

Phase identification in the Cu-In-S system by γ - γ perturbed angular correlations

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Perturbed angular correlations (PAC's) of γ rays are applied to investigate the Cu-In-S system. The radioactive ^{111}In - ^{111}Cd tracers are incorporated in the metallic indium used as starting material for crystal growth. $\text{Cu}_{1-x}\text{In}_{1+x}\text{S}_2$ samples with varying Cu:In ratio ($x=0.0, 0.03, 0.07, 0.10$) were prepared and characterized by PAC's. The stoichiometric sample ($x=0.0$) shows cubic symmetry of the In site without tetragonal distortion. For all samples with In excess the signals of metallic In ($\nu_{Q1}=e^2qQ/h=18$ MHz, $\eta_1=0$) and InS ($\nu_{Q2}=233$ MHz, $\eta_2=0.15$) appear. Consequently, a new line in the Gibb's phase triangle of the Cu-In-S system is determined. The fractions of the In and InS phases as a function of In excess are analyzed.

I. INTRODUCTION

The potential of CuInS_2 for efficient photovoltaic solar energy conversion has attracted considerable interest in this material.¹⁻³ With a direct energy gap ($E_g=1.5$ eV) in the optimum of the theoretical conversion efficiency, the development of high-efficiency solar cells should be possible. The conversion efficiencies achieved so far, however, have been limited to values below 10%.⁴ Recently we have reported a 9.7% efficient photoelectrochemical solar cell based on n - CuInS_2 .³ These conversion efficiencies, however, were obtained only by preparing samples with substantial In excess, thus leaving the single-phase region of the compound.⁵ The spherical In precipitates observed had a significant influence on the defect chemistry and acted as impurity scavengers.⁶ It appears, therefore, promising to investigate the ternary Cu-In-S system with particular emphasis on the In-rich regions in the phase triangle.

We report here the first application of PAC's of γ rays to this type of problem. By using ^{111}In atoms as radioactive PAC tracers, one obtains a microscopic view of the In environments without introducing an external perturbation. The PAC method is particularly suited to identify noncubic phases⁷ and point defects in cubic phases.⁸ For example, the tetragonal distortion discussed for several ternary chalcopyrites including CuInS_2 (Ref. 9) should reveal themselves in a PAC modulation. A phase exhibiting a well-defined electric field gradient (EFG) can be identified if it contains more than about 1% of all In atoms. Several phases containing In can be identified simultaneously at this accuracy. In this respect, the PAC method is superior to x-ray diffraction of mixed phase samples. The typical tracer concentration is 10^{10} cm⁻³ in our experiments and thus well below usual doping levels in CuInS_2 and other In containing semiconductors. There-

fore, the electronic properties will not be affected by the nuclear transmutation of ^{111}In to ^{111}Cd .

II. EXPERIMENTAL DETAILS

The radioactive ^{111}In tracers were obtained as $^{111}\text{InCl}_3$ in 0.04M HCl from Amersham Buchler. Typically 50 μl of this solution containing 200 μCi ^{111}In were used for one sample preparation. The $^{111}\text{InCl}_3$ solution was put on a metallic indium foil and the water was removed by moderate heating. In a H_2 atmosphere the $^{111}\text{InCl}_3$ was reduced to metallic ^{111}In and a homogeneous distribution of ^{111}In in In was achieved by melting. Appropriate amounts of Cu, In, and S were sealed under Ar atmosphere in a quartz tube of 1-cm diam. and 30-cm length, which was put into a two-zone tube furnace such that the sulphur was positioned at the "cold" end of the quartz tube and copper and indium at the "warm" end. The temperatures were chosen to 480 and 1150 $^\circ\text{C}$, respectively, at a reaction time of typically 4 h. The subsequent cooling down to room temperature took another 12 h.

Subsequently the γ - γ perturbed angular correlations were recorded for the 171-245-keV γ cascade in ^{111}Cd by means of a conventional four-detector setup.¹⁰ Thus the hyperfine interaction of the isometric $\frac{5}{2}^+$ nuclear state in ^{111}Cd ($T_{1/2}=85$ ns) with surrounding charges can be observed. In nonmagnetic materials we only have to consider the electric quadrupole interaction, which is determined by the interaction frequency $\nu_Q=e^2qQ/h$ and the dimensionless asymmetry parameter η . eq is the largest component of the EFG tensor and eQ is the probe's nuclear quadrupole moment. $\nu_Q=0$ is obtained for cubic symmetry, while $\eta=0$ holds for axial symmetry with at least a threefold axis. The measured 12 coincidence spectra are combined to one PAC spectrum, $R(t)$, that contains the

relevant information. In general, the PAC probes may occupy N different sites characterized by different ν_{Qi} and η_i . Site No. 0 corresponds to $\nu_Q = 0$. The PAC spectrum then takes the general form⁸

$$R(t) = A_{22} \sum_{i=0}^N f_i \left(\sum_{n=0}^3 s_{ni} \exp(-c_{ni} b_i t) \times \cos\left(\frac{3}{10} \pi c_{ni} \nu_{Qi} t\right) \right). \quad (1)$$

