Time-differential perturbed-angular-correlation study of the In_2Se_3 crystal structure

Karl Krusch and John A. Gardner

Department of Physics, Oregon State University, Corvallis, Oregon 97331

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The time-differential perturbed-angular-correlation technique has been used to investigate the temperature dependence of the electric-field gradient (EFG) at Cd impurities in the semiconducting compound In_2Se_3. Between room temperature and the melting point, four different phases could be observed. Most crystal structures which have been proposed for the α and β phases are shown to be incorrect. The β' phase (550—720 °C) has not been reported previously. The data suggest that the β phase may be a Peierls distortion of the β' phase. The EFG in the α phase is well described by a simple point-charge model suggesting that the electronic part of the EFG in α-In_2Se_3 is small.

I. INTRODUCTION

Like most III-IV compounds of the general formula A_2B_3, In_2Se_3 is a semiconductor with a number of structural modifications and complicated low-temperature phases. Although it has been the subject of several x-ray and electron microscopy studies,[1-7] the different structures and their transition temperatures are not all well established. The time-differential perturbed-angular-correlation (TDPAC) technique is a powerful tool for investigating electric-field gradients (EFG), magnetic hyperfine fields, and relaxation mechanisms at the site of radioactive tracer nuclei. Electric-field gradients are very sensitive to the local symmetry of the tracer nucleus, and it is often possible to distinguish between structures which are only slightly

different.[8] Our interest in the compound In_2Se_3 initially arose from an investigation of motional correlation times at ^{111}In-^{111}Cd probe nuclei in liquid Se using the TDPAC technique. At lower temperature a solid often precipitated, and it was assumed that this solid was In_2Se_3.[9] The necessity of characterizing the TDPAC spectrum of this precipitate and the lack of definitive structural information about higher-temperature phases of In_2Se_3 prompted us to undertake this investigation of the temperature dependence of the EFG at the site of Cd impurities in In_2Se_3.

II. EXPERIMENTAL DETAILS, DATA ANALYSIS, AND RESULTS

The radioactive isotope ^{111}In used in these measurements has a half-life of 2.83 days and decays

TABLE I. Summary of relevant nuclear characteristics of radioactive probe nuclide $^{111}In \rightarrow ^{111}Cd$.[a]

Parent half-life	2.83 days
Energies of γ-γ cascade	171—245 keV
Nuclear spin sequence	$\frac{7}{2}+ - \frac{5}{2}+ - \frac{1}{2}+$
Angular correlation coefficients:	
A_{22}	$-0.180(2)$
A_{44}	$+0.002(3)$
Intermediate nuclear state:	
half-life	84 nsec
spectroscopic nuclear quadrupole moment	$+0.83(13)$ b

[a] All data taken from S. Raman and H. J. Kim, Nucl. Data B6, 39 (1971), except quadrupole moment which is from P. Herzog et al., Z. Phys. A 294, 13 (1980).

by electron capture to the 416-keV state of ^{111}Cd.

This excited state (half-life 0.12 nsec) subsequently decays via a γ-γ cascade to the ground state of ^{111} Cd. The relevant nuclear parameters for this system are given in Table I.

The experimental setup for the time-differential perturbed angular correlation measurement consists of four NaI(Tl) scintillation counters, arranged in fixed positions symmetrically in the horizontal plane around the sample. Delayed coincidences of the 171−245 keV cascade were detected for inter-

dectector angles $\theta = 90°$ and $\theta = 180°$ by standard fast-slow coincidence circuits. The resulting four spectra were stored in separate memory banks of a multichannel analyzer as a function of the time delay t between the two γ emissions. After data were collected for approximately 24 h, the ratio

$$R(t) = \frac{2}{3}\left[\left[\frac{C_1(180°,t)C_4(180°,t)}{C_3(90°,t)C_2(90°,t)} \right]^{1/2} - 1 \right]$$

