

Electric Field Gradients at the In Site in Au-In Compounds*

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The quadrupole interaction in Au-In compounds of different stoichiometries was studied with the perturbed angular correlation technique. The electric field gradients at ^{111}Cd probes were measured and the temperature dependences of the quadrupole frequencies were determined. A new high temperature phase of AuIn above 630 K and a new metastable modification of Au_7In_3 were found.

Key words: Perturbed Angular Correlations; EFG; Intermetallic Compounds; Au-In System.

1. Introduction

Interface compound studies on the Au-In system [1, 2] have shown that AuIn_2 is formed below and around room temperature. AuIn_2 exhibits a CaF_2 structure of cubic symmetry leading to a vanishing electric field gradient (EFG) at the lattice sites. Application of the perturbed angular correlation (PAC) method to detect the other intermetallic compounds formed in the interface region at elevated temperatures requires the knowledge of the hyperfine interactions of PAC probes, present in the lattices of the bulk compounds. We report a PAC study of bulk $\text{Au}_x\text{In}_{(1-x)}$ samples with different stoichiometries. The quadrupole interaction of $^{111}\text{In}(\beta^-)^{111}\text{Cd}$ probe was observed at different temperatures. The EFG at ^{111}Cd was measured, but the actual position of probe nuclei is determined by that of the parent ^{111}In , chemically identical with one of the compound constituents.

2. Experimental Details and Data Analysis

A series of bulk $\text{Au}_x\text{In}_{(1-x)}$ samples of different stoichiometry, doped with ^{111}In , was prepared in a following way. A carrier free solution of ^{111}In in 0.04 M HCl was dried-out on the Au foil, and then the proper amounts of high purity gold and indium were melted under argon atmosphere in a resistance furnace. An appropriate annealing in sealed and evacuated quartz tubes ensured the homogeneity of the samples.

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The PAC measurements were performed at different temperatures (24 K–700 K) using a standard four BaF_2 detector setup. From these measurements the perturbation factors were obtained and fitted by the appropriate theoretical function describing the static quadrupole interaction [3]. The fitted quadrupole interaction parameters

$$v_Q = e Q V_{zz} / h \quad (1)$$

(which can be displayed by the Fourier transform of the measured perturbation function) and

$$\eta = (V_{xx} - V_{yy}) / V_{zz} \quad (2)$$

are directly related to the components V_{ii} of the diagonalized EFG tensor and to the known electric quadrupole moment Q of the 247 keV state in the ^{111}Cd probe [4]. A broadening of the EFG is described by the width δ of the Lorentzian v_Q distribution.

The temperature dependence of quadrupole frequencies measured in $\text{Au}_{70}\text{In}_{30}$ and $\text{Au}_{75}\text{In}_{25}$ samples was fitted with the equation:

$$v_Q(T) = v_Q(0) [1 - a T]. \quad (3)$$

3. Results

3.1. The AuIn Phase

The AuIn compound is stable at room temperature and melts congruently at 783 K. Its composition range is very narrow. This phase is reported to be triclinic [5] but its structure type is not defined.

The PAC spectra were taken at different temperatures between 300 K and 800 K. At about 630 K a polymorphic phase transformation was found, result-



