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Positron annihilation studies in binary solid solutions of metal beta-diketonates, using lifetime and Doppler broadening spectroscopies

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ABSTRACTS

Positron annihilation lifetime (LS) and Doppler broadening annihilation radiation lineshape (DBARL) spectroscopies measurements were performed in several binary solid solutions of the general formula $M_{(1-x)}G_{(x)}L_3$, where $M = \text{Al(III)}, \text{Ga(III)}, \text{or In(III)}$, as matrix; $G = \text{Cr(III)}, \text{Mn(III)}, \text{Fe(III)}, \text{Co(III)}, \text{Ru(III)}, \text{Rh(III)}, \text{and Ir(III)}$, as guest molecules, $L = \text{acetylacetonate (acac) or dipivaloylmethane (dpm)}$, and $X = \text{guest molecule mole fraction}$. The studied systems can be classified in two groups: the first one presenting only inhibition of positronium formation and the second one presenting inhibition and quenching effects. The inhibition and quenching constants were determined.

INTRODUCTION

In previous publications (1,2) we have discussed the positronium (Ps) formation and inhibition effect in binary solid solutions of the general formula $\text{Al}_{(1-x)}\text{G}_{(x)}(\text{acac})_3$, where $G = \text{Cr(III)}, \text{Fe(III)} \text{ and } \text{Co(III)}$, as guest molecules, and Al(acac)_3 as the matrix, studied by LS technique.

For a better understanding of the positron annihilation behaviour in this type of systems, new measurements were carried out. Owing to the properties of Cr^{+3} , Fe^{+3} , Co^{+3} , Mn^{+3} ions or their complexes as inhibitors and/or quenchers, the host $\text{Al(III)}, \text{Ga(III)}, \text{and In(III)}$ complexes (in which Ps formation is very efficient) can be regarded as "nonpolar solvents", while the guest $\text{Cr(III)}, \text{Mn(III)}, \text{Fe(III)}, \text{Ru(III)}, \text{Co(III)} \text{ and } \text{Rh(III)}$ complexes, in which any Ps is hardly formed, can be considered as solutes.

EXPERIMENTAL

The metal acetylacetonates and dipivaloylmethanates were synthesized as described in the literature (3-4), with some modifications, when necessary. The purification and characterization of the pure compounds are described elsewhere (1-2).

Solid solution preparation, positron source, the lifetime spectrometer and the lifetime spectra analysis were described in

previous publications (1,2).

The characteristics of the intrinsic Ge detector used in DBARL measurements and the parameter chosen for reporting the results (FWHM) are described in reference (5).

RESULTS AND DISCUSSION

The LS and DBARL parameters for $\text{Al}(\text{acac})_3$, $\text{Ga}(\text{acac})_3$, $\text{In}(\text{acac})_3$ and $\text{Al}(\text{dpm})_3$ are shown in Table 1. The o-Ps intensities (I_3^0), for the other pure compounds (guest molecules) are lower than 6% and the o-Ps lifetimes (τ_3) are meaningless, as discussed before (1). The FWHM values for the latter compounds are in the range (2.76-2.90) keV.

Table 1 - LS and DBARL parameters for the matrix compounds

Compound	τ_3^0 (ns)	I_3^0 (%)	FWHM (keV)	Compound	τ_3^0 (ns)	I_3^0 (%)	FWHM (keV)
$\text{Al}(\text{acac})_3$	1.23	44.0	2.44	$\text{Ga}(\text{acac})_3$	1.13	46.4	2.44
$\text{Al}(\text{dpm})_3$	1.62	59.0	2.30	$\text{In}(\text{acac})_3$	1.11	46.2	2.50

The twelve studied binary solid solutions are collected in Table 2 with their inhibition (k) and quenching (k') constants.

The systems are separated in two groups: the first one for which the only observed effect is an inhibition of Ps formation and the second one presenting both the inhibition and quenching effects.

Table 2 - The inhibition and quenching constants for the $\text{M}_{(1-x)}\text{G}_{(x)}\text{L}_3$ systems, determined by using equations $I_3 = I_3^0 / (1 + kX)$ and $1/\tau_3 = 1/\tau_3^0 + k'X$, respectively, except for No. 7 to 9.

No.	Group 1	k (X^{-1})	No.	Group 2	k (X^{-1})	k' ($X^{-1}\text{ns}^{-1}$)
1	$\text{Al}_{(1-x)}\text{Co}_{(x)}(\text{acac})_3$	256	7	$\text{Al}_{(1-x)}\text{Cr}_{(x)}(\text{acac})_3$	100	92
2	$\text{Ga}_{(1-x)}\text{Co}_{(x)}(\text{acac})_3$	255	8	$\text{Al}_{(1-x)}\text{Mn}_{(x)}(\text{acac})_3$	138	53
3	$\text{In}_{(1-x)}\text{Co}_{(x)}(\text{acac})_3$	456	9	$\text{Al}_{(1-x)}\text{Cr}_{(x)}(\text{dpm})_3$	2.9	4.8
4	$\text{Al}_{(1-x)}\text{Ru}_{(x)}(\text{acac})_3$	260	10	$\text{Al}_{(1-x)}\text{Co}_{(x)}(\text{dpm})_3$	18	1.8
5	$\text{Al}_{(1-x)}\text{Fe}_{(x)}(\text{acac})_3$	138	11	$\text{Al}_{(1-x)}\text{Mn}_{(x)}(\text{dpm})_3$	17	2.3
6	$\text{Al}_{(1-x)}\text{Rh}_{(x)}(\text{acac})_3$	18	12	$\text{Al}_{(1-x)}\text{Fe}_{(x)}(\text{dpm})_3$	13	1.4

The behaviour of the systems of Group 1 is very similar, as observed before, the system no 1, included here just for comparison (1). For this group the FWHM vs. X curves, as expected, show an increase of the FWHM parameter with the increase of the

guest molecule concentration.

For the systems number 10 to 12 of Group 2 the FWHM values increase with X , and $1/\tau_3$ values increase linearly with X , suggesting a quenching effect by oxidation mechanism. For the systems number 7 to 9, the FWHM values decrease with X , suggesting a quenching effect by spin conversion mechanism.

The corrected intensities, I_3^{corr} , were determined by using the usual expressions cited in the literature (6).

Finally, to verify the behaviour of solid solutions in which, Ps formation, both in the matrix and in the guest molecules, is efficient, we have studied the system $\text{Al}_{(1-x)}\text{Ir}_{(x)}(\text{acac})_3$. The o-Ps intensity, o-Ps lifetime, and FWHM for the pure Ir(III) acetylacetonate are: 27.00 %, 1.180 ns and 2.57 keV.

For this system I_3 decreases linearly with X , according to

$$I_3 = [I_{3(\text{Al})}^0 \cdot X_{(\text{Al})}] + [I_{3(\text{Ir})}^0 \cdot X_{(\text{Ir})}]$$

while τ_3 remains practically constant in the full range of the studied concentration.

For all the studied systems it was observed that for the corresponding mixtures, prepared as blanks, I_3 decreases linearly with the concentration and τ_3 remains constant and near the o-Ps lifetime of the matrix compound, as observed before (1,2).

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