

Study of electric quadrupole interactions at ^{111}Cd on Zn sites in RZn (R = Ce, Gd, Tb, Dy) compounds using the PAC spectroscopy

Brianna Bosch-Santos · Artur W. Carbonari ·
Gabriel A. Cabrera-Pasca · Messias S. Costa ·
Rajendra N. Saxena

Published online: 7 February 2013
© Springer Science+Business Media Dordrecht 2013

Abstract Nuclear quadrupole interactions at Zn sites in the intermetallic compounds RZn (R = Ce, Gd, Tb, Dy) have been investigated by perturbed gamma-gamma angular correlation (PAC) spectroscopy using ^{111}In (^{111}Cd) as probe nuclei. Measurements were carried out in the temperature range of 10–295 K. These compounds exhibit CsCl type cubic structure and while CeZn shows antiferromagnetic behaviour, the compounds GdZn, TbZn, DyZn are ferromagnetic. The results show that the EFG in these compounds is sensitive to the distribution of rare-earth 4f-electron charges.

Keywords Electric quadrupole interaction · Rare earths compounds · PAC

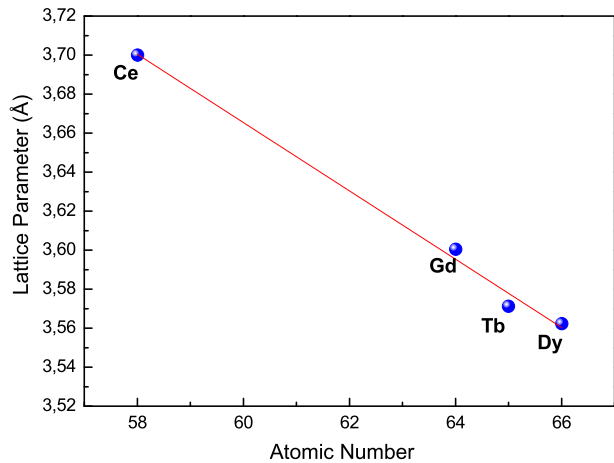
1 Introduction

Below the magnetic ordering temperature in intermetallic compounds containing rare earth elements, the measurement of hyperfine interactions are generally characterized by a combination of magnetic dipole and electric quadrupole interactions. Results of electric quadrupole interactions in both paramagnetic and magnetic phases in such compounds have shown a significant influence of the charge distribution in the 4f shell on the probe nucleus sites [1]. The investigation of this influence on RZn compounds where R is a rare earth element is interesting because the rare earth elements differ in the number of 4f electrons although having similar chemical properties mainly because these electrons do not participate in chemical bonds and present a localized magnetism associated with the 4f electrons [2]. The compound

Proceedings of the 4th Joint International Conference on Hyperfine Interactions and International Symposium on Nuclear Quadrupole Interactions (HFI/NQI 2012), Beijing, China, 10–14 September 2012.

B. Bosch-Santos (✉) · A. W. Carbonari · G. A. Cabrera-Pasca · M. S. Costa · R. N. Saxena
Instituto de Pesquisas Energéticas e Nucleares, IPEN-CNEN/SP, São Paulo, Brazil
e-mail: brianna@usp.br

Fig. 1 Lattice parameter dependence on the atomic number of rare earth atom for each compound



CeZn shows antiferromagnetic structure ($T_N \sim 30$ K) type (001) associated with a tetragonal distortion. The compounds GdZn, TbZn and DyZn on the other hand present ferromagnetic structure with Curie temperatures around 268, 204, 139 K, respectively. All RZn compounds have a CsCl type cubic structure belonging to the space group Pm-3m [3]. For TbZn however, it has been reported that a small fraction of free Tb metal remains in the sample when this compound is formed by arc melting. Terbium metal exhibits a hexagonal crystal structure belonging to the space group P63/mmc with Curie temperature, $T_C \sim 219$ K and a Neel temperature, $T_N \sim 230$ K [4]. Magnetic and electric hyperfine interactions in RZn (R = Ce, Gd, Tb, Dy) have been investigated by perturbed gamma-gamma angular correlation (PAC) spectroscopy using ^{111}Cd probe nuclei at the Zn sites of these compounds [5, 6]. The main purpose of this paper is however, to present a detailed analysis of results to investigate the influence of the 4f-electron charge density on the quadrupole interaction at the probe nucleus sites. PAC spectroscopy provides information about the hyperfine interaction between extra nuclear fields and nuclear moments of the probe nuclei at a certain atomic site in the crystalline structure, and consequently allows extracting information about the involved hyperfine parameters as well as characterization of structural and the magnetic transitions of the crystal.