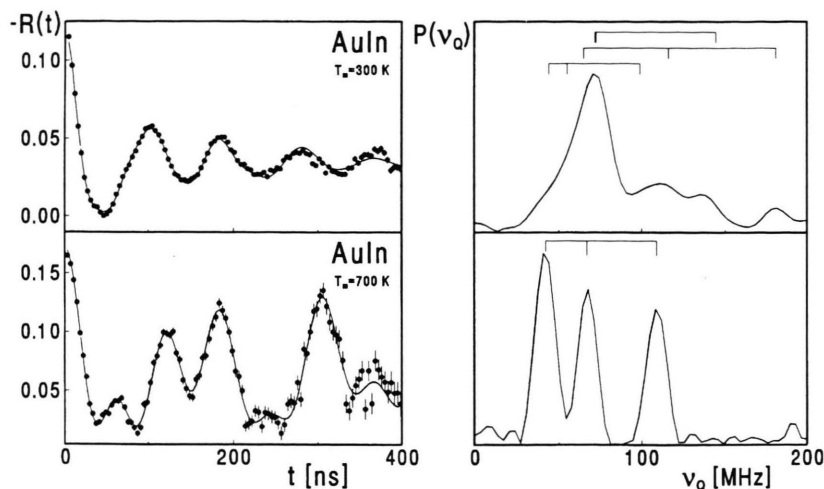


Fig. 1. PAC patterns (together with the corresponding Fourier transforms) measured at ^{111}Cd in an $\text{Au}_{50}\text{In}_{50}$ sample at different temperatures T_m .

ing in a change of the PAC pattern (see Figure 1). Above this temperature one well defined quadrupole frequency of 34.7(4) MHz with $\eta = 0.47(1)$ was measured, nearly constant up to the melting point. Below 630 K three quadrupole frequencies were necessary to fit the PAC spectra (see Figure 1 and Table 1). This reproducible and reversible transformation, obtained for 4 samples of different stoichiometries close to the 1:1 composition is incompatible with the Au-In phase diagrams given in the literature, which report a single phase AuIn compound in the whole temperature range 300 K–783 K (Figure 2). Our result is also in disagreement with the $\nu_Q = 63.4(10)$ MHz and $\eta = 0.3$ values reported for this phase in [6].

3.2. The γ and γ' Phase (Au_9In_4 and Au_7In_3)

The high temperature γ phase undergoes a transformation to the γ' phase having a different structure between 647.6 K and 637.5 K. The approximate atomic composition of the γ phase is Au_9In_4 . Its equilibrium domain at low temperature is very narrow at approximately 30 at.% In, but at higher temperatures the phase region extends from 29.5 to 39.5 at.% In [7]. It crystallizes in the Cu_9Al_4 -type structure [8]. The low temperature γ' phase of Au_7In_3 stoichiometry has a hexagonal crystal structure with 60 atoms in the elementary cell [8] and is observed in a very narrow composition range.

PAC measurements performed on the $\text{Au}_{0.70}\text{In}_{0.30}$ sample above 650 K resulted in two electric field gradients attributed to the 4(e) and 12(i) indium sites in the Au_9In_4 phase of D 8_3 γ -brass structure (Figure 3).

Table 1. The quadrupole interaction parameters of ^{111}Cd in Au-In compounds: the quadrupole interaction frequency ν_Q , the asymmetry parameter η and the parameters $\nu_Q(0)$ and a of the temperature dependence $\nu_Q(T) = \nu_Q(0)(1 - aT)$.

Compound phase	Structure	$\nu_Q(300\text{ K})$ [MHz]	η	$\nu_Q(0)$ [MHz]	a [10^{-4} K^{-1}]	Lattice site
AuIn	triclinic	30(1)	0.73(5)			
		41(1)	1.00(2)			
		59(1)	0.34(2)			
AuIn ht	?	34.7(4)*	0.47(1)			
Au_7In_3 γ'	hexagonal	84(1)	0.86(1)	91(1)	2.6(10)	6(g) 1
		101(1)	0.95(1)	107(1)	2.06(4)	6(g) 1
		111(1)	0.68(1)	121(1)	2.80(7)	6(g) 1
Au_7In_3 quenched from 700 K	?	86(1)	0.63(1)	92(2)	2.1 (6)	
		107(1)	0.65(1)	113(1)	1.7 (4)	
		116(1)	0.42(1)	120(1)	1.0 (2)	
Au_9In_4 ht γ	cubic ?D 8_3	105(4)**	0.00(1)			? 4(e) 3 m
		102(2)**	0.36(2)			?12(i) m
Au_3In ϵ'	orthorhom. DO $_8$	26.2(3)	0.19(1)	28.6(3)	3.2(2)	2(a) mm2

* data from 700 K, – ** data from $T = 655\text{ K}$.

