PERTURBED γ-γ ANGULAR CORRELATION STUDIES OF ISOSTRUCTURAL Ag_5Zn_8 AND Ag_5Cd_8 INTERMETALLIC COMPOUNDS

P. Wodniecki, B. Wodniecka, M. Marszalek and A.Z. Hrynkiewicz

Henryk Niewodniczański Institute of Nuclear Physics
E. Radzikowskiego 152, 31-342 Kraków Poland

Perturbed γ-γ angular correlation spectroscopy was applied to study hyperfine interaction parameters for ^{111}In probes in intermetallic compounds of $D8_2$ structure. The perturbed γ-γ angular correlation spectra measured in Ag_5Zn_8 and Ag_5Cd_8 phases reflect a number, population and symmetry of nonequivalent substitutional sites occupied by the indium probes. The temperature dependences of the observed electric field gradients were measured in the temperature range 37–500 K.

PACS numbers: 76.80.+y

1. Introduction

An intensive study of electric field gradients (EFG) at a site of atomic nuclei in pure noncubic metals has revealed several systematic trends as a fixed ratio of an electronic and ionic contribution to the total EFG and a $T^{3/2}$ temperature dependence of the EFG in the majority of metals [1–3]. Although the empirical $T^{3/2}$ dependence has also been found in several other systems [4–6], there is still lack of a satisfying theoretical explanation of this EFG temperature behaviour. Moreover, in rare earths as well as in many intermetallic compounds a linear decrease in EFG value with the temperature raise has been evidenced [7–10]. The perturbed γ-γ angular correlation (PAC) investigations in intermetallic phases aim to collect as large as possible number of EFG values in metallic compounds of different crystallographic structures. Information on the EFG's acting on probe atom situated in the substitutional sites of compounds contribute to the understanding of the electric field gradient behaviour in different metallic systems. The PAC technique, due to its sensitivity to the asymmetry of EFG, often enables to determine an occupation site of the probe nuclei. This fact has the great practical importance since an alloying addition can improve the ductility of an intermetallic compound [11].

Compounds with metallic bonding are formed by metallic elements which have approximately the same atomic size and a similar electronegativity. Such compounds are electron compounds if their components belong to different groups in the periodic table and their atomic sizes do not differ by more than ≈ 15 per cent. These intermetallic phases are stable over definite ranges of composition. The main effect of substituting a solute for a solvent atom is a change of the electron-to-atom ratio. The Ag_5Zn_8 and Ag_5Cd_8 are the electron compounds of γ-brass $D8_2$-type based on compositions at which this ratio has the value of 21/13. Both belong to the space group No. 217, $I\bar{4}3m$ [16]. This type of structure is a complicated one having 52 atoms in a unit cell which basically consists of $3 \times 3 \times 3$ bcc unit cells. It should be noticed that two atomic vacancies involved in a unit cell cause the atomic displacements around each vacancy.

2. Experimental details

The PAC measurements were performed with the isomeric $5/2^+$-state of ^{111}Cd ($T_{1/2} = 84$ ns) populated by the electron capture decay of ^{111}In ($T_{1/2} = 2.8$ d). A conventional four detector setup with NaI crystals combined with a slow-fast coincidence timing electronics was used. More experimental details are given in Ref. [12]. Combining four coincidence time spectra the intensity ratios $R(t)$ were obtained, which were fitted by the function

$$G_2(t) = \sum_{i=1}^{n} f_i \sum_{n=0}^{3} \{s_{2n}(\eta_i) \cos[g_n(\eta_i)\nu_{Qi}t] \exp[-g_n(\eta_i)\delta_i t]\}. \tag{1}$$

The fractions f_i correspond to the relative number of probe atoms, which are exposed to an EFG characterized by the quadrupole coupling constant $\nu_{Qi} = eQV_{zz}/h$, the asymmetry parameter $\eta_i = (V_{xx} - V_{yy})/V_{zz}$ and the frequency distribution width δ_i. The ^{111}In parent nuclei were obtained in the nuclear reaction $^{109}Ag(\alpha, 2n)^{111}In$ using 28 MeV α-particles at the Cracow cyclotron. Ag foils containing an ^{111}In isotope were then melted together with cadmium or zinc metal in an argon atmosphere and annealed at 400°C for 24 hours. X-ray diffraction experiments confirmed the $D8_2$ crystallographic structure of the obtained samples. PAC measurements between 37 and 300 K were carried out using a closed cycle helium refrigerator. In the experiments at elevated temperatures samples were encapsulated in quartz tubes under an argon atmosphere.

