Electron Paramagnetic Resonance and Spin-Lattice Relaxation in Two-Dimensional Systems*

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Abstract. The anisotropies of the EPR linewidth and g-factor were investigated in two-dimensional molecular composites of the type \([\text{NH}_3 - R - \text{NH}_3]MX_4\). Measurements were performed both in single crystals and powders over the temperature range 4.2–290 K. The spin-lattice relaxation time \(T_1\) was measured using the modulation method, as a function of temperature. The samples exhibit different structures and coupling interactions, according to the nature of the halogen X, the metal M and the organic radical R. We have analysed the influence of these parameters on spin behavior by studying the samples \([\text{NH}_3 - (\text{CH})_n - \text{NH}_3]MX_4\) with \(M = \text{Mn, Cu}; X = \text{Cl, Br, and } n = 2, 3, 4, 5\). When R is constituted by molecules with unsaturated bonds, these materials can be considered as excellent matrices for selective polymerisation reactions by irradiation or thermal processing. We have performed EPR measurements on the heated complex of propargylamine and cadmium chloride \([\text{HC} - \text{C} - \text{CH}_2 - \text{NH}_3]_2\text{CdCl}_4\). The obtained data are interpreted taking into account the strong exchange interaction and the various coupling interactions in the samples. The thermal dependences of \(T_1\) are explained by means of the Bloembergen and Wang three-reservoir model. The data show spin diffusion when the metal is manganese, and an antisymmetric exchange interaction modulated by phonons in the case of copper. The nature of the halogen plays an important role in spin dynamics and namely in spin-lattice relaxation. The results obtained on \([\text{HC} - \text{C} - \text{CH}_2 - \text{NH}_3]_2\text{CdCl}_4\) after heating under vacuum show the creation of many paramagnetic centers due to the vanishing of triple bonds and the occurrence of a strong exchange interaction.

1. Introduction

Our study concerned two-dimensional molecular composites with the general formula \([R - \text{NH}_3]_2MX_4\) (monoammonium) and \([\text{NH}_3 - R' - \text{NH}_3]_2MX_4\) (diammoni-
um), where R and R' are organic radicals, M is a metal (Cd, Mn, Cu, ...) and X is a halogen (Cl, Br, ...). R and R' radicals may contain chains with saturated or unsaturated bonds. The metallic cation may correspond either to diamagnetic ions (Cd\(^{2+}\), Pd\(^{2+}\), ...) or to paramagnetic ions (Mn\(^{2+}\), Cu\(^{2+}\), Fe\(^{2+}\), ...). Some of the previous studies compared the "monoammonium" to the "diammonium", and as far as we know, spin-lattice relaxation has never been studied in these materials. It seemed interesting to us to endeavour measurements of EPR parameters and of \(T_1\) in order to analyse spin dynamics in these compounds. Moreover, as their features depend on the nature of the metal, of the halogen and of the length of the organic radical, we have tried to establish some relations between these parameters and the magnetic properties. We have first studied a compound of the series of tetrahalogeno-metallate alkylene diammonium of the formula \([\text{NH}_3-(\text{CH}_2)_4-\text{NH}_3]_2\text{MnCl}_4\) (in short 2C\(_4\)MnCl\(_4\)). The linewidth, the g-factor and the spin-lattice relaxation time have been measured, with their angular and thermal dependences. We have tried to obtain information on the dependences of these parameters on the nature of the halogen and of the metal, by studying 2C\(_4\)MnBr\(_4\) and 2C\(_4\)CuCl\(_4\). The influence of the \(n\) parameter (number of carbons within the organic chain) has then be determined through 2C\(_n\)MnCl\(_4\) (\(n = 3, 5\)) and 2C\(_n\)CuCl\(_4\) (\(n = 2, 3\)). These results will be interpreted by using the theory of exchange narrowing developed by Kubo and Tomita [1].

Finally, we have developed a preliminary study of compounds with an unsaturated R radical. The studies which have already been carried out on this type of materials have shown the possibility to create long-range stereoregular polymers by irradiation or by solid-state thermal processing. Our interest was applied to the heated complex of propargylamine and cadmium chloride \([\text{HC}=\text{C}-(\text{CH}_2)-\text{NH}_3]_2\text{CdCl}_4\). We have performed EPR and spin-lattice relaxation time measurements on that sample.

2. Properties of Samples

The studied molecular composites crystallise in two-dimensional layers with an antiferromagnetic coupling for M = Mn and a ferromagnetic one for M = Cu. The structure is composed of two-dimensional arrays of octahedra MX\(_6\) (generally distorted), separated by organic chains "monoammonium" or "diammonium". The M–M distances in a plane are weak, thus leading to strong intrasheet superexchange couplings. The octahedra are tilted by a few degrees in relation to the plane, which produces the puckering of the sheet of octahedra. The organic chains are isolated from each other and disposed perpendicularly to the mineral sheets. The organic and mineral parts are linked by bridging hydrogens between NH\(_3\) groups and the halogen of the mineral sheets. The cohesion of the organic sheet is obtained by covalent bonds in the R’ radical in the series of "diammonium" and by Van der Vaals bonds between the terminal groups in the series of