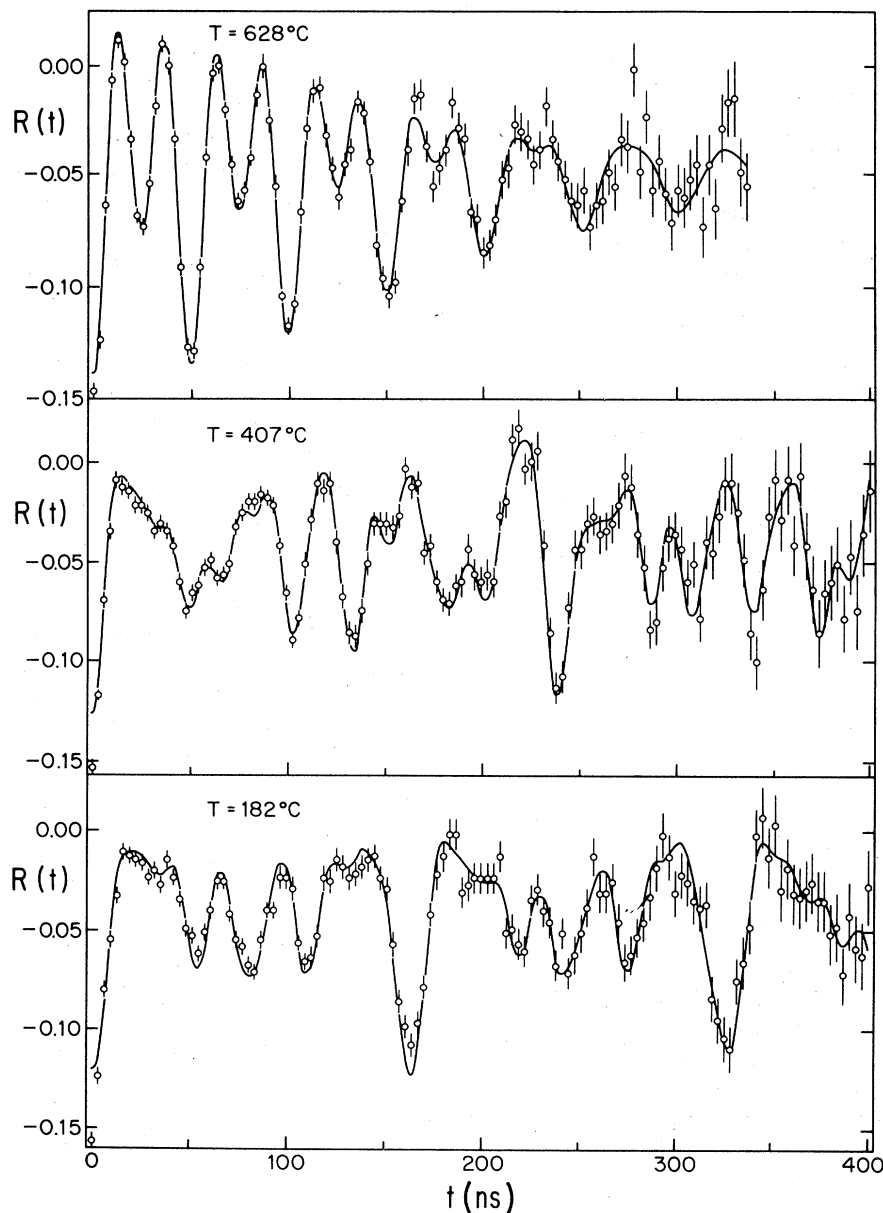was computed. Here the $C_i(\theta, t)$, $i = 1$ to 4, are the

FIG. 1. Representative $R(t)$ spectra at three temperatures. Statistical errors are shown. The solid curves are computer fits described in the text.

time spectra collected by the different detector combinations corrected for random coincidences. Representative $R(t)$ data are shown in Fig. 1. $R(t)$ is related to the perturbation function $G_{22}(t)$ for electric quadrupole interactions by[10]

$$R(t) = \frac{A_{22}G_{22}(t)}{1 - \frac{1}{2}A_{22}G_{22}(t)} .$$

$A_{22}(t)$ is the anisotropy parameter given in Table I.