2 Experimental procedure

The CeZn (Ce = 99.9 % and Zn = 99.999 % purity) sample was prepared by melting the components in a resistance furnace while the GdZn, TbZn and DyZn (Gd, Tb, Dy = 99.9 % and Zn = 99.999 % purity) samples were prepared by arc-melting the constituent elements in stoichiometric proportions in argon atmosphere. The samples were characterized by X-ray diffraction measurements and the results were analyzed with Rietveld refinement method using Rietica software [7]. The Fig. 1 shows that the lattice parameters of samples decrease with increasing atomic number of rare earth due to the effect of lanthanide contraction. Carrier-free ^{111}In was diffused into the samples at 800 °C in vacuum. PAC measurements were carried out with a usual four BaF₂ detector spectrometer using 171–245 keV gamma cascade

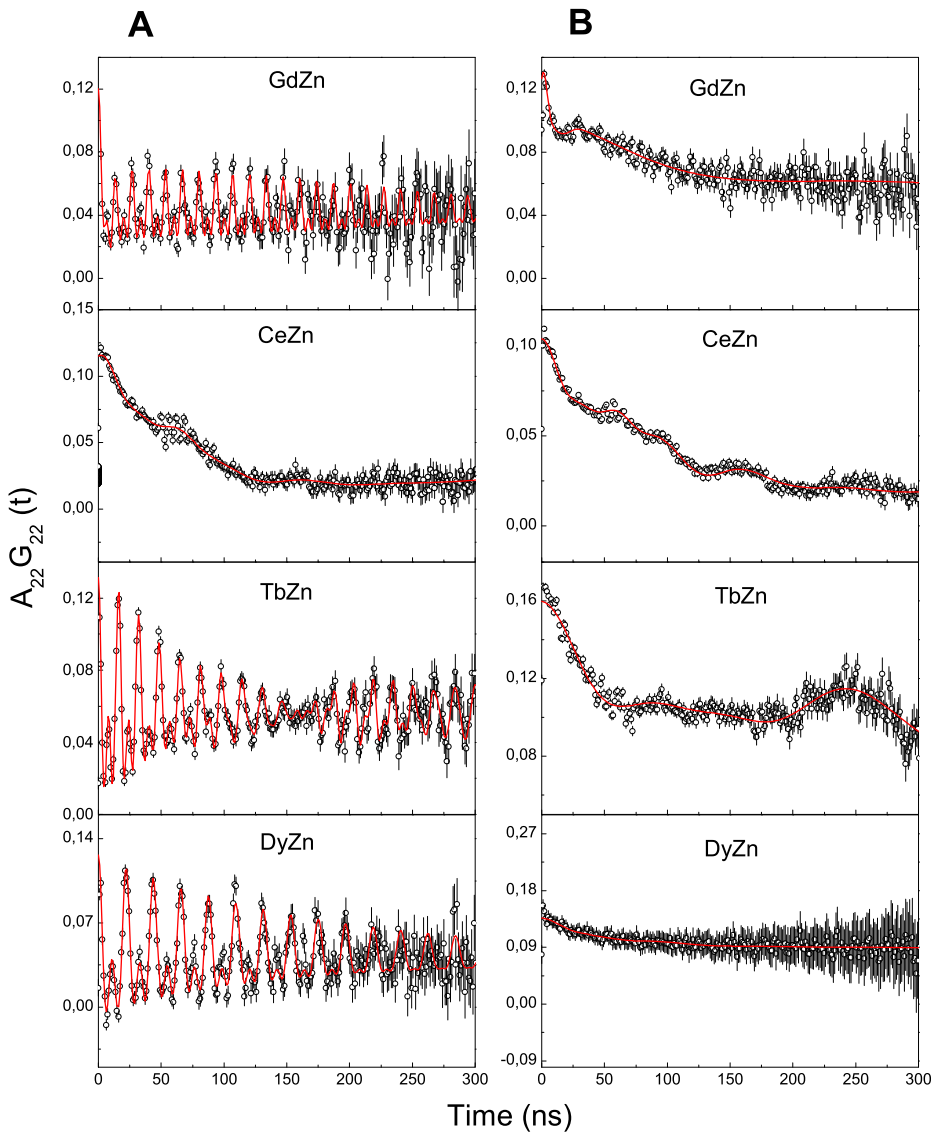
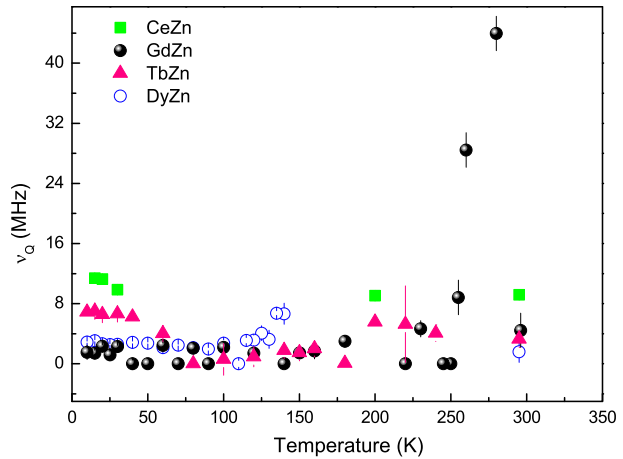


