Electron paramagnetic resonance in the $CoIn_{2-2x}Cr_{2x}S_4$ semiconductor system

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We report electron paramagnetic resonance (EPR) measurements in the diluted magnetic semiconductor (DMS) $CoIn_{2-2x}Cr_{2x}S_4$, $0.05 \leq x \leq 1$. The resonance field (H_R) is obtained from the spectra, and we have found oscillations around 410 *mT*. When temperature decreases H_R decreases also, this behavior is in agreement with a paramagnetism-ferromagnetism phase transition. In the sample x = 0.05, H_R increases from $\simeq 400\ mT$ until very high values while temperature is decreasing. The linewidth ΔHpp, for all the samples increases as the temperature decreases. Near liquid nitrogen temperatures, the EPR spectra is not observed. The behavior observed below the transition temperature is explained in terms of the exchange interaction between chromium ions. The ferrimagnetic behaviour is the responsible for the poor EPR signal at low temperatures.

Keywords: Electron paramagnetic resonance; diluted magnetic semiconductors; ferrimagnetism.

Se reportan medidas de resonancia paramagnética electrónica (RPE) en el “sistema semiconductor” magnéticamente “diluido (SMD)” $CoIn_{2-2x}Cr_{2x}S_4$, $0.05 \leq x \leq 1$. Se encuentra que el campo de resonancia (H_R) oscila alrededor de 410 *mT*, luego decrece a medida que se baja la temperatura; comportamiento que está de acuerdo con una transición de fase del tipo paramagnetismo-ferromagnetismo. En la muestra x = 0.05, H_R aumenta desde un valor de $\simeq 400$ *mT* hasta valores muy elevados, al bajar la temperatura. El ancho de línea ΔHpp, para todas las muestras, aumenta al disminuir la temperatura. Para temperaturas cercanas a la del nitrógeno líquido no se observa señal de RPE. El comportamiento observado por debajo de la temperatura de transición es explicado en términos de la interacción de intercambio entre iones de cromo. El comportamiento ferrimagnético del sistema es el responsable de que la señal sea muy débil a bajas temperaturas.

Descriptores: Resonancia paramagnética electrónica; semiconductores magnéticamente diluidos; ferrimagnetismo.

PACS: 75.50.Pp; 75.50.Gg

1. Introduction

The $CoIn_{2-2x}Cr_{2x}S_4$ system is a diluted magnetic semiconductor (DMS) with spinel structure. The parents of this system are the $CoIn_2S_4$, spin glass compound with freezing temperature of 12.6 K, that crystallizes in inverse spinel structure [1]; the $CoCr_2S_4$ is ferrimagnetic with normal spinel structure [2]. This system has two magnetic sublattices and they are of particular interest because it has, at least, one disordered magnetic ion located at octahedral A and tetrahedral B sites. It is possible to find different positional disordered degrees due to the exchange interaction distribution between the two sublattices [3]. All the magnetic behavior observed in this particular system are related with the chromium occupation of the cobalt sites and viceversa. It has been reported that all the samples studied in this work crystallize in a normal spinel structure [4]. In this work we have carried out EPR measurements as function of the temperature for different magnetic dilutions of the system. The spectrum parameters (H_R and ΔH_{pp}), as function of the temperature and the magnetic dilution, are shown.

2. Materials and Methods

Single crystals of $CoIn_{2-2x}Cr_{2x}S_4$, x = 0.05, 0.15, 0.25, 0.4, 0.5, and 1 were grown by using the chemical vapor transport technique [5]. The EPR measures were carried out in a VARIAN X band (9.5 GHz) spectrometer with a home made cavity. The spectra, as function of temperature were obtained from 4.2 K upto room temperature. The temperature was measured using calibrated carbon-glass thermometers.