The ^{111}In tracer was obtained commercially as a carrier-free solution in HCl. Samples were prepared by drying a small amount of the radioactive solution on a few pellets of Se and In which were then sealed in a 2-mm i.d. quartz tube under vacuum. The capsules were heated to a temperature just above the melting point of In_2Se_3 with occasional agitation for 12 h. Then they were cooled to approximately 800 °C and annealed for three days before data were collected. The samples were deliberately prepared with an excess of Se above the In_2Se_3 composition to minimize the possibility of producing any of the more In-rich phases. At temperatures below 750 °C, the Se solubility in In_2Se_3 and the In solubility in Se is sufficiently small that the excess Se should have no effect on the TDPAC spectra.

The observed $R(t)$ spectra were analyzed by performing least-squares computer fits to the following two-component perturbation function for an electric quadrupole interaction in polycrystalline samples[11]:

$$G_{22}(t) = f \sum_{n=0}^{3} S_{2n}\cos(\omega_{1n}t)$$

$$\times \exp(-\tfrac{1}{2}\omega_{1n}^2\delta_1^2t^2)$$

$$+(1-f) \sum_{n=0}^{3} S_{2n}\cos(\omega_{2n}t)$$

$$\times \exp(-\tfrac{1}{2}\omega_{2n}^2\delta_2^2t^2) .$$

Here, f and $1-f$ are the fractions of the ^{111}Cd nuclei which are subject to an electric quadrupole interaction characterized by the frequencies ω_{1n}, and ω_{2n}, respectively. The ω_{in} are functions of the quadrupole frequency $v_Q = eQV_{zz}/h$ and the asymmetry parameter $\eta = (V_{xx} - V_{yy})/V_{zz}$. The V_{ii} are the components of the diagonalized EFG tensor arranged so $|V_{xx}| \leq |V_{yy}| \leq |V_{zz}|$, while the δ_i describe the relative width of the Gaussian frequency distribution assumed for both lattice sites. This

function provided a good fit to all data below 720 °C, and no indication was found that more than two different symmetry sites for In atoms exist in any of the samples. The parameters obtained from these fits are given in Table II, and the derived EFG and η values are shown in Fig. 2. Between room temperature and the melting point, four different phases, denoted by α, β, β', and γ can be identified. Above 840 °C, $R(t)$ could be fit by

$$G_{22}(t) = \exp(-\lambda t) ,$$

indicating either a time-dependent interaction[12] or a very broad distribution of small electric-field gradients.[11] The fit parameters λ are given in Table II. In this temperature range, however, the composition of our samples probably departs significantly from In_2Se_3, so λ probably does not reflect the TDPAC spectrum of pure In_2Se_3.

Below 550 °C (α and β phases), the data are well fit with $\delta_1 = \delta_2 = 0$, implying two well-defined lattice sites. The two sites are equally populated ($f = 0.5$). The geometric factors S_{2n} differ slightly from the theoretical values for randomly oriented polycrystalline samples[13] and were treated as free fit parameters. Between 550 and 720 °C (β' phase) the data were best described by a single lattice site and a frequency distribution of approximately 4%. In the γ phase (720—810 °C), $G_{22}(t)$ was constant, implying a cubic In environment. The β phase shows a strong supercooling tendency, and the lifetime of the metastable β phase above 100 °C was much longer than the half life of the ^{111}In tracer. The α phase samples were made by quenching from 800 °C to room temperature and annealing at 180 °C to relieve strains as much as possible.