The observed EFG distributions were large (see Figure 4), as for the other γ -brasses [9]. Below 650 K the Au_7In_3 phase was detected. According to its structure [8] three nonaxial EFG's with equal contributions were observed in the PAC patterns (see Table 1). The corresponding unique quadrupole frequencies exhibit a linear temperature dependence (Figure 4). The fitted slope parameters of (3) are listed in Table 1.

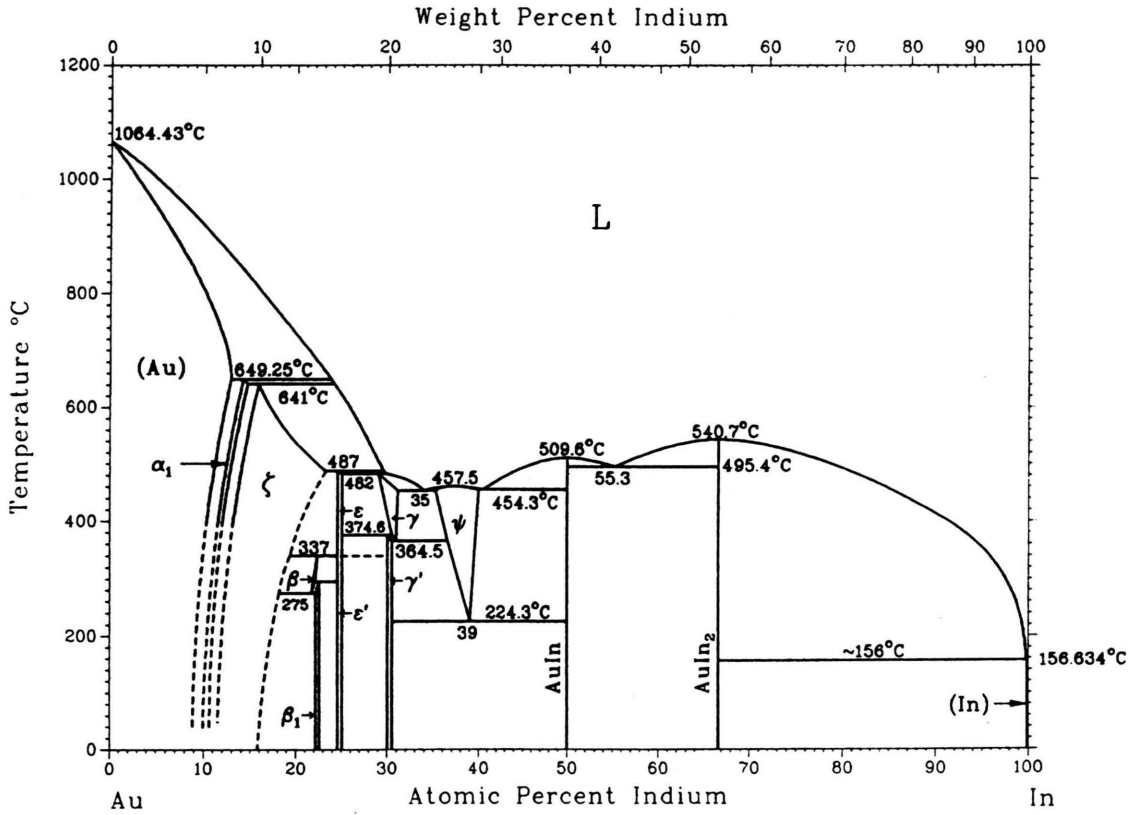


Fig. 2. Phase diagram of the Au-In system (after Okamoto et al. [13]).