Thus, each component i of a PAC spectrum corresponds to a lattice site or local environment, respectively, that is occupied by a probe with the probability f_i . Each component contributes three frequencies $c_{ni} \nu_{Qi}$ weighted by the amplitudes s_{ni} to the spectrum. The exponential term in $R(t)$ accounts for (Lorentzian shaped) frequency distributions that may occur, e.g., as a consequence of randomly distributed lattice defects.

III. RESULTS AND DISCUSSION

Figure 1 shows the PAC spectrum of ^{111}In in stoichiometric CuInS_2 . The spectrum does not show a modulation but rather a slight decrease of anisotropy with time which can be described by a Lorentzian frequency distribution around $\nu_Q = 0$ and $b_0 = 0.23(9)$ MHz. This result shows that all ^{111}In - ^{111}Cd probes are located in nearly cubic environments with very low EFG's around $11(5) \times 10^{14}$ V/cm². We attribute these EFG's to randomly distributed defects. In case of a tetragonal lattice distortion the corresponding EFG would give rise to a well-defined frequency which is obviously not observed. Mössbauer experiments with CuInS_2 doped with ^{57}Fe , however, showed two large quadrupole splittings.¹¹ One of these was attributed to $^{57}\text{Fe}^{2+}$ on substitutional In sites and the respective quadrupole splitting was explained by a tetragonal distortion ($c/a > 2.0$) of the surrounding sulphur tetrahedron. The fact that a similar quadrupolar

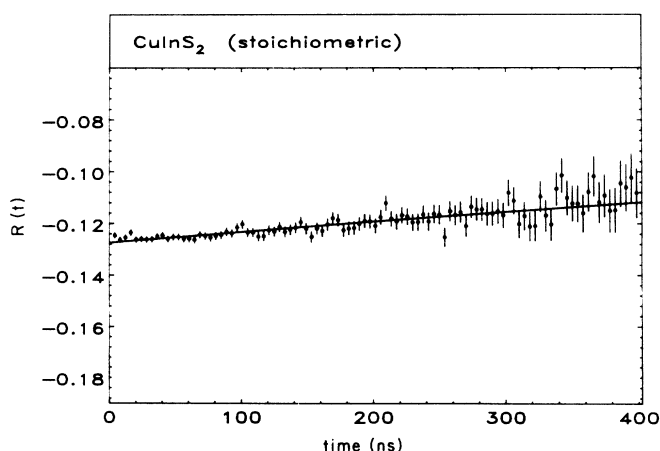


FIG. 1. PAC spectrum of stoichiometric CuInS_2 . The spectrum shows cubic symmetry for all ^{111}In - ^{111}Cd probes and gives no indication for a tetragonal lattice distortion. The slight decrease of anisotropy with time is probably an effect of randomly distributed lattice defects.

effect is not observed in our experiment may reflect the different properties of the probe atoms. It is more likely, however, that the local environment around the probe atoms is different in both experiments. It should be noted that considerable deviations from $c/a = 2.0$ have only been observed in nonstoichiometric samples.¹² For our case it is evident that the ^{111}In - ^{111}Cd probe is located on a regular In site. Therefore, we have shown that there is no substantial EFG at the In sites and thus no evidence for a deviation from $c/a = 2.0$ in accordance with earlier data.¹³

As a precursor experiment concerning the role of In excess in the Cu-In-S system, a sample with high In excess (20–30%) was prepared by melting metallic In with stoichiometric CuInS_2 . In order to leave the CuInS_2 -In line granular In_2S_3 and CuInS_2 were positioned at the “cold” end of the ampoule providing excess sulphur in the gas phase. The corresponding PAC spectrum and its Fourier transform are shown in Fig. 2. The spectrum can be decomposed into three parts [$i = 0, 1$, and 2 in Eq. (1)]. Besides the contribution of cubic CuInS_2 [$\nu_{Q0} = 0$, $f_0 = 0.58(1)$], two well-defined frequency sets due to non-cubic environments are present. The part with $f_1 = 0.21(1)$ and $\nu_{Q1} = 18(1)$ MHz ($\eta_1 = 0$) originates