III. DISCUSSION

A. The electric-field gradient

The observation of well-defined angular correlation curves for static quadrupole interactions indicates that the ^{111}Cd probe nuclei are in equilibrium with their electronic environment when the γ-γ cascade occurs. This is expected to be the case, since the 0.12-nsec half-life of the initial state of the cascade is long enough and the electrical conductivity of In_2Se_3 (Ref. 14) is large enough for the electron cores of the Cd probe to relax after the electron capture decay.

TABLE II. Quadrupole frequencies and asymmetry parameters derived from computer fits as described in text.

T (°C)	γ_Q (MHz)	η	δ	
25	115.8(4)	0	0	(site 1)
	83.5(3)	0	0	(site 2)
107	119.1(3)	0.11(4)	0	(site 1)
	82.2(3)	0	0	(site 2)
182	120.4(3)	0.11(4)	0	(site 1)
	82.3(3)	0	0	(site 2)
120[a]	143.0(6)	0.20(4)	0	(site 1)
	98.0(5)	0.35(5)	0	(site 2)
181[a]	138.0(6)	0.28(4)	0	(site 1)
	98.0(5)	0.32(5)	0	(site 2)
274	135.6(3)	0.26(3)	0	(site 1)
	98.0(3)	0.32(2)	0	(site 2)
341	132.3(4)	0.25(3)	0	(site 1)
	98.0(4)	0.31(2)	0	(site 2)
407	129.3(3)	0.26(3)	0	(site 1)
	98.7(3)	0.30(3)	0	(site 2)
510	123.4(3)	0.25(3)	0	(site 1)
	101.7(3)	0.27(2)	0	(site 2)
584	134.7(3)	0	3.9(1)%	
628	130.3(4)	0.08(4)	3.4(1)%	
667	126.5(3)	0	3.3(1)%	
716	126.5(3)	0	3.7(2)%	
759	0			
806	0			

	Time-dependent interaction			
T (°C)	λ (MHz)			
843	0.29(5)			
861	0.26(5)			
933	0.09(5)			

[a] Supercooled sample.

Electric-field gradients at probe nuclei in solids are usually taken to be the sum of a lattice part V_{zz}^{lat}, caused by the ion cores of nearby atoms, and an electronic part which arises from the influence of covalent bonds, conduction electrons, and unfilled electronic shells of the probe atom.[15] Since In_2Se_3 is a semiconductor and Cd has no unfilled d or f shells, the latter two contributions should be negligible. We have made a lattice sum calculation of V_{zz}^{lat} for the α phase using a point-charge model for the nearest-neighbor atoms. The influence of second and higher neighbor shells as well as lattice distortions due to the substitution of Cd at the In sites has been neglected. We used the structural data of Likforman et al.[3] who describe the α phase as a distorted wurzitetype structure with two equally populated In sites. No other of the numerous structures which have been proposed[5,7] has two equally-populated In sites. The charge state of the Se near neighbors is estimated from the Se-In electronegativity difference to be $-0.364e$.[16,17] To correct approximately for the polarization of the Cd electronic core, the field gradient due to the point charges is multiplied by an antishielding factor $(1-\gamma_\infty)=30$ appropriate to a Cd^{2+} ion.[18] The results are shown in Table III. If we identify site 1 as the tetragonally coordinated site and site 2 as the pentagonally coordinated one, the agreement between the calculated V_{zz}^{lat} and the experiemntally observed field gradients is suprisingly good, so any electronic contributions to V_{zz} are apparently small. The asymmetry parameters are in less good agreement, but these are very sensitive to small lattice distortions around the Cd impurity which were ignored in this calculation.