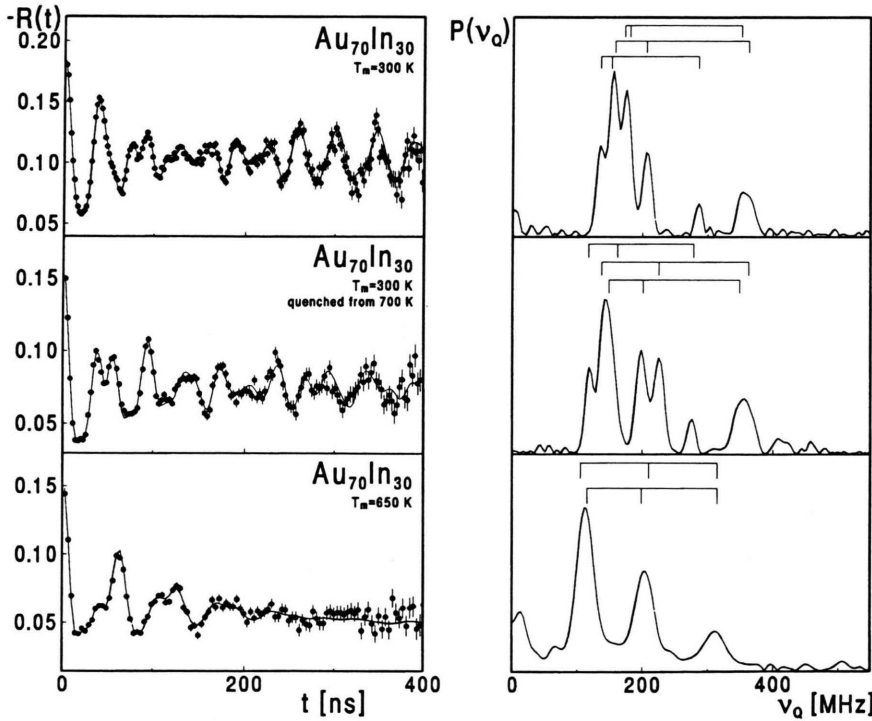


Fig. 3. PAC patterns (together with the corresponding Fourier transforms) measured at ^{111}Cd in an Au₇₀In₃₀ sample at different temperatures T_m .

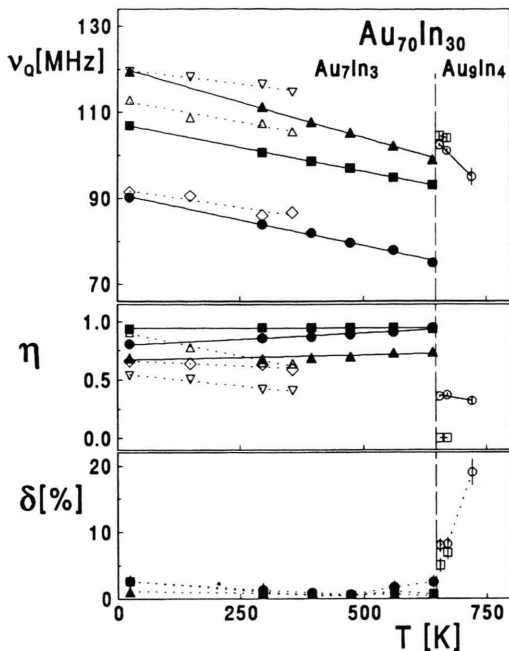


Fig. 4. Temperature dependence of quadrupole interaction parameters (quadrupole frequency ν_Q , asymmetry parameter η and the width δ of the EFG Lorentzian distribution) in an $\text{Au}_{70}\text{In}_{30}$ sample. Empty symbols below $T=400$ K correspond to the unknown phase obtained by quenching from 700 K.

The same samples quenched in water from temperatures above 700 K (700 K, 730 K and 870 K), i.e. above the γ' phase domain, exhibit three different EFGs. This result indicates the formation of a new, not previously known, phase. The corresponding PAC spectrum measured at room temperature is presented in Figure 3. Two In sites corresponding to the higher quadrupole frequency values (107 MHz and 116 MHz – see Table 1) are equally (ca. 42% each) populated. The PAC spectra taken at different temperatures proved that this new phase is stable up to 350 K and undergoes a transformation to the γ' phase at 435 K.