3. PAC results and discussion

3.1. The Ag₅Zn₈ phase

The equilibrium diagram of the Ag–Zn system shows four intermediate phases each existing over a range of homogeneity. The γ-phase, Ag_5Zn_8, forms peritectically at 667°C and has a cubic, $D8_2$-type of structure. Its homogeneity region is not determined with a very high accuracy, most of data, however, indicate that the γ-Ag_5Zn_8 phase exists for the Zn atomic concentrations of 58.5–62.7% [13]. Experiments presented here were executed on the samples of 61% and 61.6% Zn atomic concentration. Crystallographic data based on X-ray diffraction experiments [16] prove that the difference of one per cent in the atomic concentration causes an
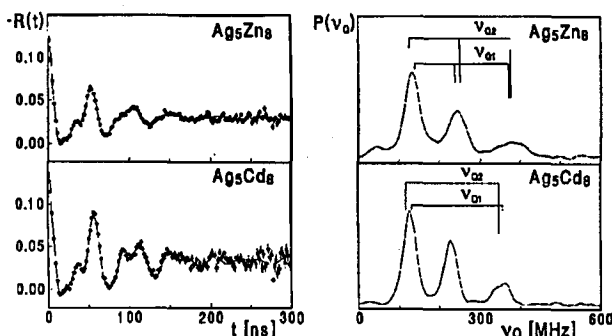
Fig. 1. PAC spectra for ^{111}In-doped Ag_5Zn_8 and Ag_5Cd_8 compounds (left panel) with the corresponding Fourier transforms (right panel).

TABLE

The quadrupole interaction parameters of ^{111}In in Ag_5Cd_8 and Ag_5Zn_8 compounds.

Compound	Site	η^{th}	η^{exp}	$\nu_Q(0)$ [MHz]	a [10^{-4} K^{-1}]
Ag_5Zn_8	Zn 24(g)	0.36	0.36(4)	129(2)	2.2(1)
	Zn 8(c)	0	0	137(3)	2.6(2)
	Ag 12(e)	0.60			
	Ag 8(c)	0			
Ag_5Cd_8	Cd 24(g)	0.36	0.36(2)	123(2)	2.3(1)
	Cd 8(c)	0	0	124(3)	2.6(1)
	Ag 12(e)	0.69			
	Ag 8(c)	0			

extremely small (about 0.5%) change in the lattice distances and therefore its influence on the EFG value is negligible.

The PAC spectrum of Ag_5Zn_8 sample shown in Fig. 1 was measured at room temperature. The fitted perturbation function exhibits two quadrupole frequencies $\nu_{Q1}=120(3)$ MHz and $\nu_{Q2}=126(4)$ MHz with asymmetry parameters $\eta_1=0.36(4)$ and $\eta_2=0$. These two fractions are sufficient to describe the $R(t)$ function which indicates that ^{111}In probe atoms occupy two nonequivalent sites in this compound. Crystallographic data report on two substitutional positions of Zn and two of Ag in the discussed phase. As the point charge model (PCM) calculations often provide reasonable estimates for the asymmetry parameter η, we have adopted it as a guide in distinguishing between different possible substitutional positions of the ^{111}In probes. The PCM calculations of the ionic contribution to the EFG, based on the known crystallographic properties [16] and done with the assumption of +1 charge on the Ag and +2 on the Zn atoms, yielded values of ηth given in Table. A comparison with the values determined experimentally indicates that indium

probe atoms most probably occupy the Zn-sites. This statement is supported by the fact that the observed probe fractions in two different environments are in agreement with the populations of 24(g) and 8(c) Zn-sites. Experimental data can be reproduced quite well with 75% relative fraction of ^{111}In interacting with non-axial EFG and 25% fraction in an axially symmetric environment.

3.2. The Ag_5Cd_8 phase

In the Ag–Cd phase diagram the Ag_5Cd_8 γ-phase, isotypic with γ-brass (D8$_2$ type), has the concentration range of 58.9–63.7 at.% Cd and is stable up to 590–640°C [13]. Moreover, a $\gamma' \leftrightarrow \gamma$ transformation in the γ-phase was found at temperature varying between 436°C at the Ag side and 470°C at the Cd side of the homogeneity range [14]. Another author [15] confirmed this transformation in the elasticity modulus measurements versus temperature, but at much lower temperature, i.e. about 330°C. It is claimed that this $\gamma' \leftrightarrow \gamma$ transformation is an order-disorder change or γ' has a slightly distorted γ-lattice.

