

MAGNETIC BEHAVIOR OF THE ALLOY $(\text{CuInTe}_2)_{1-x}(\text{TaTe})_x$ WITH $X = 0.25$

COMPORTAMIENTO MAGNÉTICO DE LA ALEACIÓN $(\text{CuInTe}_2)_{1-x}(\text{TaTe})_x$ CON $X = 0.25$

P. GRIMA-GALLARDO^{a†}, O. IZARRA^a, R. PEÑA^a, M. MUÑOZ^a, S. DURÁN^a, M. QUINTERO^a, E. QUINTERO^a AND H. ROMERO^b

a) Centro de Estudios en Semiconductores (CES), Departamento de Física, Facultad de Ciencias, Universidad de Los Andes, 5101 Mérida, Venezuela. peg@ula.ve[†]

b) Laboratorio de Magnetismo. Departamento de Física, Facultad de Ciencias, Universidad de Los Andes, 5101 Mérida, Venezuela.

† corresponding author

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The magnetic behavior of the alloy $(\text{CuInTe}_2)_{1-x}(\text{TaTe})_x$ with $x = 0.25$ had been studied using SQUID techniques. Measurements of DC magnetic susceptibility using the ZFC-FC protocol and variation of magnetization as a function of the applied magnetic field and temperature were performed. It was found the presence of magnetic nanoclusters with a mean diameter of 10 nm and a coercitive field of 0.1 KOe at $T = 5$ K.

El comportamiento magnético de la aleación $(\text{CuInTe}_2)_{1-x}(\text{TaTe})_x$ con $x = 0.25$ fue estudiado utilizando la técnica de SQUID. Se midió la susceptibilidad magnética DC utilizando el protocolo ZFC-FC y la variación de la magnetización en función del campo magnético aplicado y la temperatura. Se encontró la formación de nanoclústeres magnéticos con un diámetro promedio de 10 nm y un campo coercitivo de 0.1 KOe a $T = 5$ K.

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I INTRODUCTION

Chalcopyrite materials had been object of extensive investigation in the last years because of their applications in solar cells [1] and more recently for the discovery of room temperature ferromagnetism [2–21]. However most of the work in alloys of chalcopyrite materials with metal transition (MT) elements had been based on Mn, which has the limitation of a relative narrow solubility [22–28]. For the contrary, we had founded that other MT elements, as Fe [29], Ni [30], V [31], Nb [32] and Ta [33, 34] have a much larger solubility in the chalcopyrite matrix.

In this work we report the magnetic behavior of the alloy $(\text{CuInTe}_2)_{1-x}(\text{TaTe})_x$ with $x = 0.25$.

II EXPERIMENTAL PROCEDURE

The samples were synthesized using the melt and annealing technique as described elsewhere [35]. Stoichiometric quantities of the elements with purity of 99.99% were charged in a synthetic silica glass ampoule, which was previously subject to pyrolysis in order to avoid reaction of the starting materials with silica glass. Then, the ampoule was sealed under vacuum ($\sim 10^{-4}$ Torr) and the fusion process was carried out inside a furnace (vertical position) heated up to 1500 K at a rate of 20 K/h, with a stop of 48 h at 723 K (melting point of Te). The ampoule was shaking using a mechanical system during all the heating process in order to guarantee the complete mixing of all the elements and the formation of binary species at low temperature. Then, the temperature was gradually decreased until 600 K and this temperature was maintaining for 60 days. Finally, the sample was cooled to room temperature by switching off the furnace. For the

X-ray analysis, a small quantity of the sample, cut from the center of the ingot, was ground mechanically in an agate mortar and pestle. The resulting fine powder, sieved to 106 μ , was mounted on a flat zero-background holder covered with a thin layer of petroleum jelly. The X-ray powder diffraction data was collected at ambient temperature (25 °C), in θ/θ reflection mode using a Siemens D5005 diffractometer equipped with an X-ray tube (Cu K_α radiation: $\lambda = 1.54059$ Å; 40 kV, 30 mA) and equipped with a Ge<111> primary monochromator. A fixed aperture and divergence slit of 1 mm, a 1mm monochromator slit, and a 0.1 mm detector slit were used. The specimen was scanned from 10–80° in 2θ , with a step size of 0.02° and counting time of 40 s. Quartz was used as an external standard. The Bruker AXS analytical software was used to establish the positions of the peaks.

