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Positron Trap Studies in $\text{Zn}_{1-x}\text{Cu}_x\text{Cr}_2\text{Se}_4$ Spinel

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Abstract. The results of the positron annihilation measurements and the calculations of the vacancy parameter carried out in single and polycrystals of $\text{Zn}_{1-x}\text{Cu}_x\text{Cr}_2\text{Se}_4$ spinel series are discussed within the framework of a two state trapping model. The single crystal values of the vacancy concentration remain almost constant with increasing copper concentration x . They are higher than the polycrystal ones (which linearly increase) suggesting, that the single crystals are more defected than polycrystals. The heat treatment influences the values of the vacancy concentration showing, that oxidation and adsorption behaviour of the spinels seems to be different on the zinc rich side (where the antiferromagnetic component dominates) as compared with the copper rich side (where the ferromagnetic component dominates). In particular, the results are in good agreement with the values of the vacancy parameter which is related to the vacancy concentration.

1. INTRODUCTION

The spinels of the series $\text{Zn}_{1-x}\text{Cu}_x\text{Cr}_2\text{Se}_4$ possess a complex magnetic structure (i.e. simple spiral, ferromagnetic spiral, spin glass and ferromagnetism) [1,2]. For $x=0.3$ a semiconductor-metal phase transition was observed [2]. The positron annihilation measurements [3] revealed that: 1) the samples which possess longer positron lifetime have larger value of the vacancy parameter, 2) the low bulk intensity and the ortho-positronium intensity as well as the high source intensity suggest the existence of other traps for positrons like the surfaces of single crystals and the free volume between them and also the interaction with adhesive gas molecules (air) or oxide layers, 3) the heat treatment (at 473 K for 24 h) influences the values of the positron lifetimes and the corresponding intensities suggesting, that polycrystalline samples sintered in vacuum (of 10^{-3} mbar) give a better information of the defect state or of the bulk than the polycrystalline samples sintered in air.

2. THE PROCEDURE OF CALCULATIONS

In the simplest case of the applicability of a two state trapping model [4] the vacancy concentration c_v is given by

$$c_v = \frac{I_1}{\sigma} \left(\frac{1}{\tau_0} - \frac{1}{\tau_1} \right) \quad (1)$$

where τ_0 is a short positron lifetime constant, τ_1 is a defect lifetime, I_1 is an intensity of the defect lifetime τ_1 and σ is the specific trapping rate. The so-called specific trapping rate σ is a constant for a given defect type at a certain temperature [5]. As a positron annihilation technique is a good method for detecting cation vacancies [3], Eq.1 allows us to estimate the total concentration of cation vacancies existing both in the tetrahedral and octahedral positions of the spinel structure.

The vacancy parameter β [6] is given for the spinel structure as

$$\beta = \frac{a_{\text{cal}}^3 - a^3}{a_{\text{cal}}^3} 100\% \quad (2)$$

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where a_{cal} is a calculated lattice parameter according to the procedure described in Ref.6 and a is an experimental value of the lattice parameter for the same spinel. From the vacancy model [6] it follows that the vacancy parameter β increases with increasing anion radius. On the other hand, it was observed that the number of stable spinels decreases with increasing anion radius in the sequence: O, S, Se and Te. It suggests that the increase of the degree of imperfection of the spinel structure with increasing anion radius, as caused by the increase of defects, finally leads to the disappearance of the spinel structure [3].

3. RESULTS AND DISCUSSION

Calculations of the vacancy concentration c_v were made with the aid of Eq.1 taking the values of τ_0 , τ_1 and I_1 from Ref.3. The specific trapping rate σ was estimated in the classical way [7,8] to be equal to $3 \times 10^{-8} \text{ cm}^3/\text{s}$. The values of τ_0 for the samples with $x=0.0$ and 1.0 have been drawn from the measurements [3]. For the remaining samples the values of τ_0 are assumed in agreement with a linear decrease of the lattice parameter a with increasing copper concentration x [3]. The accuracy of the calculations was better than $\pm 0.2 \times 10^{16} \text{ cm}^{-3}$. In Table 1 are collected the values of c_v and the values of β , τ_0 , τ_1 and I_1 [3] (for comparison) obtained at room temperature for the single crystals, polycrystals sintered in air and polycrystals sintered in vacuum. In our case τ_1 is the average positron lifetime in the bulk, defects, source, surface and Kapton foil [3]. From the two and the three component analysis and from the heat treatment procedure [3] it follows that the positron trapping in the single crystals under study is mainly connected with structural defects (vacancies).

Table 1 The values of c_v and the values of β , τ_0 , τ_1 and I_1 [3] obtained at room temperature for the single crystals, polycrystals sintered in air and polycrystals sintered in vacuum of $\text{Zn}_{1-x}\text{Cu}_x\text{Cr}_2\text{Se}_4$ spinel series.

single crystals						polycrystals								
x	β (%)	τ_0 (ps)	τ_1 (ps)	I_1 (%)	c_v (cm ⁻³)	x	β (%)	τ_0 (ps)	sintered in air			sintered in vacuum		
									τ_1 (ps)	I_1 (%)	c_v (cm ⁻³)	τ_1 (ps)	I_1 (%)	c_v (cm ⁻³)
0.0	13.9	180	350	90.0	8.1×10 ¹⁶	0.0	11.04	180	235	91	3.9×10 ¹⁶	239	90.5	4.1×10 ¹⁶
0.251	14.7	176	317	90.5	7.6×10 ¹⁶	0.25	12.15	176	282	95	6.8×10 ¹⁶	281	96.0	6.8×10 ¹⁶
0.634	14.37	169	294	94.5	7.9×10 ¹⁶	0.75	13.07	167	242	87	5.4×10 ¹⁶	223	89.0	4.5×10 ¹⁶
0.92	14.45	164	292	94.5	8.4×10 ¹⁶	0.9	14.18	165	293	91	8.0×10 ¹⁶	280	88.0	7.3×10 ¹⁶
						1.0	14.16	163	304	94	8.9×10 ¹⁶	260	83.0	6.3×10 ¹⁶

Table 1 shows that: 1) the values of c_v and β are larger for single crystals in comparison with those values for polycrystals, 2) the values of c_v for polycrystals sintered in air are lower in semiconducting region (where the antiferromagnetic component dominates) and they are larger in the metallic region (where the ferromagnetic component dominates) in comparison with those values for polycrystals sintered in vacuum, 3) the value of $c_v = 4 \times 10^{15} \text{ cm}^{-3}$ [8] and the value of $\beta = 5.5\%$ which have been obtained for the NiFe_2O_4 ferrite are significantly lower in comparison with those values for the spinels under study. It suggests that the total concentration of cation vacancies increases with increasing anion radius in the sequence: O and Se.

One can conclude that: 1) the single crystals are more defected per cm^{-3} than polycrystals. This is probably caused by the different methods of preparation used for single crystal and polycrystalline samples [3], 2) the vacancy parameter is related to the vacancy concentration in the materials with the spinel structure.

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