Ag_5Cd_8 samples measured with the PAC method had the concentrations of 59.5 and 61.3 at.% Cd. The $R(t)$ function and its Fourier transform are presented in Fig. 1. The fitted perturbation function contains two quadrupole interactions ($\nu_{Q1} = 115(3)$ MHz, $\eta_1 = 0.36(2)$ and $\nu_{Q2} = 114(4)$, $\eta_2 = 0$) corresponding to the two nonequivalent lattice sites occupied by the In probes. The asymmetry parameters of both fractions are almost identical with the corresponding values for Ag_5Zn_8 compound. A comparison with the calculated η values when +2 charge on Cd atoms is assumed does not allow to determine the position of the probes. However, some charge transfer between the Ag and Cd ions enables to reproduce the measured η values if the substitution of cadmium sites by the probe atoms is assumed (see Table). The ratio of the calculated EFG values is then in agreement with the experimentally obtained. It should be noticed that the small changes in atomic position parameter values can also influence the calculated asymmetry parameter values.

The fitted relative fractions of the measured EFG's oscillate around the 3:1 ratio. Close values of the both quadrupole frequencies and rather broad frequency distribution, however, decrease an accuracy of the fraction determination, especially above room temperature. Nevertheless, the fitted parameters of $G_2(t)$ function for the fixed 3:1 fraction ratio, are, in the limit of errors, equal to these obtained when the both fractions were treated as free fit parameters. This indicates that the ^{111}In probes are randomly distributed in 24(g) and 8(c) sites of cadmium.

3.3. Temperature dependence of the EFG's

As the fractions of two observed EFG's are in the ratio of about 3:1 for both investigated compounds in the full temperature range, we decided to fix this ratio in the fit procedure. For the same reason the value of η_1 was fixed as 0.36. Results of PAC experiments performed at different temperatures for Ag_5Cd_8 and Ag_5Zn_8 are presented in Fig. 2. Experimental points, representing the ν_Q values, follow a linear dependence, according to the formula
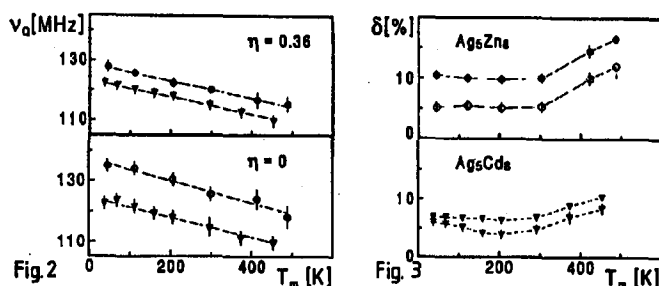
$$\nu_Q(T) = \nu_Q(0)[1 - aT]. \tag{2}$$

Fig. 2. Temperature dependence of the quadrupole frequencies for Ag_5Zn_8 (circles) and Ag_5Cd_8 (triangles). The data for 24(g) probe site are presented in the upper part and for 8(c) probe site in the lower part of the figure

Fig. 3   Widths of the Lorentzian distributions of the quadrupole frequencies versus temperature for Ag_5Zn_8 (upper part) and Ag_5Cd_8 (lower part) samples. Full symbols refer to the 24(g) and empty to 8(c) probe sites.

The values of $\nu_Q(0)$ and slope parameters a, obtained from the fitting procedure, are collected in Table. It should be, however, pointed out that the Lorentzian distributions widths δ of the measured quadrupole frequencies are relatively large and increase with temperature which influences the accuracy of the ν_Q values. Figure 3 shows a rapid increase in δ parameters above $T_m \approx 420$ K. The PAC patterns measured at temperatures above ≈ 670 K had a very broad distribution of quadrupole frequencies making the determination of ν_Q very unprecise. As this broadening of quadrupole frequency distribution at high temperatures has a reversible character, some changes in the crystallographic structure taking place at the temperature close to the phase transition has to be responsible for such a phenomenon.

4. Summary

The PAC measurements for Ag_5Zn_8 and Ag_5Cd_8 compounds on ^{111}In probes demonstrated two nonequivalent positions of probe atoms. In both samples about 75% of probes is exposed to EFG with asymmetry parameter $\eta = 0.36$. The remaining 25% of probe atoms exhibit an axially symmetric EFG. Probe atoms substitute most probably the 24(g) and 8(c) positions of Cd and Zn. The electric field gradient values are similar for both positions and equal *ca.* 6×10^{17} V/cm^2.

