



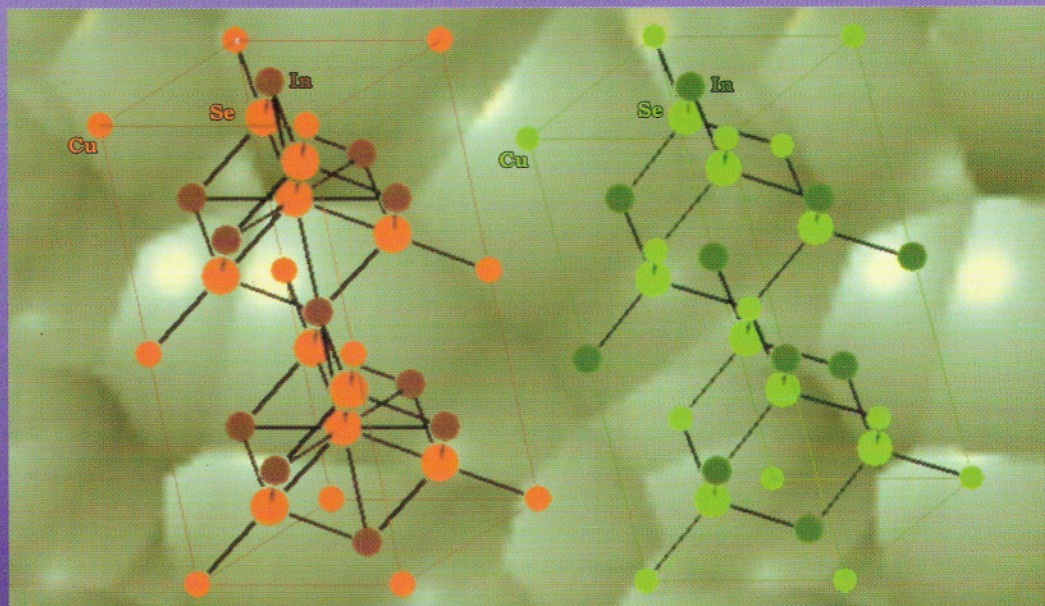
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Editor's Choice

Electrical transport properties of ZnO films for front contacts of solar cells


Optical, electrical and structural characterization of CuInSe₂ thin films
(C. Calderón et al., pp. 1910 and 1915)



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Electric field gradients at indium sites in spinels measured by perturbed angular correlations

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The Electric Field Gradient (EFG) at ^{111}Cd isotope (produced by the Electron Capture (EC) decay of ^{111}In) has been measured using Perturbed Angular Correlations (PAC) technique in many spinels. In the present work, data arising from such experiments were collected. The experimental EFG values, obtained at room temperature, at the B site of normal spinels are compared with those calculated considering the monopole moment of the ions and the dipole polarization of the anions. This comparison allows the determination of the u -parameter, which gives the anion position in the lattice.

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1 Introduction

Spinel is a group of compounds with the general formula AB_2X_4 , where A and B are cations and X is a bivalent anion (like O, S or Se). Many of the spinels have interesting electronic and magnetic properties, in this manner suitable for various technological applications. One special feature of the spinel structure is its structural and electronic flexibility, capable of incorporating a wide range of cations of different size and valence in both of the sites (octahedral and tetrahedral) in the structure. There are many papers and books dealing with the problem of ion distributions and many techniques have been applied to the study of physical properties of the spinels. A hyperfine interaction method such as Mössbauer Spectroscopy has been extensively used to determine the Electric Fields Gradients (EFG) at the cation sites [1]. Beside the Mössbauer Spectroscopy, the Perturbed Angular Correlation (PAC) technique using ^{111}In tracers is an appropriate method for determining EFG at lattice sites. In the present work, data arising from experiments in spinels, where the $^{111}\text{In}(\text{EC})^{111}\text{Cd}$ probe nuclei were introduced into the samples during its preparation or afterwards by thermal diffusion or ion implantation, are reviewed. The experimental EFG values will be compared with those calculated by direct summation considering the monopole moment of the ions and taking into account the dipole polarization of the anions. In the next sections the spinel structure and the experimental method are described. In Section 4, a few examples of PAC spectra are shown and EFG parameters for several spinels are summarized. Details on the calculations of EFGs in spinels are given in Section 5.