Phase transition temperatures were obtained from Differential Thermal Analysis (DTA) measurements using Perkin-Elmer DTA-7 equipment with gold as reference material. The charge was of powdered alloy of approximately 100 mg weight. Values of the transition for the materials were obtained from the peaks on the DTA. Each phase transition temperature value was determined from the base line intercept of the tangent to the leading edge of the peak in the difference signal. Both heating and cooling runs were carried out for each sample, the average rates of these runs being approximately 10 K/min. The error in determining absolute temperatures is of about ± 8 K.

DC magnetic susceptibility and $M(H,T)$ measurements were performed on a Quantum Design SQUID magnetometer, equipped with a superconducting magnet able to produce fields up to 5 T. The samples in the form of powder were compacted with a cotton piece inside the sample holder in order to prevent any

movement. Zero-Field-Cooling and Field Cooling (ZFC-FC) measurements were carried out in the temperature range 2–300 K. The ZFC protocol consists in cooling the sample from high temperature, to the lowest measuring temperature in a zero magnetic field. Then a static magnetic field of 0.5 kOe is applied and magnetization measured during warming up. The FC consists in cooling the sample in a small DC field and measuring the magnetization during cooling without remove the field.

Virgin magnetization curves and hysteresis loops were obtained at 5, 25, 50 and 100 K with an applied magnetic field in the range 0–50 kOe.

III EXPERIMENTAL RESULTS AND DISCUSSION

In figure 1, the DC magnetic susceptibility of the alloy $(\text{CuInTe}_2)_{1-x}(\text{TaTe})_x$ with $x = 0.25$ is displayed.

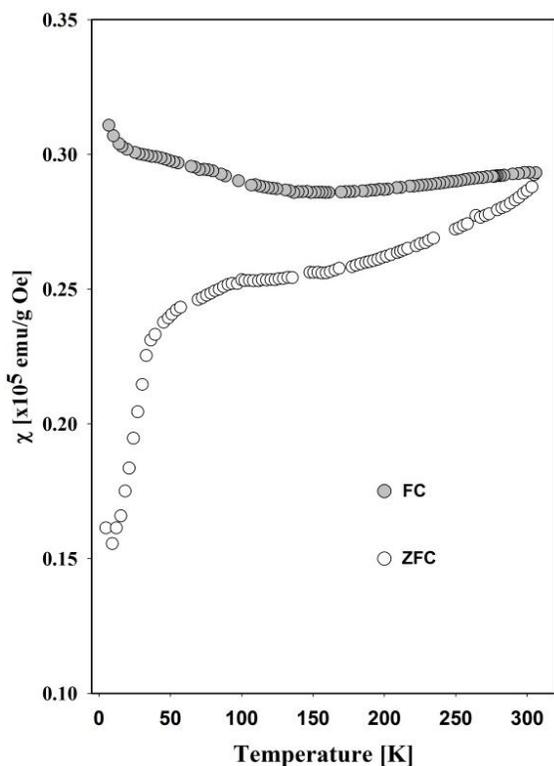


Figure 1. Magnetic susceptibility of the alloy $(\text{CuInTe}_2)_{1-x}(\text{TaTe})_x$ with $x = 0.25$; ZFC: white circles, FC: grey circles.

The furcation of the ZFC and FC curves is an indication of collective freezing of magnetic clusters. The mean magnetic moment of the cluster, μ_c , can be obtained by the expression [36]:

$$\mu_c = \left(\frac{3P_{at}K_B T \chi_m}{N} \right)^{\frac{1}{2}}, \quad (1)$$

where P_{at} is the atomic weight of the magnetic atom, K_B is the Boltzmann constant, χ_m is the mass magnetic susceptibility (in emu/gOe) at the temperature T , and N is the number of magnetic atoms in the experimental mass (0.108 g).

