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Eu Valence in $\text{EuAg}_{5-x}\text{Ga}_x$ ($x = 0.5$ and 1)

K. ŁĄTKA^{a,*}, J. PRZEWOŹNIK^b, J. ŻUKROWSKI^c, YU. VERBOVYTSKY^d AND A.P. GONÇALVES^e^aMarian Smoluchowski Institute of Physics, Jagiellonian University, Prof. S. Łojasiewicza 11, 30-348 Kraków, Poland^bDepartment of Solid State Physics, Faculty of Physics and Applied Computer Science, AGH University of Science and Technology, Al. A. Mickiewicza 30, 30-059 Kraków, Poland^cAcademic Centre for Materials and Nanotechnology, AGH University of Science and Technology, Al. A. Mickiewicza 30, 30-059 Kraków, Poland^dDepartment of Hydrogen Technologies and Hydride Materials Science, Karpenko Physico-Mechanical Institute of the NAS of Ukraine, Naukova Str. 5, 79-060 Lviv, Ukraine^eC2TN, DECN, Instituto Superior Técnico, Universidade de Lisboa, Estrada Nacional 10, 2695-066, Bobadela LRS, Portugal

The results of ^{151}Eu Mössbauer studies carried out in transmission mode at room temperature for $\text{EuAg}_{5-x}\text{Ga}_x$ ($x = 0.5, 1$) were reported in detail. The Mössbauer data clearly demonstrate the stable divalent state of Eu for both intermetallics. The fitting procedure allowed to estimate V_{zz} components of the electric field gradient tensor existing at Eu sites in the discussed compounds.

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1. Introduction

Recent investigations have shown that the $\text{EuAg}_{5-x}\text{Ga}_x$ ($x = 0.5$ and 1) alloys crystallize in the hexagonal CaCu_5 type of structure with space group $P6/mmm$ (no. 191) [1, 2] but their magnetic properties point to a rather complicated magnetic structures with ferrimagnetic-like behavior [2]. It has been shown that magnetic susceptibility and magnetizations results are consistent with Eu being in stable divalent state. For example, the refined Eu saturation magnetic moments found for these compounds [2] are very close to $7\mu_B$ which is the full free-ion magnetic moment expected for the Eu^{2+} ion with $S = 7/2$ and a spectroscopic splitting factor of $g = 2$.

One of the main advantage of ^{151}Eu Mössbauer spectroscopy is a huge change in isomer shifts, ranging from -15 mm/s for Eu^{2+} ions to $+5$ mm/s in the case of Eu^{3+} ions [3]. This fact makes this method a very sensitive tool for the studies of charge densities at Eu nucleus $\rho(0)$, enabling deeper insight to the electronic properties of different Eu materials showing stable as well as instable Eu valencies. In this way, such studies have great impact on solid state Eu chemistry. Similarly to the trivalent gadolinium ion, the divalent europium is in the $^8S_{7/2}$ electronic state with a spherical distribution of the $4f$ electronic charge being insensitive to crystal field effects; hence the ^{151}Eu nucleus in a divalent europium compound is a good probe for a lattice contribution to the electric field gradient.

The aim of this work is to present preliminary ^{151}Eu Mössbauer spectroscopy results obtained for two intermetallic compounds, $\text{EuAg}_{5-x}\text{Ga}_x$ ($x = 0.5, 1$) at 293 K. Especially, the obtained isomer shifts and V_{zz} components of electric field gradient tensor (EFG) give information concerning the observed Eu valencies and the crystal electric field parameters (CEF) A_2^0 .

2. Experimental

The samples used in the presented measurements were obtained in previous investigations and their synthesis procedures and crystallographic properties are exactly described [1, 2].

The ^{151}Eu Mössbauer spectroscopy measurements were performed in transmission geometry at room temperature using a standard, constant acceleration Mössbauer spectrometer operating in triangular mode and a 5 mCi $^{151}\text{Sm}(\text{SmF}_3)$ source. The incoming 21.5 keV gamma rays were recorded by means of thin $\text{NaI}(\text{Tl})$ scintillation detector. The calibration of the spectrometer drive motion was performed with a commercial $^{57}\text{Co}(\text{Rh})$ source and a metallic $\alpha\text{-Fe}$ foil. The surface density of the Mössbauer absorber was of about 30 mg/cm². The obtained resonance absorption spectra were fitted in the Lorentzian approximation taking into account the pure quadrupole interaction Hamiltonian where quadrupole moment constants for ground (0 keV) and excited (21.5 keV) states of ^{151}Eu took the following values $Q_g = 0.903(10)b$ and $Q_e = 1.28(2)b$, respectively [4, 5].