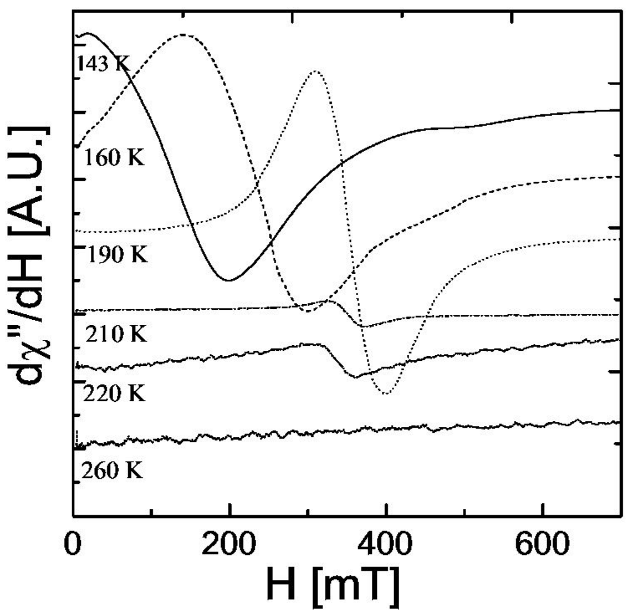

FIGURE 1. Temperature dependence of the EPR spectrum for the $CoIn_{1.2}Cr_{0.8}S_4$.

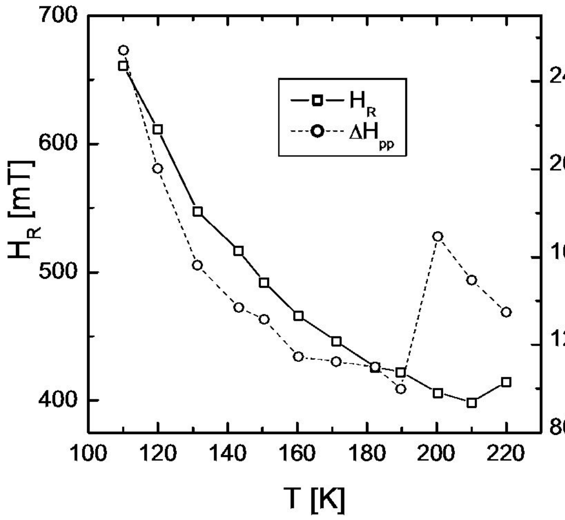

FIGURE 2. Temperature dependence of the H_R and ΔH_{pp} for the $CoIn_{1.9}Cr_{0.1}S_4$ compound.

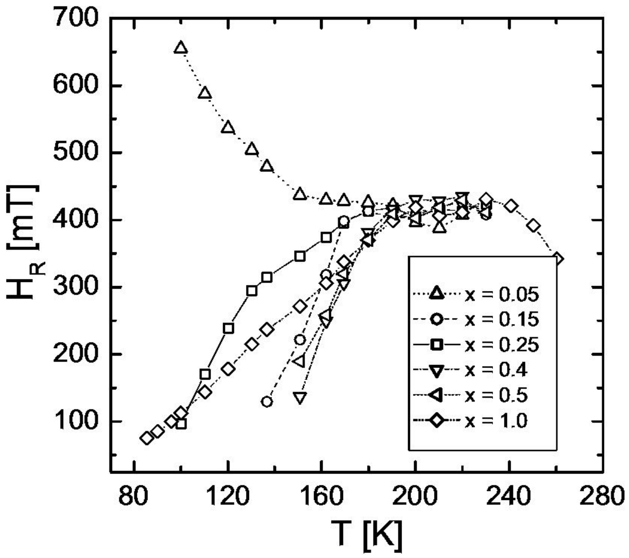

FIGURE 3. Temperature dependence of the H_R for the $CoIn_{2-2x}Cr_{2x}S_4$ compound, x = 0.05, 0.15, 0.25, 0.4, 0.5 and 1.

3. Experimental Results

EPR spectra, as function of the temperature, $4.2 \leq T \leq 300$ K, were obtained for all the samples studied. The H_R and ΔH_{pp} parameters were obtained from each spectrum.

