PREFERENTIAL SITE OCCUPATION OF INDIUM IN β-Ga$_2$O$_3$

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The hyperfine interactions of ^{111}Cd in gallium oxide doped with ^{111}In have been studied as a function of temperature (300 - 1323 K) by means of the time differential perturbed angular correlation technique. The observed hyperfine interactions are assigned to the the β - form of gallium oxide . X - ray diffraction analysis support this conclusion. It is found that indium replace gallium at only one site of both possible sites in the monoclinic β - structure. This site is probably the sixfold coordinated one. On the other hand, a time dependent interaction is detected at temperatures below 800 K.

1. INTRODUCTION

In recent years, the hyperfine interactions of ^{111}Cd in oxides have been extensively studied /1/. In the case of In2O3 a time dependent interaction has been found and connected with the decay by Electron Capture of ^{111}In to Cd^{111}. Although some necessary conditions for the existence of the time dependent interaction have been established, it is not yet clear under which conditions this interaction is presented and in which way it depends on the physical properties of the host. The case of Ga2O3, seems to be well appropriated to search for similar effects.

Gallium oxide exists in several crystalline forms α, β, γ, σ, and ε. The β type is the most stable crystalline modification and has been the most studied in crystal /2/ or in film form /3/. Optical/4/, magnetic /5/ and hyperfine properties /6/ of β - Ga2O3 doped with transition metals have been reported. The crystal structure consists in a distorted cubic closed packed lattice of oxygen ions with Ga in distorted tetrahedral and octahedral sites.

2. Experimental procedure and results.

Aqueous solution of gallium nitrate was prepared using high purity components. Indium nitrate aqueous solution prepared from carrier free ^{111}In was added. The solution was dried and calcined a few hours at 473 K. At this temperature gallium oxide appears /7/. At temperature higher than 1143 K is expected that all the forms converge to the β one /8/. This fact was corroborated by X - ray diffraction measurements. Figure 1 displays results obtained at RT and show how the β form is established with the annealing sequence.

The Time Differential Perturbed Angular Correlation experiments were carried out using a standard fast slow coincidences equipment with two detectors of CsF scintillators. Measurements were carried out as a function of temperature in the range RT - 1325 K. Typical results obtained in this way are shown in Figure 2. The TDPAC spectra displayed in Figure 2a show the transformations of the indium surroundings after annealings. These spectra are well fitted only assuming two sites for In in the host structure. The quadrupole interaction at each site is described by the standard expression for the perturbation factor:

$$G_2(t) = \sum_n S_{2n} \cos(\omega_n t) \exp(-\delta \omega_n t) \qquad (1)$$
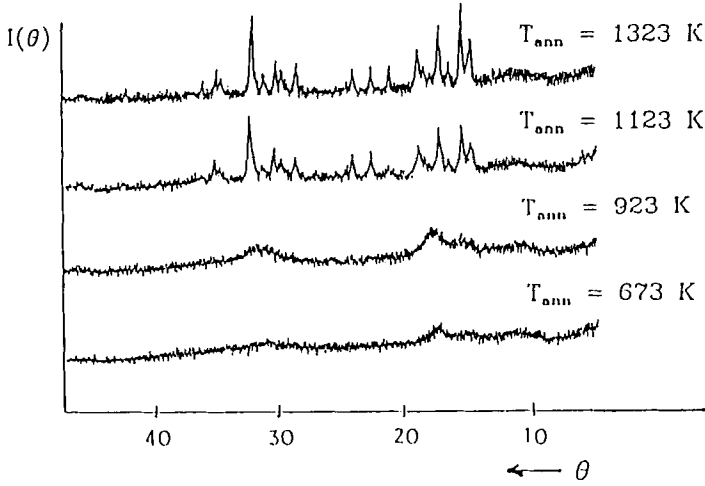
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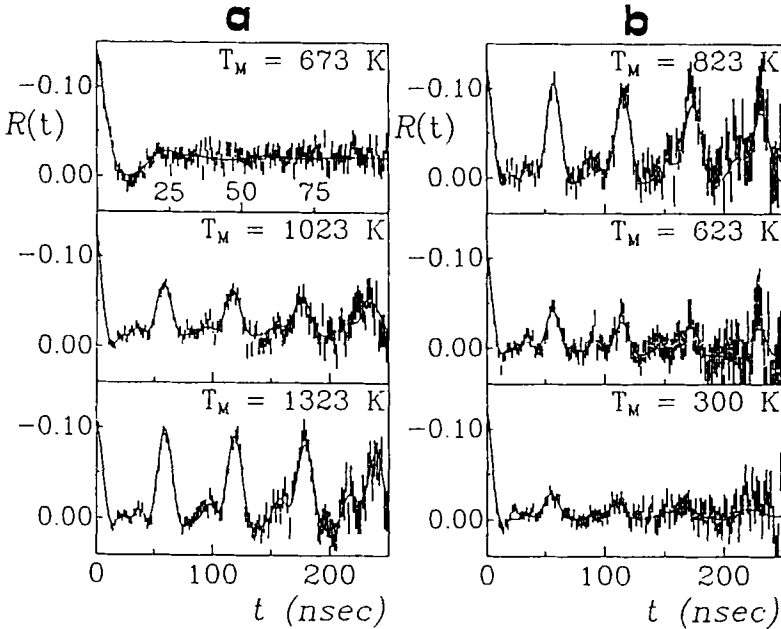Figure 1: X - Ray diffraction patterns of Gallium Oxide as a function of annealing temperature.