2 Spinel structure and EFGs at lattice sites

Spinel has the same general crystal structure as the mineral spinel MgAl_2O_4 . The spinel has space group $\text{Fd}\bar{3}\text{m}$, cations at the special positions 8a (tetrahedral coordination) and 16d (octahedral coordination), and oxygen anions that occupy the general positions 32e [2]. The structure is characterized by two

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parameters, the lattice constant a and the anion parameter u . In an ideal spinel the anions form a cubic sublattice with $u = 0.375$, but normally the anions are displaced along a $[111]$ direction and the position parameter u must be specified. In a normal spinel, the single A cation occupies the tetrahedral site and the two B cations the two equivalent octahedral sites. In an inverse spinel, one B cation occupies the tetrahedral site and the other B cation and one A cation randomly occupy the two octahedral sites. In the completely random distribution, a statistically averaged occupation occurs in each site. The cation distribution is conveniently characterized by specifying the inversion parameter, λ , defined as the fraction of B cations at tetrahedral sites, i.e., $(A_{1-2\lambda}B_{2\lambda})(A_{2\lambda}B_{2-2\lambda})X_4$. All the spinels considered in this article are normal or essentially normal ($\lambda \ll 0.5$).

The tetrahedral sites have cubic point symmetry and then zero electric field gradients are expected. This symmetry is preserved even when the size of the large divalent ions causes a displacement of the four surrounding anions along the $\langle 111 \rangle$ -directions. On the other hand, the octahedrally coordinated sites have trigonal symmetry and the principal axis of the EFG tensor is along one of the $\langle 111 \rangle$ -directions.

3 The PAC technique

The nuclear quadrupole interactions of ^{111}Cd nuclei were observed by the PAC technique. The decay of the excited level of ^{111}Cd , populated by the electron capture decay of ^{111}In , occurs by a γ - γ cascade, which is very appropriate for PAC experiments. The angular correlation of these γ -rays is perturbed if there are external fields acting on the intermediate nuclear level. These fields appear in the perturbation factor $G_2(t)$, where t is the time the nucleus spent in the intermediate level. The perturbation factor is determined using a set-up of four detectors arranged in a plane at 90° each of other and counting the γ -rays of the cascade, as a function of the time elapsed between them, emitted at 90° and 180° . For a static quadrupole interaction the perturbation factor has the form

$$G_2(t) = \sum_{n=0}^3 s_{2n} e^{-\delta\omega_n t} \cos(\omega_n t).$$

The frequencies ω_n are related to the quadrupole frequency $\nu_Q = eQV_{zz}/h$ by $\omega_n = g_n(\eta)\nu_Q$. The coefficients S_{2n} and $g_n(\eta)$ are known functions of the asymmetry parameter $\eta = [V_{xx} - V_{yy}]/V_{zz}$, where V_{ii} denote the principal components of the EFG tensor. Theoretical perturbation factors of the form $A_2 G_2(t)$ folded with the measured time resolution curve are fitted to the experimental functions. The exponential term accounts for a distribution of the EFG components of width δ . The frequencies can also be extracted by Fourier analysis. The spectra are Fourier transformed as described elsewhere [3].

In Fig. 1 typical PAC spectra obtained for two spinels are shown. These correspond to room temperature measurement after fast cooling from 1123 K. In both cases, there are two components, which correspond to probes subjected to different EFGs. One component is associated with probes at regular lattice sites in a normal spinel. The other one is associated with probes perturbed by defects and inverted ions [4]. In Table 1 the quadrupole interaction parameters corresponding to probes at regular sites are collected. This component corresponds to 70% of the probes and accounts for the three peaks in the Fourier transform. Normally, the asymmetry parameter shows small deviation from axial symmetry ($\eta < 0.16$). Table 1 includes results obtained by other experimental groups.

4 Electric field gradient calculations

EFGs can be calculated *ab initio* through an appropriate band structure description of the compound. But a particular problem that arises in relation with PAC measurements is that we need to calculate the EFG at an impurity site. The ^{111}Cd probe is located at the site of the radioactive precursor ^{111}In . The introduction of an impurity atom in the lattice complicates the calculation. A direct summation method is used in this paper. The contributions of the point charges of the ions and the induced dipole moments on the anions to the Electric Field (EF) and to the EFG were considered. The electric field is non-zero at the anion site. Since the induced moments contribute to the electric field it must be calculated with a self-

