX_3 show certain trends in the lattice constant value across the lanthanide series and

---

[*] Corresponding author. Department of Physics, Abbottabad University of Science and Technology, Havelian, Abbottabad, Pakistan.
E-mail address: shafiqdurraniuom@gmail.com (M. Shafiq).

http://dx.doi.org/10.1016/j.intermet.2017.08.014
Received 23 May 2017; Received in revised form 16 August 2017; Accepted 21 August 2017

exhibit the characteristic lanthanide contraction. In RX_3 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 andYb) is larger than trivalent ion by almost 10% [19,21]. The structural and magnetic properties of RIn_3 (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 RSn_3 (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 RIn_3 and RSn_3 compounds have antiferromagnetic (AFM) ordering with the exceptional Pauli paramagneticmaterial $LaIn_3$, and paramagnetic materiales $LaSn_3$, $CeSn_3$ and $PrIn_3$ [24–26]. The structural, electronic and magnetic properties of RSn_3 compounds (R = La, Ce, Pr, Nd, Sm, Eu, Gd, Yb) have been investigated using the 23.8 keV Mössbauer resonance of ^{119}Sn [27]. The Fermi surface properties and the de Haas–van Alphen (dHvA) effect in RX_3 compounds were reported by Ōnuki and Settai [26].

In this paper we explore the electric field gradients of RX_3 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 affects 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 consistence with the experimental values. As lanthanides are strongly correlated systems with localized 4*f* 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 $CeIn_3$. 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:

$$H\tilde{\psi} = \varepsilon\tilde{\psi} + H_{so}\tilde{\psi} \qquad (1)$$

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

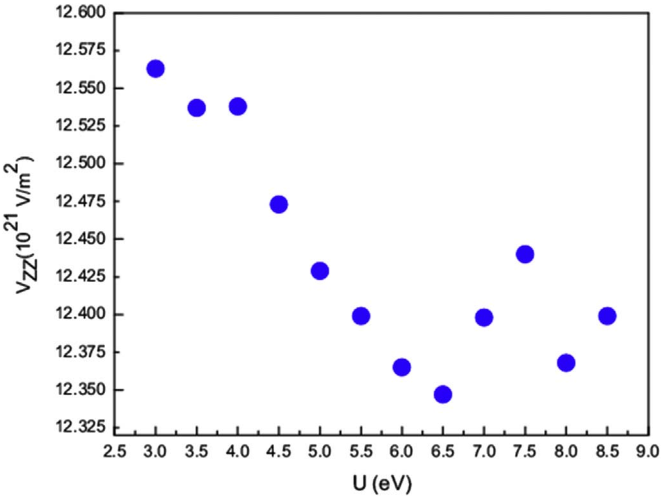


Fig. 1. The Electric field gradient of $CeIn_3$ using different Hubbard parameters GGA + U.

$$H_{so} = \frac{\hbar}{2Mc^2}\frac{1}{r}\frac{dV}{dr}\begin{pmatrix}\vec{\sigma}\vec{l} & 0\\ 0 & 0\end{pmatrix} \qquad (2)$$

with $\vec{\sigma}$ is Pauli spin matrices.

The radii of the muffin-tin spheres have been chosen as 2.50 a.u for the rare-earth elements as well as for Sn and In. To achieve convergence, the basis set is expanded in terms of plane waves up to $R_{MT}K_{max} = 7$. For the valence wave function inside muffin-tin spheres, the maximum value of the angular momentum is considered as $l_{\max} = 10$. In the interstitial region, the charge density is Fourier expanded up to $G_{\max} = 12$. The convergence of the total energy is tested and hence the total energy is converged for 6000 k-points with a dense k mesh of 165 k-points in the irreducible wedge of the Brillouin zone with a grid size of 18 × 18 × 18.

3. Results and discussion

A nucleus with the nuclear spin quantum number $I \geq 1$ possesses nuclear quadrupole moment Q, which can interact with the electric field gradient (EFG). The EFG is a traceless symmetric tensor of rank 2 with five independent components and originates due to the deviation of the electron charge distribution from the spherical distribution in the vicinity of the nucleus (≤0.2 Å) [6]. In particular, EFG is defined as the second derivative of a classical electrostatic potential with respect to Cartesian coordinates $V_{ij} = \partial^2 V/(\partial x_i \partial x_j)$ at nuclear position. The two main independent components are principle component V_{zz} and asymmetry parameter $\eta = (V_{xx} - V_{yy})/V_{zz}$, where the standard convention $|V_{zz}| \geq |V_{yy}| \geq |V_{xx}|$ is chosen for principle axes. This also guarantees that η varies between 0 (axially symmetric) and 1 ($V_{xx} = 0$) [1,35]. These two components are used in the analysis of the EFG measurements. In the principle axes system where EFG tensor is diagonal, the main component V_{zz} of EFG has been obtained by using the following relation [36]:

$$V_{ZZ} = \lim_{r\to 0}\sqrt{\frac{5}{4\pi}}\frac{V_{20}}{r^2} \qquad (3)$$

where V_{20} is the radial potential and is given by Ref. [36]:

$$V_{20}(r=0) = \frac{4\pi}{5}\int_0^{R_{MT}}\frac{\rho_{20}}{r}dr - \frac{4\pi}{5}\int_0^{R_{MT}}\frac{\rho_{20}}{r^3}\left(\frac{r}{R_{MT}}\right)^5 r^2 dr + 4\pi\sum_K V(\hat{K})J_2(KR_{MT})Y_{20}(\hat{K}) \qquad (4)$$

where J_2 is the spherical Bessel function, Y_{20} is the spherical harmonic for $l = 2$, $m = 0$ and ρ_{20} is the component of charge density, ρ_{LM} for L = 2, M = 0 when it is expressed by lattice harmonics, i.e., LM form.