Doing that, we obtain $\mu_c = 5.21 \times 10^3 \mu_B$. This value is typical of ferromagnetic clusters [37]. From crystallographic

information we can also calculate the magnetic moment for unit cell.

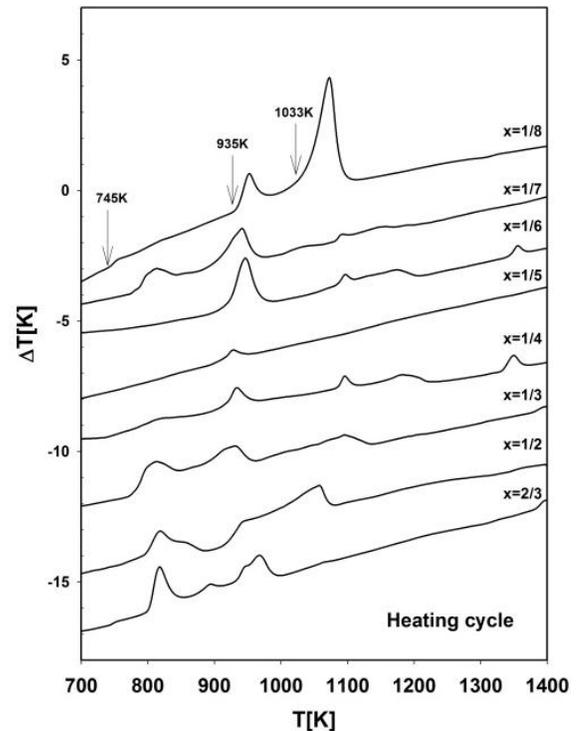


Figure 2. Differential Thermal Analysis (DTA) for $(\text{CuInTe}_2)_{1-x}(\text{TaTe})_x$ alloys. Heating cycle.

Quintero *et al.* have studied in detail the alloys of the type $(\text{I-III-VI}_2)/(\text{Mn-VI})$ [38–40] combining XRD, DTA and optical absorption techniques. They proposed that there are two kinds of ordered chalcopyrite (α and α') and two kinds of disordered sphalerite (β and β') phases. This suggestion has been corroborated by *ab initio* calculations, identifying the phase α with the ordered chalcopyrite, α' with a semi-ordered phase with mixed-symmetry, β' and β with stannite and sphalerite structures, respectively [41]. Existence of the ordered stannite structure for $x = 2/3$ was also suggested for the alloy $\text{CuMn}_2\text{InTe}_4$ [42] and observed experimentally in the $(\text{AgInSe}_2)_{1-x}(\text{HgSe})_x$ alloys [43]. Moreover, detailed XRD measurements and respective Rietveld refinements in CuFeInSe_3 [44], CuFeAlSe_3 , CuFeGaSe_3 [45], CuNiInSe_3 , CuNiGaSe_3 [46], and CuTaInSe_3 [47], indicate that these alloys crystallize in a tetragonal semi-ordered structure, space group $P4_2c$ (N° 112) whereas $\text{CuTa}_2\text{InTe}_4$ [48] and $\text{CuFe}_2\text{InSe}_4$ [49] crystallize in the stannite structure, space group $I4_2m$ (N° 121).

These results suggest that the phase sequence process as a function of composition (x) for $(\text{I-III-VI}_2)_{1-x}(\text{MT-VI})_x$ alloys (MT: Metal Transition) could be $\alpha \rightarrow \alpha' \rightarrow \beta'$, with α' acting as an intermediate phase before a reordering of the cationic sublattice which occurs at $x = 2/3$.

With regards to $(\text{CuInTe}_2)_{1-x}(\text{TaTe})_x$, the solubility of Ta in the CuInTe_2 chalcopyrite matrix is less than $x = 0.125$ as it can be observed in figure 2. Effectively, it is well known that the chalcopyrite phase of CuInTe_2 shows two phase transitions: the melting (1062 K) and order-disorder (945 K) [50]. The

presence of a third peak at 745 K for the composition $x = 1/8$ is evidence of a new crystal structure. For $x = 0.25$, the DTA curve shows, at least, five thermal transitions.