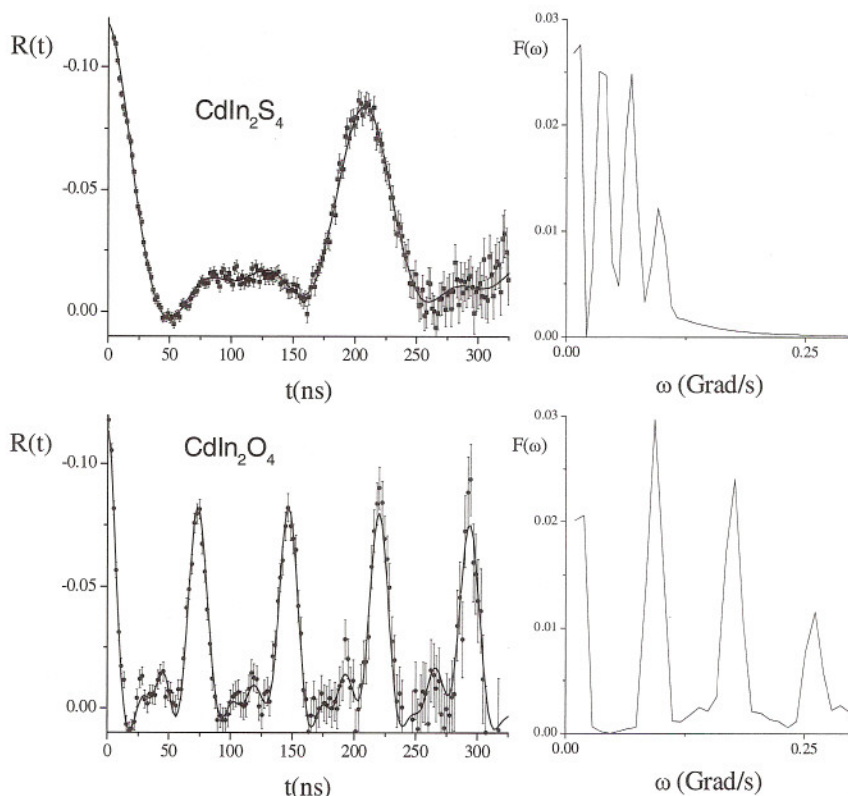


Fig. 1 Typical PAC spectra obtained at room temperature in two spinels. The Fourier transforms of the spectra are displayed on the right.

consistent method [5]. To calculate the induced dipole moment the dipole polarizability α must be known. To find appropriate values for the polarizabilities of the ions is difficult since the polarizability depends on the environment. For oxygen we used the value $\alpha = 0.8 \text{ \AA}^3$, which appears as an appropriate value for spinels [5]. We find that a value $\alpha = 1 \text{ \AA}^3$ for S and Se allows to reproduce the experimental EFGs. From the experimentally determined quadrupole interaction frequency ω_Q the component V_{zz} of the EFG tensor at the probe nuclei site was calculated. The quadrupole moment used was $Q(\text{Cd}) = 0.83$ [6]. The EFG at the probe nuclei is related to the EFG at the ion site, listed in Table 1, by

$$V_{zz}^n = (1 - \gamma_\infty) V_{zz},$$

where γ_∞ is the Sternheimer antishielding factor, which takes into account the contribution of the closed electron shells of the probe to the EFG. For Cd^{+2} , $\gamma_\infty = -29.27$ was used [7]. We have considered the contributions of all ions in a sphere with radius 50 \AA to the EFG, assuming pure ionic bonding and neglecting distortions around the probe. The u -values calculated in the present work for reproducing the measured EFGs are given in Table 1. The u -values reported in the literature are given with the references. The calculated EFG is axially symmetric.

5 Discussion and conclusions

The experimental values of η depend on the sample story and then must be connected with defects [4]. The value of ω_Q is less sensible to the defect content of the sample [4]. This could explain why the model, based in a perfect crystal lattice, although does not reproduce the experimental small deviation from axial symmetry, gives a reliable value for the principal EFG component. The agreement between

Table 1 PAC results obtained with spinels and calculated u -values. The lattice parameters and u -values reported in the literature are listed. The quadrupole interaction frequency measured by PAC at room temperature are given. References are given in square brackets. The principal component V_{zz} of the EFG tensor at the ion site is given. The u -values required for reproducing the V_{zz} -values are listed in the last column.

spinel	a (Å)	u (rep.)	ω_Q (Mrad/s)	V_{zz} (10^{20} V/cm ²)	u (calc.)
Co ₃ O ₄	8.084	0.389 [8]	48 [14]	2.43	0.386
CdIn ₂ O ₄	9.115	0.385 [8]	14.1 [4]	1.48	0.386
CdFe ₂ O ₄	8.690	0.391 [9] 0.389 [10]	25.8 [15]	2.70	0.388
ZnFe ₂ O ₄	8.416	0.385 [11]	14.9 [15]	1.56	0.385
ZnCo ₂ O ₄	8.047		24.3 [this work]	2.54	0.385
CdIn ₂ S ₄	10.797	0.386 [8]	5.01 [16]	0.52	0.386
HgIn ₂ S ₄	10.810	0.388 [8]	5.36 [16]	0.56	0.386
ZnAl ₂ S ₄	10.005	0.390 [8]	5.81 [17]	0.61	0.386
CdCr ₂ S ₄	10.239	0.390 [8]	11.62 [18]	1.22	0.387
	10.207	0.375 [12]			
CdCr ₂ Se ₄	10.721	0.389 [13]	9.20 [17]	0.96	0.387
	10.721	0.383 [12]			
HgCr ₂ Se ₄	10.74	0.389 [13]	9.67 [17]	1.01	0.388

the determined u -values and those reported in the literature using other experimental techniques is very good. The ability of the model to reproduce the EFG at Indium sites in the non-oxide spinels is also very good and makes the assumed polarizability values for S and Se reliable.

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