In order to check reproducibility of this result an additional set of PAC measurements for three samples with the atomic indium concentrations close to 30 at.% was executed. For all these specimens, quenched from ca. 870 K, the same PAC pattern characteristic for the previously unreported phase was evidenced. This phase, observed as a 100% contribution in the samples of 30 at.% indium concentration, was also evidenced for some other sample stoichiometries after quenching, but not as the single phase product.

It should be emphasized, that the same samples of 30 at.% indium concentration, quenched from temperatures below the γ - γ' phase transition, do not exhibit this new structure but the PAC spectra typical for the γ' phase.

One should also mention the result of Goral and Eyring [10] obtained in a high resolution microscopy study of gold-indium bilayers. They report the existence of a superstructure form of the Au_7In_3 γ' phase with a doubling of the hexagonal a axis. It is an open question, whether the phase observed in our experiments is identical with the superstructure mentioned above.

3.3. The ϵ' Phase (Au_3In)

The Au_3In phase has a composition of ≈ 25 at.% In and is isotypic with Cu_3Ti [11]. Between 572 and 612 K it undergoes an order-disorder transformation ($\epsilon' \leftrightarrow \epsilon$) and decomposes peritectically at 765.5 K [7]. ϵ' and ϵ represent ordered and disordered orthorhombic structures.

In $\text{Au}_{75}\text{In}_{25}$ one nonaxial electric field gradient was evidenced in the PAC pattern (Figure 5) and ascribed to the Au_3In compound of DO_a structure [12]. Its value also linearly decreases with the rise of temperature (Figure 6 and Table 1). An order-disorder phase transformation in Au_3In , manifested by the increase of the widths δ of quadrupole frequency distributions above 600 K (Figure 6), was observed in agreement with the phase diagram [13].

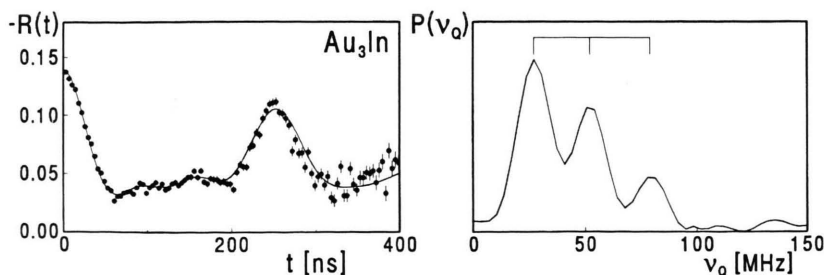


Fig. 5. Room temperature PAC spectrum with the corresponding Fourier transform measured at ^{111}Cd in the Au_3In compound.

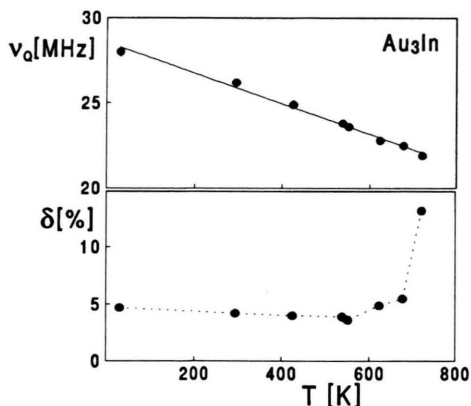


Fig. 6. Temperature dependence of the quadrupole frequency ν_Q and the width δ of EFG distribution at ^{111}Cd in the Au_3In compound.

3.4. The ψ Phase ($\text{Au}_{62}\text{In}_{38}$)

This compound was identified by Schubert *et al.* [14] as isotypic with Ni_2Al_3 . According to the phase diagram (Figure 2) this phase is formed between 500 and 540 K and extends from 35.5 to 39.5 at.% In at 730 K [7], narrowing to ≈ 39 at.% at 497 K.