The diffraction pattern of sample $x = 0.25$, showed in Figure 3, is composed by a tetragonal chalcopyrite-like phase and a secondary phase identified as Ta_2Te_3 [51].

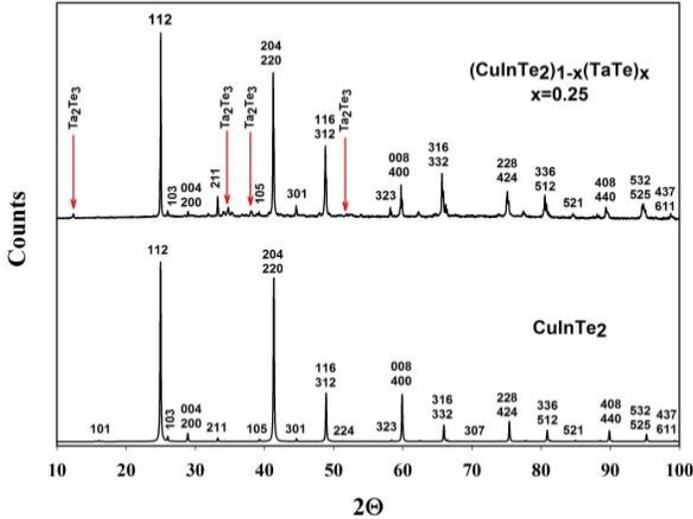


Figure 3. X-ray diffraction patterns of sample $x = 0.25$ (top) and $CuInTe_2$ (bottom). Arrows signal the presence of a secondary phase identified as Ta_2Te_3 .

Based in DTA and x-ray diffraction measurements, and the previous discussion about the crystallographic evolution of $(I-III-VI_2)_{1-x}(MT-VI)_x$ alloys we can conclude: a) the sample $x = 0.25$ is two phases. The mean phase is tetragonal, close to chalcopyrite, but DTA curve excludes the $I42d$ space group; b) the composition value of the sample ($x = 0.25$) is far from the value $x = 2/3$ for which the cationic reordering takes place, so the $I42m$ space group is also excluded; c) discard leads to the conclusion that sample $x = 0.25$ belongs to the $P42c$ space group.

It is worth to note here that there is very little information about the phase Ta_2Te_3 . Apart its crystal structure we are not found any information about its magnetic behavior, in consequence, we cannot evaluate how this secondary phase can affect the magnetic behavior of the mean phase. However, as Ta_2Te_3 represents less than 5 % in the diffraction pattern, we will assume that it will affect very little.

For the $P42c$ space group, there are 8/7 atoms of Ta^{+2} by unit cell. Using Hund's rules, the magnetic moment of $Ta^{+2} = 3.87 \mu_B$, in consequence, the magnetic moment for unit cell is $(3.87 \mu_B)(8/7) = 4.42 \mu_B/\text{unit cell}$.

The number of unit cells by cluster is given by:

$$N_{uc} = \mu_p / p \mu_{uc} = 1178. \quad (2)$$

The volume of the cluster is then:

$$V_c = N_{uc} V_{uc} = 5.6 \times 10^2, \text{ nm}^2 \quad (3)$$

Where V_{uc} is the volume of the tetragonal unit cell: a^2c ($a = 6.186 \text{ \AA}$ and $c = 12.428 \text{ \AA}$) [33]. Finally, the mean diameter of

the clusters assuming spherical symmetry is:

$$D_p = \left(\frac{6V_p}{\pi} \right)^{1/3} = 10 \text{ nm}. \quad (4)$$

The hysteresis loops for $T = 5, 25, 50$ and 100 K are showed in Figures 4 to 7. The sequence of measurements was: from $H = 0$ to $+20 \text{ kOe}$ (virgin curve), then from $H = +20 \text{ kOe}$ to -20 kOe and finally from $H = -20 \text{ kOe}$ to $+20 \text{ kOe}$. In the figures, the white circles represent the experimental measurements and the lines a guide for the eyes.