In Fig. 1 we have shown the temperature dependence of the EPR spectrum for x = 0.4. The resonance field increases as the temperature increases, reaching its maximum at the critical temperature previously reported [4]; H_R lightly decreases above this critical temperature. The temperature dependence of H_R in all the studied samples is shown in Fig. 3. The resonance field oscillates around 410 *mT* in almost all the samples studied, then it falls for temperatures below the critical temperature; this behavior agrees with a paramagnetism-

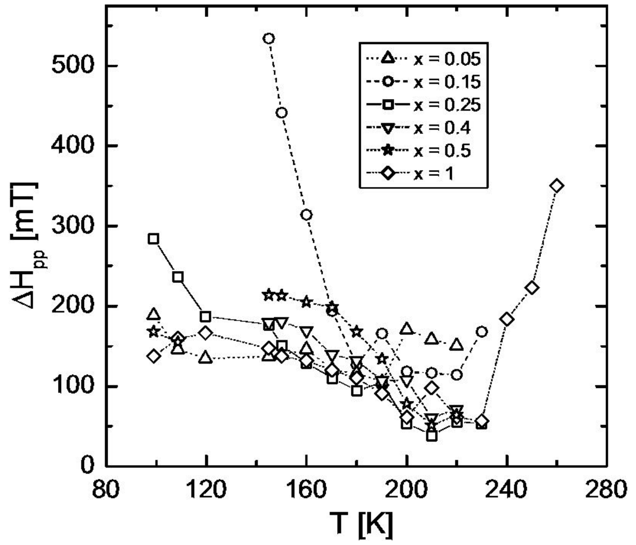

FIGURE 4. Temperature dependence of the ΔH_{pp} for the $CoIn_{2-2x}Cr_{2x}S_4$, x = 0.05, 0.15, 0.25, 0.4, 0.5 and 1.

ferromagnetism second order phase transition [6]. The diluted sample, $x = 0.05$, has a different behavior; as the temperature decreases, H_R increases from ≈ 400 *mT* up to very high values, ≈ 650 *mT*.

In Fig. 2, we show the temperature dependence of H_R and ΔH_{pp} for x = 0.05 in the complete temperature range. Concerning H_R, it monotonically decreases until reaching a minimum around T = 210 K. The line width behavior shows a discontinuity in the temperature region where H_R is minimum, this abrupt change of the line width should be associated with an increment in the exchange interaction between chromium ions, which is a characteristic behavior of a paramagnetism-ferromagnetism phase transition. When the temperature is decreased H_R and ΔH_{pp} increase, this behavior look like to that shown by the spin glass compounds at low temperatures [7]. One could think that when lowering the temperature a competition occurs among the Cr-Cr interactions and those of Co-Cr with frustrations of the spin, producing a spin glass phase; this is in agreement with previous results of magnetic susceptibility [3]. When the temperature is decreased from room temperature up to liquid nitrogen temperature, the line-width decreases reaching a minimum in the critical temperature for all the samples, as you can see in Fig. 4. This behavior is in accordance to an increment in the exchange interaction of the Cr-Cr, which is associated with a much more magnetic ordering in the system. The last results and the one obtained for H_R are in very good agreement with a paramagnetism-ferromagnetism phase transition. However, when the temperature is lowered the resonance line presents a high noise/signal ratio, this ensures a paramagnetism-ferrimagnetism phase transition in all the samples with $x > 0.05$. Below the transition temperature, the behavior is explained in terms of an increase in the exchange interaction with the first neighbors of the chromium ions. The disappearance of the EPR signal, at very low temperatures, could be explained by a ferrimagnetic behavior with a decrease and further compensation of the magnetization. For highest concentrations, $x \geq 0.25$, a strong competition occurs between the dipolar exchange and the exchange interaction; this is responsible for the decrease in the slope of the line-width curve as the chromium ions increase. When the dipolar broadening gets more intense, the EPR signal increases in width, and when the exchange interaction gets more intense the linewidth tend to decrease. In all the samples studied above the transition temperature, in the paramagnetic phase, it was not possible to observe an EPR signal due to the poor magnetization of the samples, and probably to the short relaxation times of the spin in the system.

4. Summary

The compound $\mathrm{CoIn_{1.9}Cr_{0.1}S_4}$ has a ferrimagnetic phase transition at 200 K, as decreasing the temperature, a spin glass like behavior takes place as indicative of a strong dipolar broadening. For samples $x > 0.05$, a ferrimagnetic phase occurs in the temperature range $200 \leq T \leq 220$, in these samples the exchange interaction between chromium ions is the dominant effect. In the paramagnetic region, the spin relaxation time is very short, disappearing the EPR signal.

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