Distributions of the quadrupole frequencies measured in both compounds are relatively broad (especially for Ag_5Zn_8) in comparison with those observed in many other intermetallic compounds [6, 9, 17, 18], the reason of which, however, is not clear. Multiple preparations of investigated samples with different annealing times and temperatures did not decrease the observed frequency distributions. It should be pointed out that in the complicated structure of γ-brasses two atomic vacancies are involved in a unit cell and the structure loses its centrosymmetry as a result of atomic displacements around each vacancy [19, 20]. These displacements taking place also in the nearest neighbourhood of ^{111}In probes can contribute to the raise of the measured quadrupole frequency distributions. It is also possible that the atomic distribution in the studied compounds is not fully ordered. In the

Cu_5Cd_8 $D8_2$ γ-brass the interchange of Cu and Cd atoms between the 12(e) and 24(g) positions was found [21]. Thus, it cannot be also excluded that certain part of In probe atoms substitute Ag, however no additional EFG corresponding to such ^{111}In site was evidenced in the PAC spectra.

The temperature dependence of the EFG's in Ag_5Zn_8 and Ag_5Cd_8 is linear in the observed temperature range. The slope parameters a are very similar for both compounds and slightly differ for different probe sites (the larger one is observed for axially symmetric 8(c) position).

References

[1] R. Vianden, *Hyperfine Interact.* **15/16**, 189 (1993).

[2] R.S. Raghavan, E.N. Kaufmann, P. Raghavan, *Phys. Rev. Lett.* **34**, 1280 (1975).

[3] J. Christiansen, P. Heubes, R. Keitel, W. Klinger, W. Loeffler, W. Sandner, W. Witthun, *Z. Phys. B* **24**, 177 (1976).

[4] S.H. Devare, R.G. Pillay, S.K. Malik, S.K. Dhar, H.G. Devare, *Hyperfine Interact.* **10**, 949 (1981).

[5] M.K. Kurup, K.G. Prasad, K. Raghunathan, R.P. Sharma, *Hyperfine Interact.* **23**, 89 (1985).

[6] P. Wodniecki, B. Wodniecka, M. Marszałek, A.Z. Hrynkiewicz, *Hyperfine Interact.* **80**, 1033 (1993).

[7] R. Vianden, E.N. Kaufmann, R.A. Naumann, G. Schmidt, *Hyperfine Interact.* **7**, 247 (1979).

[8] M. Behar, L.G. Brunnet, J.A.H. da Jornada, R.P. Livi, F.C. Zawislak, *Hyperfine Interact.* **15/16**, 261 (1983).

[9] B. Wodniecka, M. Marszałek, P. Wodniecki, A.Z. Hrynkiewicz, *Hyperfine Interact.* **80**, 1039 (1993).

[10] M. Forker, W. Steinborn, *Phys. Rev. B* **20**, 1 (1979).

[11] S.C. Huang, E.L. Hall, *Acta Metall. Mater.* **39**, 1053 (1991).

[12] J. Christiansen, *Hyperfine Interactions of Radioactive Nuclei*, Springer-Verlag, Berlin 1983.

[13] Landolt–Börnstein, *Strukturdaten der Elemente und intermetallischen Phasen*, Springer-Verlag, Berlin 1971.

[14] M. Hansen, *Constitution of Binary Alloys*, McGraw-Hill, New York 1958.

[15] W. Köster, *Z. Met.kd.* **32**, 154 (1940).

[16] W.B. Pearson, *A Handbook of Lattice Spacing and Structures of Metals and Alloys*, Pergamon Press, London 1958.

[17] P. Wodniecki, M. Uhrmacher, *Appl. Phys. A* **57**, 469 (1993).

[18] M. Marszałek, B. Wodniecka, P. Wodniecki, A.Z. Hrynkiewicz, *Hyperfine Interact.* **80**, 1029 (1993).

[19] A.J. Bradley, J. Tewlis, *J. Proc. R. Soc. A* **112**, 678 (1926).

[20] Y. Koyama, J. Yoshida, H. Hoshiya, Y. Nakamura, *Phys. Rev. B* **40**, 5378 (1989).

[21] O. v.Heidenstam, A. Johansson, S. Westman, *Acta Chem. Scand.* **22**, 653 (1968).