3. Results and discussion

The recorded spectra are shown in Fig. 1. It is worth noticing that Eu ions occupy only one crystallographic

*corresponding author; e-mail: uflatka@cyf-kr.edu.pl

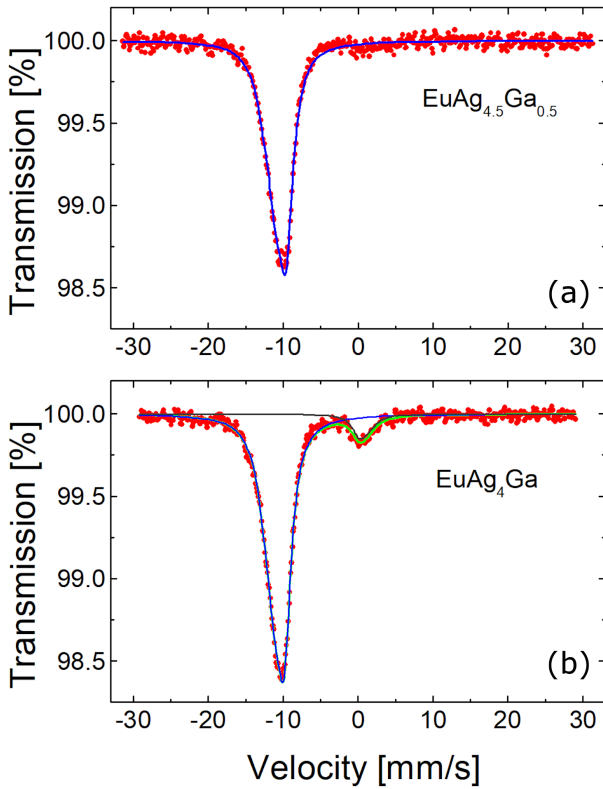


Fig. 1. ^{151}Eu Mössbauer spectra obtained for $\text{EuAg}_{4.5}\text{Ga}_{0.5}$ (a) and EuAg_4Ga (b) at room temperature. The continuous lines represent the least-squares fits to the experimental points.

position 1a in the Wyckoff description for the determined hexagonal structure [1, 2]. In agreement with the single non-cubic position of Eu ions, in the compounds under study, the spectra were fitted under assumption that a pure electric quadrupole interaction is present for the observed lines at room temperature. As a matter of fact, both compounds order magnetically at rather low temperatures i.e. below 19.8 K and 8.2 K for $\text{EuAg}_{4.5}\text{Ga}_{0.5}$ and EuAg_4Ga , respectively, as determined by magnetic susceptibility measurements [2]. Therefore, the magnetic part of the full hyperfine Hamiltonian should have to be included in a fitting procedure in case of spectra recorded at low temperature region i.e. below the mentioned above temperatures. One broadened line obtained for $\text{EuAg}_{4.5}\text{Ga}_{0.5}$ proves that this compound is essentially of single phase while for EuAg_4Ga a second line with 7.4(5)% intensity and, characteristic for a trivalent Eu^{3+} compound, was detected nearby $v = 0$ mm/s velocity. This second line can be tentatively ascribed to the existence of Eu_2O_3 impurity that could develop during preparation procedures. The derived Mössbauer parameters for both compounds are collected in Table I. Especially, the obtained isomer shift values (related to the spectrum observed with the standard absorber in the EuF_3 chemical form) for the main components are $-10.45(1)$ mm/s and $-10.64(1)$ mm/s for $\text{EuAg}_{4.5}\text{Ga}_{0.5}$ and EuAg_4Ga , respectively. These values, being finger-

prints, are characteristic for the stable divalent europium in both compounds as observed also for other Eu intermetallics. It is clearly seen from Table I that both isomer shifts as well as EFG values are quite comparable for investigated compounds. This means that the local chemical environments do not change much when going from one compound to another.

