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EPR study of the diluted magnetic semiconductor $CuGa_{1-x}Mn_xTe_2$

J. Pérez[a], P.J. Silva[b], C.A. Durante-Rincón[a,1], J. Primera Ferrer[a], J.R. Fermin[a,*,1]

[a] Departamento de Física, Facultad de Ciencias, Universidad del Zulia, Apartado. Postal 526, Maracaibo 4001, Zulia, Venezuela
[b] Laboratorio de Física de la Materia Condensada, Centro de Física, Instituto Venezolano de Investigaciones Científicas (IVIC), Carretera Panamericana Km. 11, Apartado 21827, Caracas 1020-A, Venezuela

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Abstract

Electron paramagnetic resonance (EPR) experiments were made in the diluted magnetic semiconductor $CuGa_{1-x}Mn_xTe_2$, in the temperature range $70 < T < 300$ K. The samples were synthesized by direct fusion of stoichiometric mixtures of the elements, with Mn composition from $x = 0.0$ to 0.25. The EPR spectra were measured as function of temperature, Mn composition, and field orientation. The temperature variation of the resonance field shows a critical point at about 235 K, and is associated with a transition from the ferromagnetic to the superparamagnetic state. The resonance field was also measured as a function of the field angle, and displays a well-defined uniaxial symmetry. This uniaxial field depends on the Mn concentration and is due to tetragonal distortions induced by Mn^{2+} at Ga sites, and the demagnetizing effects due to formation of ferromagnetism (FM) Mn-clusters.

Keywords: Superparamagnetism; Magnetic anisotropy; Paramagnetic resonance; Diluted magnetic semiconductor; Clustering

1. Introduction

Diluted magnetic semiconductors (DMS) are alloys in which a magnetic ion is randomly distributed into the solid host, and have been the subject of intensive experimental and theoretical work during the last decades [1]. The fundamental magnetic, electronic, and optical properties of these systems are quite different from their pure semiconductor counterpart, and over the last years; it has been shown that these properties are greatly influenced by the presence of charged carriers and the localized magnetic moments of the ions, leading to strong magnetotransport and magnetooptical effects. These phenomena have been widely studied and understood in Mn-based DMS in which the magnetic moments of the Mn ions interact antiferromagnetically. Recently, a new generation of transition metal-based compounds such as $CdMnGeP_2$ [2], GaMnAs [3], and NiMnGa [4], has been attracting much attention. These materials have opened a door into the field of new magnetic materials and ferromagnetic/semiconductor hybrid structures for applications in spintronics and spin-related devices [5]. The main features of these alloys are the presence of vacancies, interstitial atoms, and anti-site atoms, and it is expected that when diluted into the solid matrix, the magnetic ion interact with these defects forming pairs with low configuration energy. Theoretically, the origin of magnetic ordering in ferromagnetic DMS could be connected to point defects responsible for the magnetic ion shelter and p-type carrier concentration induced by holes generation [6]. Experimentally, several techniques are available for studying the magnetic properties of DMS. However, electron paramagnetic resonance (EPR) has proven to be one of the ideal techniques to study magnetic impurities in semiconductors [7,8]. This is because the EPR spectrum is very sensitive to properties such as local anisotropies, magnetic interactions between intrinsic defects, and magnetic and structural inhomogeneities in the sample.

Ternary I–III–VI_2 alloys are well known by their potential applications in the industry of solar cell devices [9]. The most studied are those of the family Cu-III–VI,

*Corresponding author. Fax: +58 261 7598099.
E-mail address: jfermin@luz.edu.ve (J.R. Fermin).
[1] Also an invited researcher at CIDETIU-URBE, Maracaibo, Venezuela.

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which possess high absorption coefficient and energy gap near to the optimum range for conversion of solar energy [10]. Although, the capability of DMS of the type I–III–VI_2 as candidates for ferromagnetic/semiconductor hybrid structures is actually an unexplored issue. The aim of this work is addressed to study the magnetic properties of the I–III–VI_2 DMS $CuGa_{1-x}Mn_xTe_2$, employing the EPR technique. The resonance spectra are studied as a function of the ion concentration, temperature, and magnetic field orientation.

2. Experimental

Samples of the I–III–VI_2 DMS $CuGa_{1-x}Mn_xTe_2$ with Mn composition $x = 0.0$–0.25 were prepared by direct fusion of the stoichiometric mixture of the elements of at least 5 N purity in graphite crucibles inside evacuated quartz ampoules ($\approx 10^{-6}$ Torr). To minimize the risk of explosion due to exothermic reaction between the group III element and Te, the ampoules were heated in a vertical furnace very slowly at 5 K/h up to 1100 °C. Kept at this temperature for 24 h, the samples were rocked at regular intervals to achieve a homogeneous mixing of the liquid phase of the reacting mixture, and then cooled to 500 °C at a rate of 5 K/h. At this temperature the ampoules were annealed for 4 days. The as-grown ingots were cut in slices of thickness of about 0.5 mm. These samples showed p-type conductivity, as observed by a thermal probe. This result lends support to the idea that in these alloys, Mn atoms enter into the $CuGaTe_2$ tetragonal lattice substituting the Ga^{3+} as $Mn^{2+} + p^{+}$ [11].

