Electric Quadrupole Interaction of $^{111}\text{Cd}$ in Semiconductors*

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The time differential perturbed angular correlation technique was applied to study the electric quadrupole interaction in various semiconductors. The quadrupole coupling of $^{111}\text{Cd}$ in the InX and In$_2$X$_3$ compounds (X = S, Se, Te) are reported.

In the orthorhombic InS we observed one quadrupole frequency which increases linearly with temperature. The behaviour is the same in InTe. In InSe, however, the electric field gradient (EFG) scales with a $T^{3/2}$ power law, well known from former investigations in metals and semimetals.

The In$_2$X$_3$ semiconductors show several modifications. In$_2$S$_3$ exists in three phases and has been investigated in the temperature range 25 K $\leq T \leq$ 1200 K. In $\beta$-In$_2$S$_3$ (stable up to 693 K) two interaction frequencies have been observed. The high temperature modification $\gamma$-In$_2$S$_3$ shows one EFG. In cubic $\alpha$-In$_2$S$_3$ no EFG could be measured. In$_2$Se$_3$ exists in four modifications. The different phases and transition temperatures are not definite yet. In the $\beta$-phase (stable between 473 K and 823 K) we observed two energetically equal structures with different interaction frequencies. Such a case has not yet been reported. In$_2$Te$_3$ has been investigated in the $\beta$-phase only. The observed interaction is temperature independent.

While in metals and semimetals most data can be well described by a $T^{3/2}$-dependence, semiconductors show different results.

Introduction

Nuclear quadrupole coupling has been intensively studied in metals. NQR as well as TDPAC experiments lead to the well known $T^{3/2}$ power law for the temperature dependence of the EFG [1]. It could be shown that for metals not only the lattice parameters but also the conduction electrons are essential for the EFG [2].

Measuring the EFG in semimetals and semiconductors offers the possibility to change the electron density either by adding impurities or by varying the temperature, whereas in metals the electron density is temperature independent. Investigations of the classic semimetal antimony and its alloys Sb$_1-x$M$_x$ (M = Ag, Cd, In, Sn) showed quite a different behavior in contrast to metals [3].

First experiments in the semiconductor tellurium ($E_g = 0.33$ eV) indicated an increase of the EFG with increasing temperature [4]. This result is unlike the above mentioned one. Further investigations in the isostructural compounds Sb$_2$Te$_3$ and Bi$_2$Te$_3$, narrow gap semiconductors as tellurium ($E_g = 0.15$ eV respectively $E_g = 0.3$ eV), yield the same data [3].

The magnitude of the EFG is about the same in all cases. It could be shown that the probe nuclei $^{111}\text{Cd}$ occupy interstitial lattice sites and the EFG will mainly be determined by a covalent bond of Cd to the next Te neighbours. Studies in the cubic insulator CdCl$_2$ confirm this thesis, where $^{111}\text{In}$ and the isomeric level in $^{111}\text{Cd}$ were used as parent activities [5]. In the second case only one interaction was observed, proving that the $^{111}\text{In}$ atoms are seated on interstitials.

1. Method

The TDPAC technique is based on the observation of the correlation between emission directions of two successive radiations emitted during a nuclear decay cascade exposed to extranuclear fields. The angular correlation of $\gamma$-rays emitted in a nuclear cascade can be expressed in terms of Legendre polynomials

$$ W(\theta, \phi) = \sum A_k A_k^* P_k(\cos \theta). $$

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The coefficients $A_k^2$ and $A_k^3$ depend on the spin of the decaying level and the multipolarity of the $\gamma$-radiation. If during the lifetime $\tau$ of the excited level an extranuclear EFG acts on the nucleus, the interaction of the nuclear quadrupole moment and the EFG leads to a perturbation of the angular correlation and consequently causes a characteristic modulation of the exponential decay curve. The coincidence counting rates therefore are described by

$$N(\theta, t) = N_0 \cdot \exp\left(-\frac{t}{\tau}\right) \cdot W(\theta, t) + U_0.$$ 