TABLE I

Hyperfine interaction parameters derived from the ^{151}Eu resonance spectra obtained for the $\text{EuAg}_{4.5}\text{Ga}_{0.5}$ and EuAg_4Ga intermetallic compounds at 293 K.

Compound	δ_{is}^* [mm/s]	V_{zz} [10^{21} V/m 2]	Relative area [%]	MisFit [%]
$\text{EuAg}_{4.5}\text{Ga}_{0.5}$	$-10.45(1)$	$7.52(11)$	100	$1.4(2)$
EuAg_4Ga	$-10.64(1)$	$6.91(9)$	$92.6(3)$	$0.41(7)$

*The isomer shifts of the recorded ^{151}Eu Mössbauer spectra are given here relative to the $^{151}\text{Sm}(\text{SmF}_3)$ source at 293 K.

The derived V_{zz} component (under assumption that $\eta = 0$) of the EFG tensor for each investigated compound can serve for the estimations of CEF parameters, A_2^0 , in isostructural compounds. The experimental determination of the V_{zz} at the Eu nuclei is of general interest for a better understanding of the electronic properties presented by different rare earth compounds. The CEF parameter A_2^0 is commonly given by the simple relation [6, 7]:

$$A_2^0 = -V_{zz}(1 - \sigma_2)/[4(1 - \gamma_\infty)]$$

Here, σ_2 is a screening coefficient estimated to be about 0.6 for any rare earth ion and γ_∞ (with $(1 - \gamma_\infty)$ of about 60) [7] is the Sternheimer antishielding factor of the EFG produced by the lattice charges (i.e. the polarisation of the core electrons). The quantity A_2^0 is then a universal factor applicable to all isostructural compounds of rare earths, provided that the structural parameters do not significantly vary with the rare earth. The next term of CEF, i.e. A_2^2 is directly related to the asymmetry parameter $\eta = V_{xx} - V_{yy}/V_{zz}$ in the form

$$A_2^2 = \eta A_2^0.$$

This term is always zero for a site with axial symmetry since then $\eta = 0$. It has to be underlined that V_{zz} itself is an important solid state property, and generally its absolute value can be easily obtained from the numerical fitting procedures of the Mössbauer spectra if quadrupole interactions are present (see Ref. [8] for example).

4. Conclusions

The Mössbauer spectra can be fitted in a proper way taking into account only one single position of Eu ions for the observed main components. The obtained isomer shifts are characteristic for divalent Eu ions. The observed broadening of the individual experimental lines results from quadrupole splittings of excited and ground nuclear states of Eu nucleus at a given Eu non-cubic crys-

talline position. The proper fitting procedure of the obtained spectra for both compounds deliver the values of V_{zz} and these values enable estimation of the respective CEF A_2^0 parameters.

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References

- [1] Yu. Verbovytsky, M.F.C. Pereira, A.P. Gonçalves, *J. Alloys Comp.* **584**, 447 (2014).
- [2] K. Łątka, J. Przewoźnik, Yu. Verbovytsky, A.P. Gonçalves, *J. Alloys Comp.* **650**, 572 (2015).
- [3] F. Grandjean, G.J. Long, in: *Mössbauer Spectroscopy Applied to Inorganic Chemistry* Eds: G.J. Long, F. Grandjean, Plenum Press, New York 1989, Vol. 3, p. 513.
- [4] Y. Tanaka, R.M. Steffen, E.B. Shera, W. Reuter, M.V. Hoehn, J.D. Zumbro, *Phys. Rev. C* **29**, 1897 (1984).
- [5] Mössbauer Effect Data Center (MEDC). *Properties of isotopes relevant to Mössbauer spectroscopy. ^{151}Eu isotope properties*, Retrieved June, 12, 2018.
- [6] G. Czjzek in: *Mössbauer Spectroscopy Applied to Magnetism and Materials Science*, Eds. G.J. Long, F. Grandjean, *Modern Inorganic Chemistry Series*, series Ed. J.P. Fackler, Plenum Press, New York 1993, Ch. 9, pp. 373–429.
- [7] G. Czjzek, V. Oestreich, H. Schmidt, K. Łątka, K. Tomala, *J. Magn. Magn. Mater.* **79**, 42 (1989).
- [8] R. Pöttgen, K. Łątka, *Z. Anorg. Allg. Chem.* **636**, 2244 (2010).