Four samples of 36.7, 38.6, 39.5 and 39.7 at.% indium concentrations were prepared, and for all of them measurements over a wide temperature range were performed. A typical PAC spectrum measured at room temperature, i.e. below the temperature range of the discussed phase, is presented in Figure 7. One quadrupole frequency of 156(1) MHz with the corresponding asymmetry parameter $\eta = 0.57(1)$ was observed in this

experiment with a width δ of the frequency distribution of about 10%. This frequency exhibits a linear decrease with temperature described by the parameters $\nu_Q(0) = 163(2)$ MHz and $a = 1.7(3) \cdot 10^{-4} \text{ K}^{-1}$ (see (3)). The value of the δ parameter increased drastically above ≈ 550 K, and the PAC spectra taken in the temperature region reported for the Au_3In_2 phase are strongly damped (see Figures 7 and 8). All the PAC spectra taken between the Au_3In_2 phase boundaries (500 K – 730 K) resulted in similar spectra with a very large frequency distribution. This findings do not confirm the existence of an ordered phase in that region of the phase diagram. The 3-days annealing of the samples at the appropriate temperatures as well as the quenching did not improve the PAC spectra. The lack of a clear PAC signal, i.e. of a well defined axially symmetric EFG attributed to the one indium site, reported for this structure by Schubert *et al.* [5], is surprising and can only be explained by a disordered character of the discussed phase. It should, however, be pointed out that our result corroborates the phase diagram reported by Hansen *et al.* [15], where the Au_3In_2 phase is not evidenced.

3.5. The Solid Solution

This phase of h.c.p. A3-type structure [7, 11] has the indium solubility range between 13 and 23 at.% and decomposes peritectically. The PAC measurement for the $\text{Au}_{84}\text{In}_{16}$ sample resulted in a broad frequency distribution around $\nu_Q = 10.6(8)$ MHz. The large δ value of ca. 22% reflects the disordered structure of a solid solution.

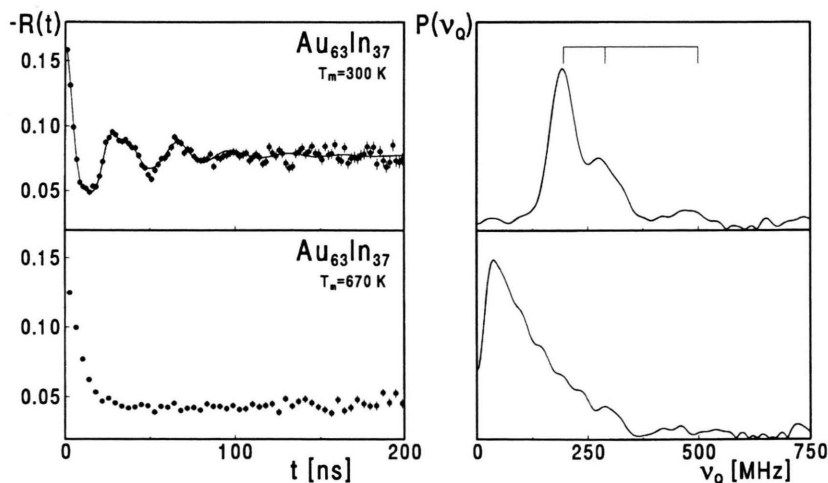


Fig. 7. PAC spectra with the corresponding Fourier transforms measured at ^{111}Cd in an $\text{Au}_{63}\text{In}_{37}$ sample at different temperatures T_m .

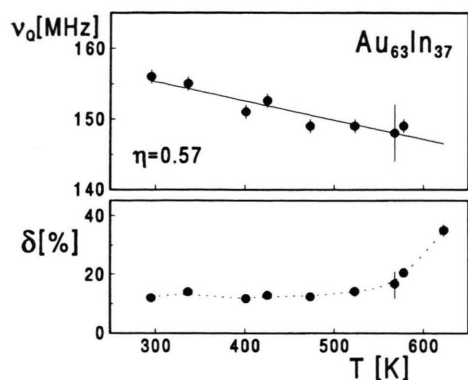


Fig. 8. Temperature dependence of the quadrupole frequency ν_Q and the width δ of EFG distribution at ^{111}Cd in an $\text{Au}_{63}\text{In}_{37}$ sample.