The labels indicate the values of the magnetic saturation (M_s), the remanent magnetization (M_r) and the coercitive field (H_c)

In Table 1, the parameters obtained from the hysteresis curves are summarized.

Table 1. Parameters obtained from the hysteresis loops.

| Temperature (K) | Magnetic Saturation ($\times 10^3 \text{ emu/g}$) | Remanent Magnetization ($\times 10^3 \text{ emu/g}$) | Coercitive Field (kOe) |
|-----------------|---|--|------------------------|
| 5 | 6.5 | 7.5 | 0.22 |
| 25 | 6.1 | 8.2 | 0.17 |
| 50 | 6.2 | 7.0 | 0.13 |
| 100 | 6.0 | 6.0 | 0.11 |

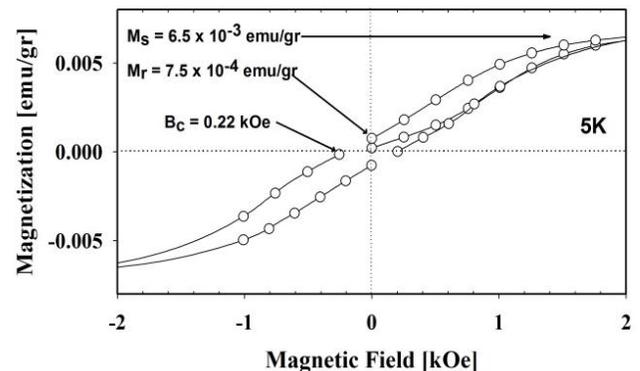
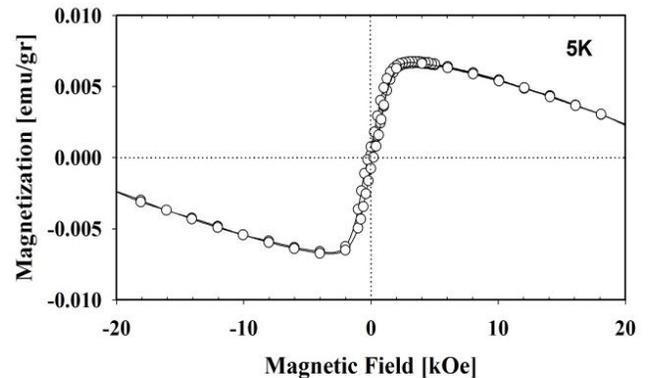


Figure 4. Top: Hysteresis loop of the alloy $(CuInTe_2)_{1-x}(TaTe)_x$ for $x = 0.25$ and $T = 5 \text{ K}$. Bottom: Amplification around $H = 0$ showing the values of M_r , M_s and B_c .

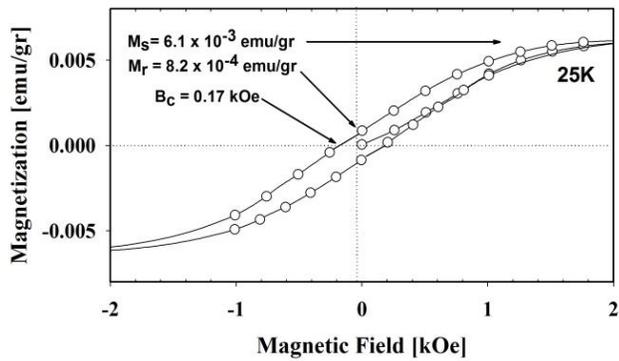
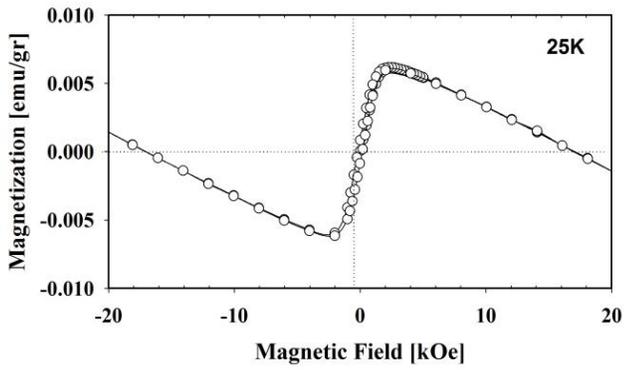