A time constant background caused by random events is taken into account by $U_0$. In the case of the perturbed angular correlation, the relation

$$W(\theta, t) = 1 + A_{22} G_{22}(t) P_2(\cos \theta)$$

holds. For static randomly oriented interaction the perturbation function is given by

$$G_{22}(t) = s^{20}(\eta) + \sum s^{2n}(\eta) \exp\left[-\frac{1}{2}(\delta \omega_2^2) t\right] \cos \omega_n(\eta) t$$

with $\omega_n = n \omega_0$ ($\eta = 0$) and $\omega_0 = 3 \pi v_Q / 10$, where $v_Q = e Q V_q / h$. The term $\delta \omega_2^2$ stands for a possible spread in the interaction frequency $\omega_n$, either Gaussian or Lorentzian.

### 1.1. Probe Nucleus

In all cases we made use of the radioactive noble isotope $^{111}\text{In}$, which decays by electron capture with a 2.8-day half-life to nuclear levels in $^{111}\text{Cd}$. The excited $^{111}\text{Cd}$ nuclei decay via a $\gamma$-$\gamma$-cascade to the ground state, including the $5/2^+$ state at 247 keV with a lifetime $\tau = 122$ ns and a quadrupole moment $Q = 0.77$ barn.

### 1.2. Sample Preparation

The samples were prepared by electroplating the radioactive $^{111}\text{In}$ onto In-foil. Subsequently the stoichiometric composition of In and the corresponding component X = S, Se, Te were sealed in an evacuated glass tube. The capsules were heated above the melting point and the obtained melts cooled down to room temperature. To get polycrystalline modulation patterns the samples were powdered. Annealing procedures were necessary in some cases to obtain reasonable spectra. X-ray diffraction studies proved the crystal structure of the composition.

### 1.3. Experiment, Data Handling

The experimental arrangement was a conventional $180^\circ/90^\circ$ four detector set up. Via a Single-Channel-Analyzer (SCA), counters A and B select the 173 keV events $\gamma_1$ when the intermediate $5/2^+$ level is populated, and counters C and D the 247 keV radiation $\gamma_2$, respectively, emitted during the decay into the ground state. Thus time spectra AC ($180^\circ$, $t$), BC ($90^\circ$, $t$), AD ($90^\circ$, $t$) and BD ($180^\circ$, $t$) are recorded. The counting rates were reduced according to

$$R(t) = \frac{2}{3} \left[ \sqrt{\frac{AC(180^\circ, t) \cdot BC(90^\circ, t) - AD(90^\circ, t)}{BD(180^\circ, t)}} - 1 \right]$$

after background correction. This ratio equals the effective amplitude times the perturbation function:

$$R(t) \cong A_{22}^{\text{eff}} G_{22}(t).$$

Finally up to two functions $G_{22}(t)$ were fitted to the data by a least squares fit procedure.

The relevant data derived from TDPAC measurements are

- the amplitude $A_{22}^{\text{eff}}$, 
- the quadrupole coupling constant $v_Q$, 
- the relative frequency distribution $\Delta v_Q / v_Q$, 
- the asymmetry parameter $\eta$.

### 2. Results

#### InX Compounds:

**I. InS:** InS was investigated in the temperature range $21 \text{ K} \leq T \leq 843 \text{ K}$. We observed one interaction frequency and a positive slope $\Delta v_Q / \Delta T$ of the temperature dependence. Yet the EFG is very well defined, indicated by a very small frequency distribution $\delta = 0.4\%$, and not axially symmetric. The average asymmetry parameter is $\eta = 0.15$. The measured quadrupole coupling constant $v_Q$ varies between 225.25 Mc and 241.7 Mc. A time spectrum is shown in Fig. 1 and the temperature dependence in Figure 2a.

**II. InSe:** the observed temperature range was $20 \text{ K} \leq T \leq 865 \text{ K}$. The time spectra were fitted with one frequency and an asymmetry parameter $\eta = 0$. The frequency distribution is about $\delta = 2\%$. The temperature dependence can be described by a
Electric Quadrupole Interaction of $^{111}$Cd in Semiconductors

$T^{3/2}$ power law and the EFG decreases from $v_Q = 141$ Mc to $v_Q = 107$ Mc (Figure 2 b).