3.6. The α_1 Phase (Au_7In)

The α_1 phase is stable around 11.5 at.% In and decomposes by a peritectic reaction. Its hexagonal crystallographic structure is reported as DO_{24} (Ni_3Ti) type [11] or the Nd-type [7]. The PAC pattern measured for the $\text{Au}_{88.1}\text{In}_{11.9}$ sample annealed for one day at 780 K was described by a large frequency distribution around 11.3(6) MHz ($\delta = 33(3)\%$). Therefore, it appears better to regard the structure as being of the Nd-type and not of the Ni_3Ti -type, since the latter is a definitely ordered structure for which two unique axially symmetric EFGs should be expected.

4. Conclusions

The quadrupole interaction parameters for the ^{111}Cd probe in different phases of the Au-In system were determined. The results of PAC measurements for Au_3In , Au_9In_4 , Au_7In_3 , α_1 and ζ phases are in agreement with the corresponding structures given in the literature.

For the $\text{Au}_{70}\text{In}_{30}$ sample a new metastable structure modification was found. In the AuIn compound a polymorphic transition was observed at ca. 630 K.

The results for the $\text{Au}_{62}\text{In}_{38}$ stoichiometry do not confirm the existence of the ordered phase isotypic with Al_3Ni_2 . Also an attempt to observe the β_1 phase (of 22 at.% average indium concentration) with $\text{Cu}_{10}\text{Sb}_3$ type structure [16], where one unique nonaxially symmetric EFG is expected, failed.

Detailed XRD investigations of the Au-In alloys around 30 and 50 at.% indium concentration are needed to clarify the structure of the new phases observed with the PAC method. Further experiments concerning the formation of the intermetallic Au-In compounds at the interfaces of bi- and multilayer Au-In samples are in progress.

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- [1] V. Simić and Z. Marinković, *Thin Solid Films* **41**, 57 (1977).
- [2] W. Keppner, R. Wesche, T. Klas, J. Voigt, and G. Schatz, *Thin Solid Films* **143**, 201 (1986).
- [3] H. Frauenfelder and R. M. Steffen, in K. Karlsson, E. Matthias, and K. Siegbahn (eds.), *Alpha-, Beta- and Gamma-Ray Spectroscopy*, Vol. 2, North-Holland, Amsterdam 1963, P. 1118.
- [4] P. Herzog, K. Freitag, M. Reuschenbach, and H. Walitzki, *Z. Phys. A* **294**, 13 (1980).
- [5] K. Schubert, U. Rösler, and L. Härle, *Naturwissenschaften* **40**, 437 (1953).
- [6] H. Haas and D. A. Shirley, *J. Chem. Phys.* **58**, 3339 (1973).
- [7] S. E. R. Hiscocks and W. Hume-Rothery, *proc. R. Soc. London, Ser. A* **282**, 318 (1964).
- [8] M. Pusej and K. Schubert, *J. Less-Common Met.* **41**, 33 (1975).
- [9] P. Wodniecki, B. Wodniecka, M. Marszałek, and A. Z. Hryniewicz, *Acta Physica Polonica A* **88**, 333 (1995).
- [10] J. P. Goral and L. Eyring, *J. Less-Common Met.* **116**, 63 (1975).
- [11] J. Wegst and K. Schubert, *Z. Metallkd.* **49**, 533 (1958).
- [12] *Pearson's Handbook of Crystallographic Data*, P. Villars and L. D. Calved (eds.), 1991.
- [13] H. Okamoto and T. B. Massalski, *Binary Alloy Phase Diagrams* 1987.
- [14] J. Schubert, H. Breimer and R. Gohle, *Z. Metallkd.* **50**, 146 (1959).
- [15] M. Hansen, *Constitution of Binary Alloys*, McGraw-Hill, 1958.
- [16] K. Schubert, M. Balk, S. Bhan, H. Breimer, P. Esslinger and E. Stolz, *Naturwissenschaften* **46**, 647 (1959).