Figure 5. Top: Hysteresis loop of the alloy $(\text{CuInTe}_2)_{1-x}(\text{TaTe})_x$ for $x = 0.25$ and $T = 25$ K. Bottom: Amplification around $H = 0$ showing the values of M_r , M_s and B_c .

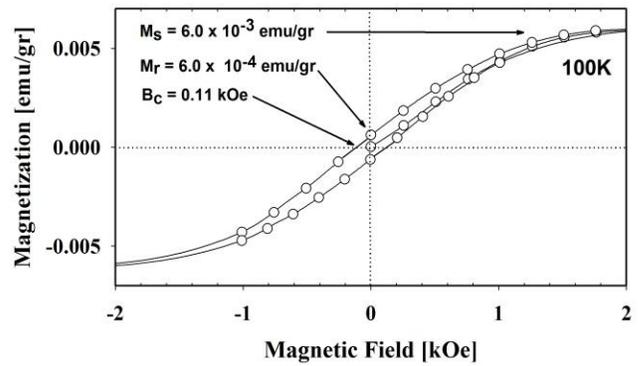
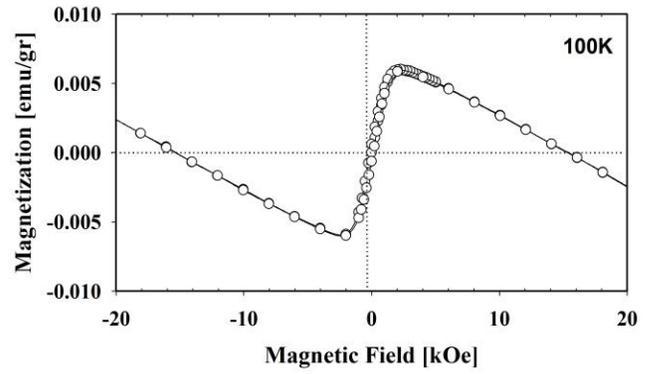


Figure 7. Top: Hysteresis loop of the alloy $(\text{CuInTe}_2)_{1-x}(\text{TaTe})_x$ for $x = 0.25$ and $T = 100$ K. Bottom: Amplification around $H = 0$ showing the values of M_r , M_s and B_c .

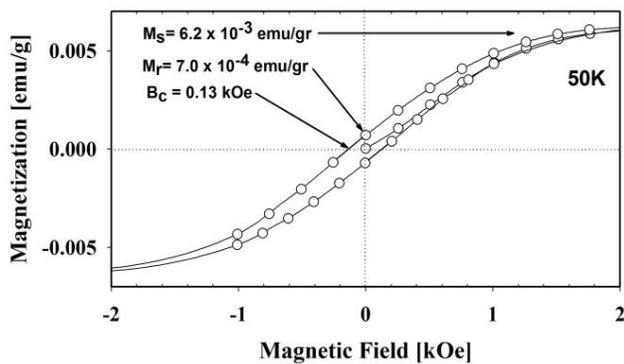
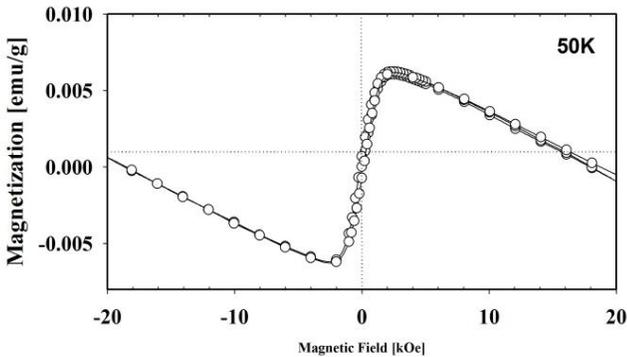


Figure 6. Top: Hysteresis loop of the alloy $(\text{CuInTe}_2)_{1-x}(\text{TaTe})_x$ for $x = 0.25$ and $T = 50$ K. Bottom: Amplification around $H = 0$ showing the values of M_r , M_s and B_c .