Fig. 2 Perturbation functions for $^{111}\text{In}(^{111}\text{Cd})$ probe in RZn measured at **a** 10 K and **b** 295 K. *Solid lines* are the last squares fit of the theoretical functions to the experimental data

in ^{111}Cd resulting in twelve coincidence spectra $W(\theta, t)$. These spectra were analyzed by means of TDPAC software to obtain the perturbation function $A_{22}G_{22}(t)$ which, contains detailed information about the hyperfine interactions and allows the determination of electric quadrupole frequency (ν_Q) [8]. The value of electric quadrupole moment Q for the intermediate energy level of the gamma cascade in ^{111}Cd is known $Q = 0.80$ b.

Fig. 3 Temperature dependence of quadrupole frequency (ν_Q) for ^{111}Cd probe at Zn sites in RZn



3 Experimental result

PAC spectra measured at 10 K and 295 K for all the studied compounds are shown in Fig. 2. The spectra for GdZn, TbZn, and DyZn show two probe sites. The major fraction with approximately 70 % population was assigned to ^{111}In substituting Zn ions [5, 6]. The spectra at 10 K show combined electric plus magnetic interactions. Below respective transition temperatures the minor fractions in GdZn, and DyZn disappear and only a single site is observed in each case. In the case of TbZn, on the other hand two probe sites continue even below the transition temperature. As mentioned before the major fraction is due to the probe substituting regular Zn sites in cubic TbZn. The minor fraction is due to probe nuclei substituting small quantity of metallic Tb, with hexagonal structure, present in the sample. Both sites in TbZn sample show magnetic interactions. From the known cubic structure of these compounds one expects a zero EFG. However from the data presented here one can clearly observe a weak quadrupole interaction in these compounds. The observed EFG most probably is due to the probe nuclei substituting a position of the Zn atom in these compounds which causes some distortion in the structure.

The CeZn compound showed only electric quadrupole interaction at all temperatures because the Zn sites are between two magnetic planes with spins arranged in opposite directions and, consequently, cancels each other. Results of the temperature dependence of the quadrupole frequency ν_Q for studied compounds is presented in Fig. 3. One can observe a sudden change in the quadrupole frequency near the respective Curie temperatures due to the tetragonal distortion which are present in RZn compounds near ferromagnetic transitions.

In Fig. 4a it is clearly observed that V_{zz} follows a linear dependence with Z presenting a strong decrease in V_{zz} with the increase of the atomic number. This behavior can be also observed in Fig. 4b where the root mean square radius ($\langle r^2 \rangle_{4f}$) of the 4f shell also decrease with atomic number, suggesting that probably the V_{zz} at Zn sites when occupied with ^{111}Cd probe nuclei is sensitive to the 4f shell charge distribution and the overlap of valence electrons of the probe nuclei with the 5d and 6s electrons of the rare earth element which, are hybridized by the interaction with the layer 4f [1] causing a distortion in the cubic structure for these compounds. Forker