Figure 2: TDPAC spectra of ^{111}In in Gallium oxide, as a function of a) increasing annealing temperature (which coincides with measurement temperature) and b) measurement temperature.

The dependence on temperature of the hyperfine parameters for both sites are shown in figure 3. At the highest temperature only one site is populated. On cooling down the sample the hyperfine structure is kept up to

800 K. At lower temperature a time dependent interaction appears (Fig 2b). In order to fit these spectra we have used the following expression for the theoretical R(t):

$$R(t) = A_{22} \ [g_s + g_d \ \exp(-\lambda t)] \ G_2(t) \tag{2}$$

where A₂₂ is the experimental anisotropy, λ gives account of the relaxation introduced by the fluctuating field and G₂(t) is given by equation (1). g• and gd accounts for the relative importance of the static and dynamic interactions.
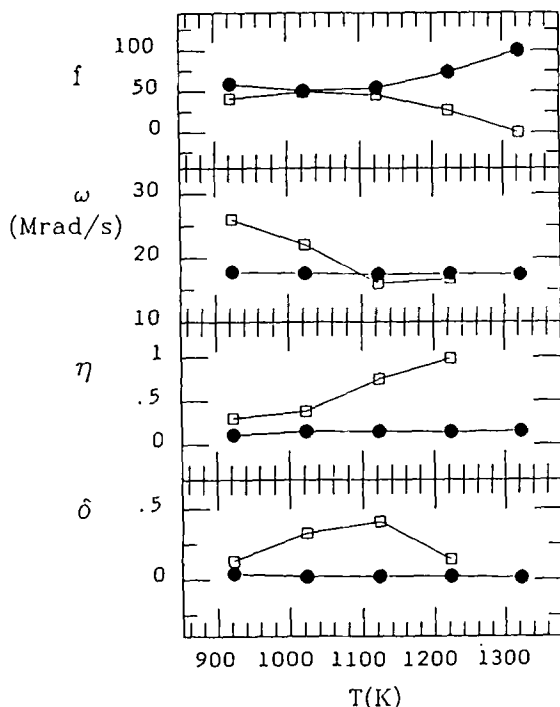

Figure 3: The hyperfine interactions parameters for the two sites (● □) of indium in gallium oxide are shown as a function of annealing temperature. The relative population f of the sites are plotted in the first box.

3.   Discussion and conclusions.

From the knowledge of the transformations of gallium oxide and the X-ray diffraction analysis, we can assign the highest temperature result to the β-form. The hyperfine interactions parameters are:

$$\omega_Q = 17.4_1 \ \text{Mrad/s} \qquad\qquad \eta = .15_1$$

The crystal structure of β − Ga₂O₃ has two sites for the metallic ion. After the formation of β − form indium occupies two sites in the crystal. The population ratio is 1:1. Both sites are probably the gallium ones in that structure. Annealing treatments produce the depletion of one site in profit of

the other one. The preferential site must be the octahedrally   coordinated one, as should be expected by comparison with the sixfold coordination of indium in the two sites of In_2O_3.

The time dependent interaction which appears below 800 K, has similar characteristics to the one found in indium sesquioxide. The expression (2) is appropriated to describe the perturbation and includes the perturbation factor discussed in Ref. 1. There are at least two possible physical models connected with such a perturbation factor. The consequence of these two possibilities will be discussed in a forthcoming paper. In spite of this ambiguity   we can compare the present results with those of indium oxide and get a value for the difference ΔE of the activation energy for the removal of the dynamic   effect in both compounds. In figure (4) is plotted the ratio ζ between the dynamic gd and the static ge contributions versus temperature . From the shift in the curves we can estimated a ΔE = 14 mev.

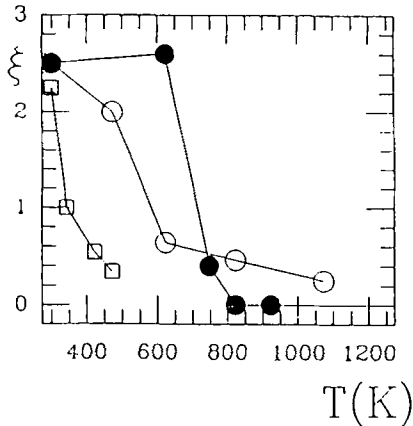Figure 4: The parameter ζ = gd/ge is plotted versus measurement temperature . Data for ^{111}In in Ga2O3 (●), In2O3 (○)   and   In2O3:Sn (▢) are included. The data for indium oxide, pure and tin doped, were   taken from Ref.1.

References

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