Additionally, it clearly observed from the curves at high magnetic fields that a diamagnetic component accompanied the ferromagnetic one. The value of this diamagnetic component can be obtained from the slope of the hysteric curves, giving: -3.07×10^{-4} ; -4.74×10^{-4} ; -1.30×10^{-4} and -5.17×10^{-4} emu/g for 5, 25, 50 and 100 K, respectively.

The values of the coercive field (symmetric for opposite polarity of magnetic field: $H_c = -H_c$) as a function of temperature is displayed in figure 8. The experimental points had been fitted with the equation:

$$H_c = H_0 \left[1 - \left(\frac{T}{T_B} \right)^n \right]. \quad (5)$$

The fitted parameters given: $H_0 = 0.35$ kOe, $T_B = 564$ K and $n = 0.21$.

According to the classic Mean Field theory for non-interacting and randomly oriented clusters the coefficient " n " must be close to 0.5 [52] whereas we are obtained a much lower value that suggest, for the contrary, a strong interaction between them. This is coherent with the relative flat behavior of the FC curve in the magnetic susceptibility. Moreover, the relation between the remanence and saturation magnetizations, is close to 0.1 which disagrees with the expected value of 0.5 predicted by the Stoner-Wohlfarth model [53]. Another indication that the

magnetic behavior of this alloy is far from an ideal system.

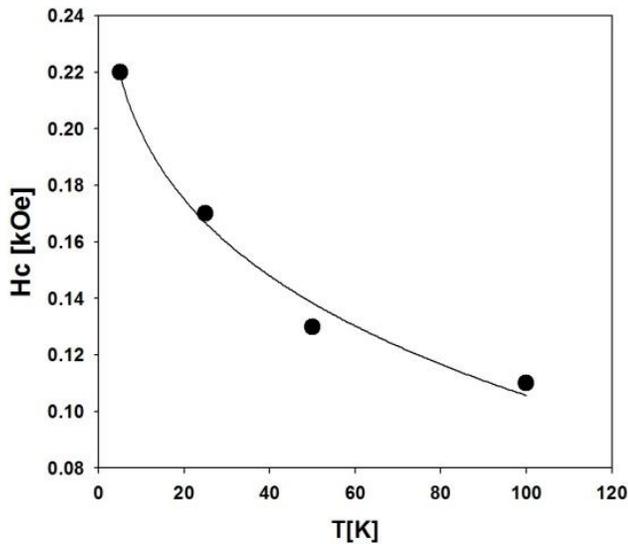


Figure 8. Measured coercive field as a function of temperature: 5, 25, 50 and 100 K for the alloy $(\text{CuInTe}_2)_{1-x}(\text{TaTe})_x$ for $x = 0.25$. Black circles: experimental; line: fit with equation (5).

CONCLUSIONS

The magnetic behavior of the alloy $(\text{CuInTe}_2)_{1-x}(\text{TaTe})_x$ with $x = 0.25$ has been investigated using Squid techniques. The DC magnetic susceptibility shows hysteresis of ZFC and FC curves in the entire range of temperature measurements 82-300 K) which is typical of cluster glass magnetic systems. From the values of the magnetic susceptibility at 300 K the mean magnetic moment and diameter of the clusters have been calculated. Hysteresis loops show that coexist two magnetic components, one ferromagnetic another diamagnetic. From the relation between remanence and saturation magnetizations, the variation of the coercive field with temperature and the flat character of the FC curve it is inferred that this alloy does not follow the Stoner-Wohlfarth model due to strong magnetic interactions between clusters.

IV ACKNOWLEDGMENTS

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