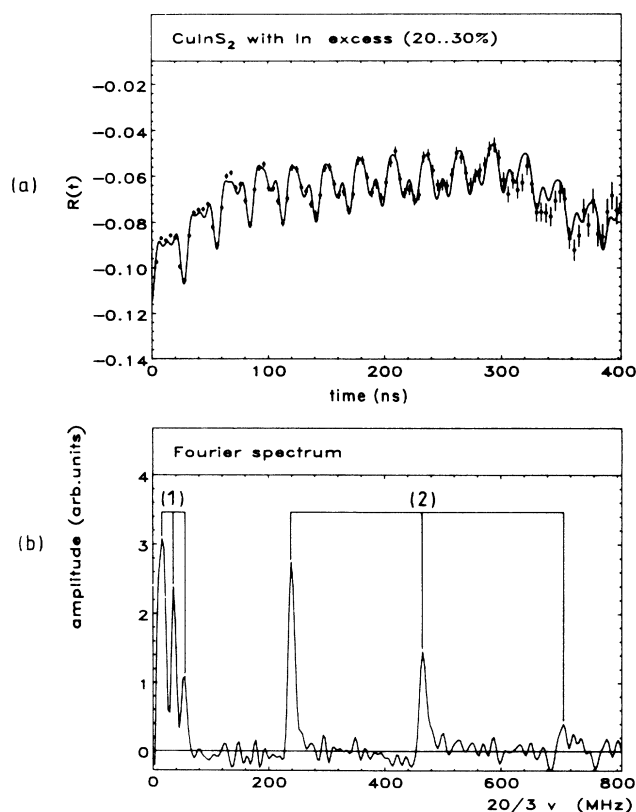


FIG. 2. PAC spectrum (a) and its Fourier transform (b) of a sample prepared from stoichiometric CuInS_2 and metallic In. The Fourier spectrum demonstrates the appearance of two non-cubic components. The hyperfine parameters $\nu_{Q1} = 18$ MHz ($\eta_1 = 0.0$) and $\nu_{Q2} = 233$ MHz ($\eta_2 = 0.15$) extracted from a least-squares fit [solid line in (a)] allow the identification as metallic In and InS , respectively.

from metallic In.¹⁰ The second frequency set [$f_2=0.21(1)$, $\nu_{Q2}=233(1)$ MHz ($\eta_2=0.15$)] results from ¹¹¹In probes in crystalline InS occlusions.¹⁴ Thus we have shown for the first time that CuInS₂ and InS coexist in thermal equilibrium. This enables us to draw a new line in the Gibb's phase triangle of the Cu-In-S system as shown in Fig. 3. We note that the PAC signals of the various In₂S₃ phases are also well known.¹⁴ No such signal is observed in our experiment. Therefore, the appearance of a In₂S₃ phase is definitely excluded.

The new line offers the new possibility to prepare CuInS₂ in equilibrium with InS. The molecularity along this line is changed by varying the Cu:In ratio. Therefore, we have prepared samples with nominal composition Cu_{1-x}In_{1+x}S₂ with $x=0.03, 0.07,$ and 0.10 . The respective PAC spectra are displayed in Fig. 4. Besides the prominent modulation induced by the InS phase, all spectra reveal a small content of metallic In. The remaining part of the signal is due to the cubic CuInS₂ phase. The observed effective anisotropy is considerably reduced for the Cu_{0.9}In_{1.1}S₂ sample (Fig. 4, top). The fractions of the InS and In phases deduced from the spectra of Fig. 4 are shown in Fig. 5 as a function of In excess. The appearance of the metallic In phase is unexpected and indicates a deviation from the nominal stoichiometry. This deviation must be due to an irreversible loss of sulphur in the evacuated ampoule upon heating. How this loss of sulphur affects the observed fractions of phases is illustrated in Fig. 5. Besides the individual fractions their sum is also plotted. For comparison the fraction of InS which would have been expected from nominal stoichiometry when moving along the CuInS₂-InS line (see Fig. 3) is also given in Fig. 5. Only for the sample with the largest In excess (10%) the expected InS fraction matches with the sum of the observed In and InS fractions, suggesting that the loss of sulphur exclusively affects the InS phase and that the produced CuInS₂ is stoichiometric within our experimental limits. For lower In excess a different behavior

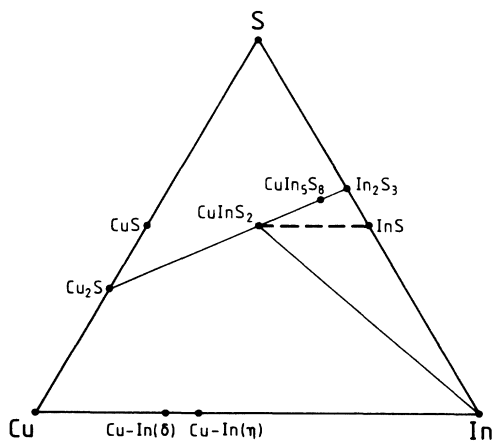


FIG. 3. Gibb's phase triangle of the Cu-In-S system. The line connecting Cu₂S in In₂S₃ stems from Ref. 11. Our data show for the first time that CuInS₂ coexists with InS in thermal equilibrium (broken line) and confirm the line between CuInS₂ and In.