Similar calculations cannot be done at present for the higher-temperature phases, because detailed structural data are not available. It is known however that In_2Se_3 contracts significantly in the $\alpha \rightarrow \beta$ transition.[19] Qualitatively, one expects a larger V_{zz}^{lat}
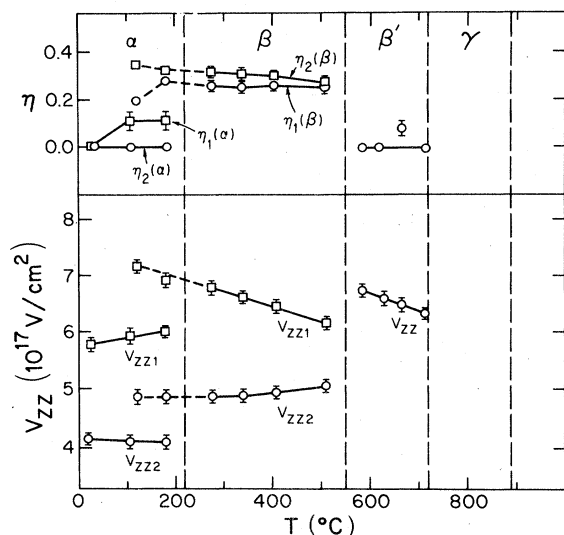
FIG. 2. Electric-field gradients and asymmetry parameters derived from computer fits. The two sites in the α and β phase are equally populated. The single site in the β' phase has a frequency distribution of 4%. The lines joining points have no theoretical significance.

when the atoms are closer together, and this is consistent with the larger V_{zz} found in the β phase.

B. Structure of In$_2$Se$_3$

These TDPAC measurements show, that all ^{111}Cd tracer atoms occupy one of two distinguishable In sites in the α and β phases of In$_2$Se$_3$. Both sites are equally populated and apart from one site in the α phase, all have less than axial symmetry. There have been a number of x ray and electron diffraction investigations of In$_2$Se$_3$, and several mutually inconsistent crystal structures for the α (Refs. 3, 5, and 7) and β (Refs. 4 and 7) phases have been proposed. For the α phase, only the structure proposed by Likforman et al.[3] is even qualitatively consistent with the TDPAC results as discussed above. For the β phase, the only structure which may be qualitatively consistent with the TDPAC results are those proposed by Semilitov,[4] but his structural investigation was too imprecise

for any meaningful comparison. The β' phase has not been previously reported. In order to escape observation by numerous investigators the β and β' phases probably are structurally similar, and the $\beta \rightleftharpoons \beta'$ transition probably has a relatively small specific-heat anomaly. This observation, along with the temperature dependence of the field gradients in the β and β' phases leads us to speculate that β is a Peierls distortion of β'. Both, the relatively large V_{zz} distribution of the β' single site and the convergence of the two V_{zz} and η values with rising temperature in the β phase are suggestive of this possibility. It should be emphasized that the appearance of the β' phase is not an artifact of the data analysis. The TDPAC data of this phase could be fit as well to a two-lattice-site model with only slightly different interaction frequencies. Both frequencies fall within the width of the Gaussian distribution determined by the one-site model and are significantly different from the values in the β phase.

We find the γ phase to be cubic as reported by Likforman et al.[2] but can obtain no further information from TDPAC. Unfortunately, we also can deduce no structural properties from our data above 800 °C because of the Se excess in our samples. In this temperature region a monoclinic δ phase has been reported.[1] These TDPAC data are taken at temperature intervals which are too widely spaced to reveal accurately the transition temperatures. The $\alpha \rightarrow \beta$ transition temperature of 220 °C and the $\beta' \rightarrow \gamma$ transition temperature of 720 °C reported by Likforman et al.[2] are consistent with our measurements. The $\beta \rightarrow \beta'$ transition occurs at approximately 550 °C.

ACKNOWLEDGMENTS

TABLE III. Comparison of experimental and calculated EFG for the α phase.

Site	V_{zz} (10^{17} V/cm^2)	η
No. 1 (experimental)	4.17(65)	0 ($T = 25$ °C)
		0.1 ($T > 25$ °C)
Fourfold coordinated (calculated)	4.21	0.23
No. 2 (experimental)	5.78(91)	0
Fivefold coordinated (calculated)	4.67	0.19

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