The EPR measurements were performed in an x-band VARIAN spectrometer, employing a home made cylindrical cavity with Q factor of the order of 2000, working in the TE_{100} mode. The magnetic field is supplied by an electromagnet mounted onto a 0–360° base that allowed us to rotate the sample with respect to the direction of the applied field. With this we were able to study the angular symmetry of the EPR field. All spectra were taken at 9.35 GHz cavity, and in the temperature range $77\,K < \cap$ $T < 300\,K$. The temperature was calibrated using a carbon-glass thermometer. The samples were cut into rectangular plates with one of the edges parallel to the direction of minimum resonance field. The magnetic field was applied parallel to the plane of the plate.

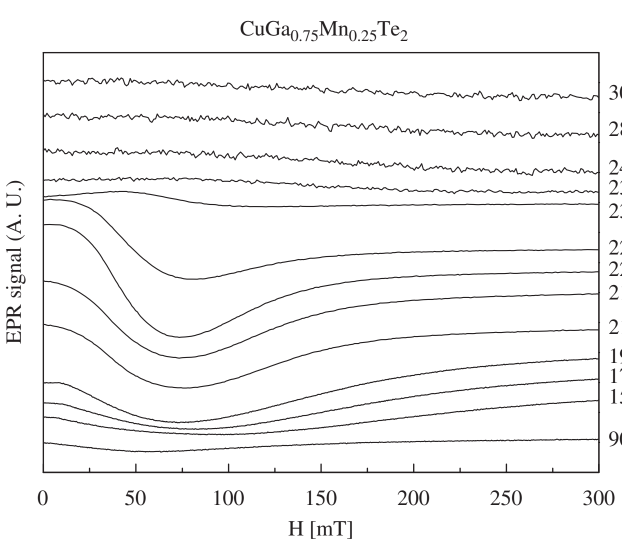

Fig. 1. EPR spectra of $CuGa_{0.75}Mn_{0.25}Te_2$ for several temperatures.

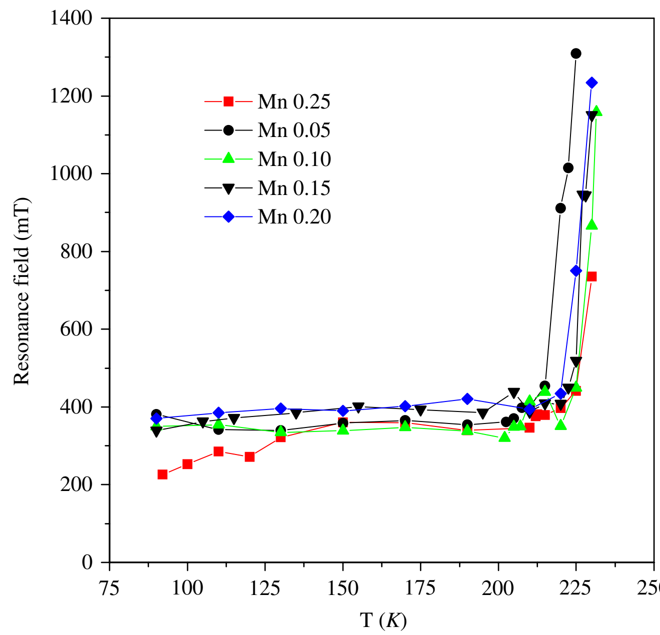

Fig. 2. Temperature dependence of the resonance field for all Mn concentrations.

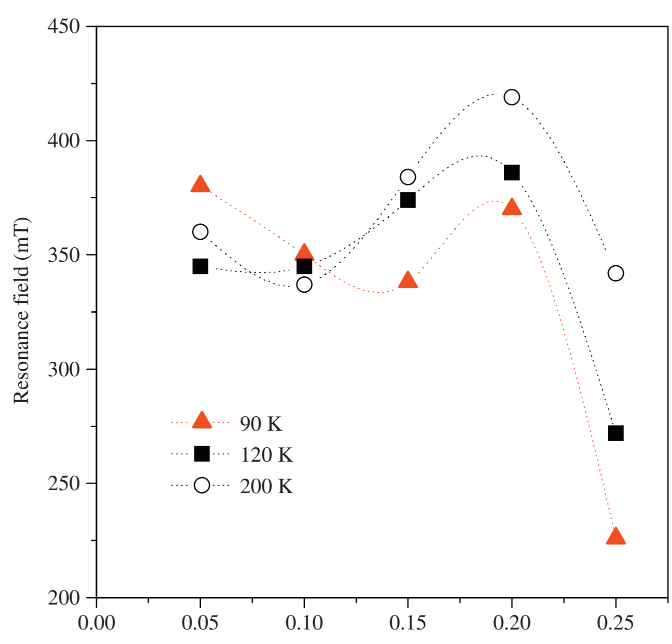

Fig. 3. Dependence of the EPR field with respect to x, measured at three different T. Note that the value of x_c is temperature independent.