III. InTe: InTe has been measured at temperatures between 84 K and 817 K. Similarly to tellurium and its compounds Sb$_2$Te$_3$ and Bi$_2$Te$_3$ we observed an increase of the quadrupole coupling with temperature (Figure 2 c). The strength of the interaction is in the same range as in the above mentioned compound. The time spectra have been fitted with one frequency only and a relatively broad frequency distribution $\delta = 10\%$.

3. In$_2$X$_3$-Compounds

The In$_2$X$_3$-semiconductors all exist in several sometimes complicated modifications. The data received reflect this fact.

I. In$_2$S$_3$: In$_2$S$_3$ exists in three phases and has been investigated in the temperature range 25 K $\leq T \leq 1172$ K. $\beta$-In$_2$S$_3$ is stable up to 693 K. In its defective spinel type structure the probe nuclei occupy octahedral and tetrahedral sites. Therefore two interaction frequencies have been observed, one nearly constant ($v_Q = 70$ Mc), the second decreasing with increasing temperature (118 Mc $< v_Q < 150$ Mc). In cubic $\alpha$-In$_2$S$_3$ no EFG could be observed. The high temperature modification $\gamma$-In$_2$S$_3$ has a layered trigonal structure. Here one frequency has been observed, decreasing with increasing temperature (103 Mc $< v_Q < 120$ Mc). The results are shown in Figure 3 a.

II. In$_2$Se$_3$: In$_2$Se$_3$ exists in four modifications. The different phases and transition temperatures are not definite yet. In $\beta$-In$_2$Se$_3$, which exists between 473 K and 823 K, we observed two energetically equal structures with different interaction frequencies. Such a case has not yet been reported. The sample A (Fig. 3 b) has been held at a temperature of 77 K for 48 h. The results fit very well to the ones of Krusch and Gardner [6]. The second sample B (Fig. 3 b) showed a different behaviour. The interaction frequencies vary in both cases with temperature.

III. In$_2$Te$_3$: In$_2$Te$_3$ has been investigated in the $\beta$-phase only. The observed interaction frequencies are $v_Q = 145$ Mc and $v_Q = 100$ Mc and practically temperature independent (Figure 3 c).
Fig. 3. Temperature dependence of the EFG in In$_2$X$_3$-compounds.
4. Discussion

As mentioned in the introduction we wanted to study the EFG at regular lattice sites. The presented data prove this supposition. Both in InS and in InSe we observed well defined EFG's, expressed by the small frequency distribution. Both compounds offer one site for In-atoms. In InTe, however, there are two possible In-sites (one in tetrahedral, the other in hexahedral coordination). The frequency broadening of about 10% indicates that the EFG at both sites is about the same but cannot be analyzed by the applied technique. Thus both sites are regularly occupied by probe nuclei.

Another proof is given by the ratio of the amplitudes of the two interaction frequencies. As an example $\beta$-In$_2$S$_3$ is shown in Figure 4a. Within the experimental error this ratio is $A_{22,2}/A_{22,1} = 3$. Structural analysis of the lattice shows two sites for the In-atoms in the ratio 24:8. This is another proof for the regular distribution of probe nuclei at intrinsic lattice sites.

Furthermore, the temperature dependence of the distribution factor $\delta$ reflects on lattice dynamics close to the phase transitions. As an example the data of In$_2$S$_3$ are shown in Figure 4b. The increase in the transition regions is caused by the beginning alteration of the lattice and relaxation processes, until the new phase crystallizes. Then $\delta$ will decrease again.

There are only few investigations of the EFG in semiconductors. As for a long time the positive slope $\Delta \nu_q/\Delta T$ seemed to be specific for semiconductors the present data show that there is no general criterion to describe the temperature dependence of the EFG.

In the narrow gap semiconductors like Te, Bi$_2$Te$_3$ and Sb$_2$Te$_3$ the EFG increases with increasing temperature. This behaviour may be due to changes in the charge carrier concentration in the conduction band.

The compounds discussed here — having relatively high band gaps — show different temperature dependences. One can not exclude that in this case lattice vibrations may influence the EFG as well as changes in the charge carrier concentration.

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