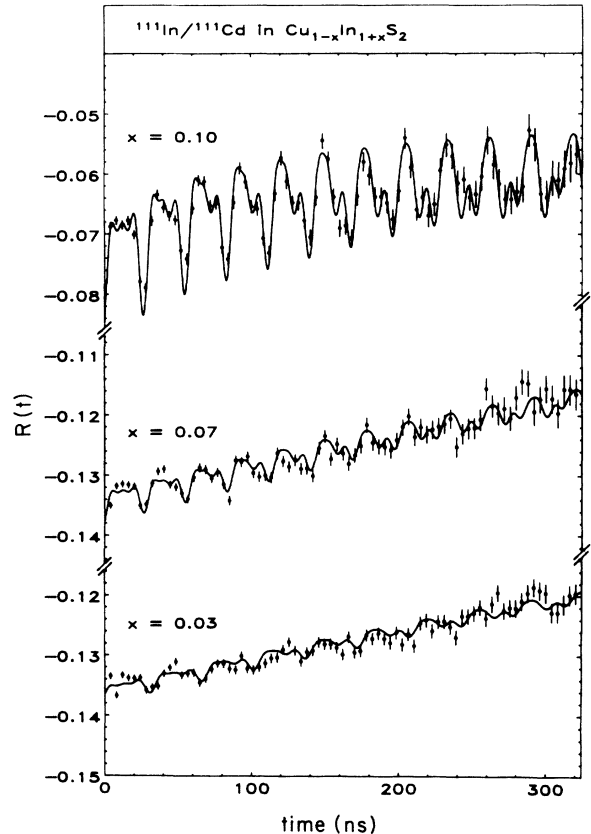


FIG. 4. PAC spectra for Cu_{1-x}In_{1+x}S₂ samples with $x=0.03, 0.07,$ and 0.10 . All spectra contain both the metallic In- and the InS-PAC signal at different fractions.

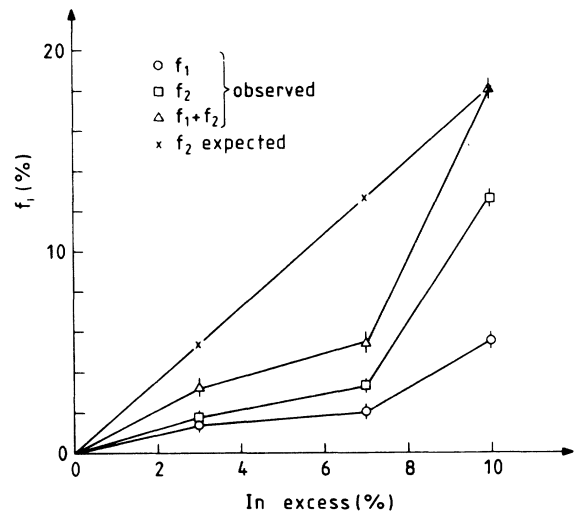


FIG. 5. The fractions of the In (f_1) and InS phase (f_2) as a function of In excess. The data are extracted from the spectra of Fig. 4. Besides the sum of these experimentally determined fractions (f_1+f_2) also the InS fraction as it would have been expected from the nominal stoichiometry is plotted. The sum of In and InS and the expected InS fraction only match in the case of $x=0.10$.

is found, i.e., the sum of the fractions is considerably lower than the expected InS value. Besides the sulphur loss responsible for the appearance of the In phase this result demonstrates that a In rich CuInS₂ exists. From the data we infer an In excess of $x = 1.5$ and 4.5 at.% within the Cu_{1-x}In_{1+x}S₂ phase, respectively, if a possible sulphur loss is neglected.

At present, the origin of the pronounced change between 7% and 10% total In excess is not known. The different properties of CuInS₂ for 10% In excess are also evident from the top of Fig. 4. The spectrum shows a reduced effective anisotropy presumably due to a fast relaxation process for part of the probes typical for ¹¹¹In PAC

in insulators.¹⁰ Therefore, we assume that intrinsic, probably compensated CuInS₂ has been formed.

In conclusion, we have shown that PAC's with ¹¹¹In-¹¹¹Cd tracer atoms are well suited to investigate the Cu-In-S phase system. An extension of the present work to other parts of the phase diagram and to thin film samples is in progress.

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