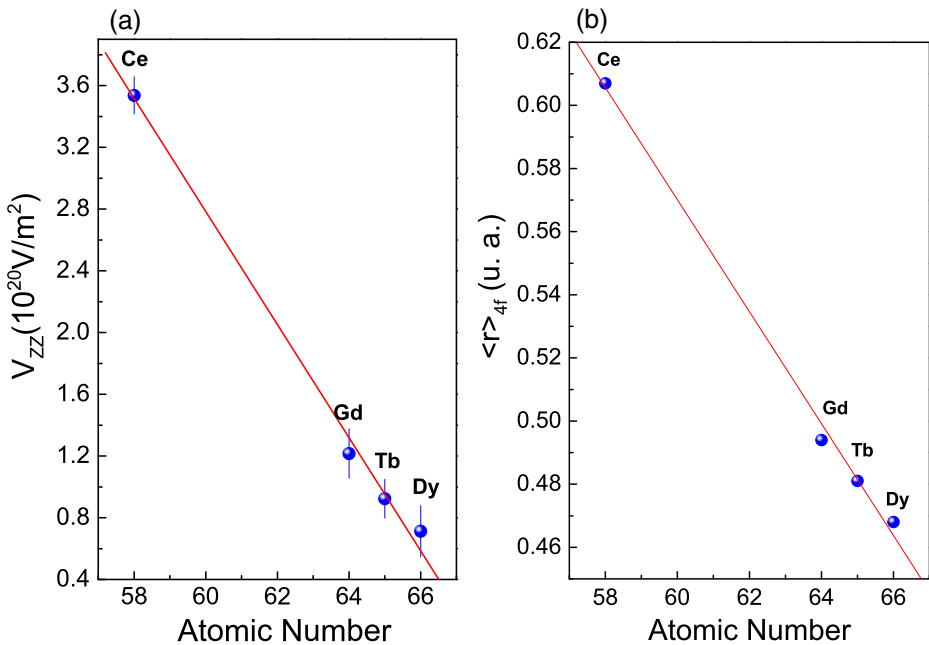


Fig. 4 **a** Electric field gradient V_{zz} at 295 K, and **b** root mean square radius ($\langle r \rangle_{4f}$). Both are plotted against rare-earth atomic number. The *continuous line* represents a linear regression

et al. [1] observed the same behavior in R_2In compounds, but these compounds have a hexagonal structure. The decrease of the V_{zz} can be compared with the decrease of the lattice parameter with increasing rare-earth atomic number as the lattice parameter is strongly dependent on the $4f$ shell of the rare-earth element. Therefore, the major contribution to V_{zz} must come from the interaction of the probe nuclei with the rare-earth $4f$ electron shell.

4 Conclusions

The electric quadrupole interaction of ^{111}Cd probe nuclei replacing Zn atoms in RZn ($\text{R} = \text{Ce}, \text{Gd}, \text{Tb}, \text{Dy}$) compounds have been investigated by PAC spectroscopy as a function of temperature. The values of V_{zz} and the root mean square radius of the $4f$ shell show strong dependence on the rare earth atomic number and decrease with increasing rare-earth atomic number. This is an evidence that the major part of V_{zz} originates from the distribution of $4f$ charges of rare-earth atoms when using ^{111}Cd with probe nuclei. Moreover, the V_{zz} increases with the decrease of the unit cell volume showing that V_{zz} depends on the distance between charges.

Acknowledgements Partial financial support for this research was provided by the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) and Fundação de Amparo para Pesquisa do Estado de São Paulo (FAPESP). AWC and RNS thankfully acknowledge the support provided by CNPq in the form of research fellowships.

References

1. Forker, M., Mubeler, R., Bedi, S.C., Dionysio-Olzon, M., Dionysio de Souza, S.: Magnetic and electric hyperfine interactions in the rare-earth indium compounds R₂In studied by ¹¹¹Cd perturbed angular correlations. *Phys. Rev. B* **71**, 094404 (2005)
2. Morin, P., Rouchy, J., Du Tremolet De Lacheisserie, E.: Magnetoelastic properties of RZn equiatomic compounds. *Phys. Rev. B.* **16**, 3182–3193 (1977)
3. Gignoux, D., Schmitt, D.: Handbook of magnetic materials. *KHS* **10**, 239–413 (1997)
4. Delaney, D.W., Lograsso, T.A.: Magnetostriction of growth textured Tb-Zn alloys. *J. Magn. Magn. Mater.* **205**, 311–318 (1999)
5. Bosch-Santos, B., Cabrera-Pasca, G.A., Carbonari, A.W.: Study of the magnetic properties of GdZn compound using PAC spectroscopy with ¹⁴⁰Ce and ¹¹¹Cd as probe nuclei. *Hyperfine Interact.* **197**(1–3), 105–109 (2010)
6. Bosch-Santos, B., Cabrera-Pasca, G.A., Carbonari, A.W., Costa, M.S., Saxena, R.N.: Magnetic hyperfine field in TbZn compound measured by PAC spectroscopy using ¹¹¹Cd and ¹⁴⁰Ce as probe nuclei. International Nuclear Atlantic Conference, Belo Horizonte, MG, Brazil, 24–28 October (2011)
7. Howard, C.J., Hunter, B.A.: Australian Nuclear Science and Technology Organization Lucas Heights Research Laboratories A Computer Program for Rietveld Analysis of X-Ray and Neutron Powder Diffraction Patterns. Rietica, N. S. W. (1997)
8. Atomic Energy Review: The use of selective nuclear techniques for the elucidation of chemical bonding, vol. 17, pp. 479–551 (1979)