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Magnetic behaviour of $Cu_2FeGeSe_4$

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Abstract

Measurements of magnetic susceptibility χ as a function of temperature T and of magnetisation M as a function of applied magnetic field H at a number of fixed temperatures were made on polycrystalline samples of $Cu_2FeGeSe_4$. The χ versus T data show that an antiferromagnetic transition occurs at 20 K and that a second transition occurs at $\sim$8 K, indicating a transition to weak ferromagnetic form. The M versus H curves indicated that at all temperatures below $\sim$70 K bound magnetic polarons (BMP) occur, in the paramagnetic, antiferromagnetic and weak ferromagnetic ranges. Below 8 K, the M versus H curves exhibited magnetic hysteresis, and this is attributed to the interaction of the BMPs with tetragonally anisotropic matrix. The B versus H curves were well fitted by a Langevin-type of equation, and the variation of the fitting parameters determined as a function of temperature. These showed that above 20 K the total BMP magnetisation fell almost linearly with increasing temperature and effectively disappeared at 70 K. The number of BMPs remained practically constant with temperature having a mean value of $6.55 \times 10^{18}/cm^3$. The analysis gave a value of 213 μ_B for the average magnetic moment of a BMP, corresponding to 42.4 Fe atoms. Using a simple spherical model, this gives the radius of a BMP as 12.0 Å.

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Keywords: Quaternary magnetic semiconductors; Bound magnetic polarons; Hysteresis effects

1. Introduction

Compound semiconductor materials for which an appreciable fraction of the cations is atoms of iron, manganese or similar elements show interesting magnetic properties and all of these materials can be labelled magnetic semiconductors (MS). The particular magnetic behaviour occurring in any given case depends to a large extent on the distribution of the magnetic atoms in the lattice. Thus for MS alloys in which these atoms are at random in the cation lattice, for lower concentrations the material mainly shows spin-glass form, a change to antiferromagnetic form occurring when the concentration exceeds about 0.6 [1]. For compounds, where the arrangement of magnetic atoms on the cation lattice is regular, the exchange between

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these atoms is usually antiferromagnetic and, in the simplest case, collinear antiferromagnetic behaviour occurs. However, various effects can occur which complicate this simple form, resulting in different magnetic behaviours. The behaviour of interest in the present work is that of bound magnetic polarons (BMPs) [2–4].

In these materials, BMPs can arise due to the presence of non-ionised acceptors or donors [4]. These must have relatively high concentrations for the BMP effects to be observed but not so high that impurity bands are formed. The bound hole (electron) interacts with the spins of the magnetic ions within the sphere of its Bohr orbit and tends to produce ferromagnetic alignment in those spins. Thus, in a simple model, the material can be considered as an irregular assembly of ferromagnetic spheres in a matrix which may be antiferromagnetic or paramagnetic, depending upon the temperature conditions, etc.

This behaviour can be investigated by various types of magnetic measurements, the most common being measurements of magnetic susceptibility χ as a function of temperature T and measurements of magnetisation M as a function of magnetic field H at various temperatures. McCabe et al. [5] used these types of measurement to investigate the behaviour of BMPs in the antiferromagnetic p-type MS alloy $Cu_2Mn_{0.9}Zn_{0.1}SnS_4$ which has the tetragonal stannite structure. They showed that BMPs were present up to a temperature of about 60 K. The Néel temperature of this alloy is near 8 K and so BMPs were observed in both the antiferromagnetic and paramagnetic range.

In the present research programme, the magnetic properties of I_2–Fe–IV–VI_4 compounds are being investigated, for the cases of I = Cu, Ag, IV = Si, Ge, Sn and VI = Se, Te. Here the results for the compound $Cu_2FeGeSe_4$ are considered. Guen and Glaunsinger [6] reported that this compound showed antiferromagnetic form and that it had the tetragonal stannite structure. Later work on the structures of these types of compound [7] confirmed the stannite form for $Cu_2FeGeSe_4$ and gave lattice parameter values of $a = 5.591$ Å and $c = 11.030$ Å. Here, the variations of the magnetic properties with temperature in the range 2–300 K are considered. These can be attributed to the Fe^{2+} ions, since the copper is Cu^{+} and so will not contribute. Preliminary results of this investigation have been reported previously [8], where in addition to preliminary magnetic data, electrical measurements showed that the compound was p-type and that the particular sample investigated had a hole concentration of $1.1 \times 10^{19}/cm^3$ at room temperature. Resistivity measurements as a function of temperature gave a hole binding energy of $E_h \approx 42$ meV.

2. Sample preparation and experimental techniques

The polycrystalline samples of $Cu_2FeGeSe_4$ used in the work were prepared by the melt and anneal technique, described in detail previously [8]. Measurements of magnetic susceptibility χ as a function of temperature T in the range 2–300 K were made using a Quantum Design SQUID magnetometer with an external magnetic field of 1×10^{-2} T. The resulting variation of χ with T was used to determine the temperatures at which magnetic transitions occurred and to estimate, where possible, the type of transition. Two sets of measurements were made to determine the variation of the magnetisation M as a function of applied magnetic field H at various fixed temperatures. One set of measurements was made using the high magnetic field facilities at Toulouse. The field is produced by the discharge of a capacitor bank into a resistive copper coil. The maximum field (35 T) is reached within 100 ms and the decreasing time is 300 ms. In order to measure the magnetisation, two pick-up coils are mounted to give zero-induced voltage in the absence of the sample. The signal in the presence of the sample is proportional to the time derivative of its magnetisation. The second set of measurements was made using the SQUID system described above, the maximum field in that case being 6 T.

3. Results

For the case of magnetic susceptibility measurements, curves of χ versus T and $1/\chi$ versus T are shown in Figs. 1 and 2, respectively. From Fig. 1, it

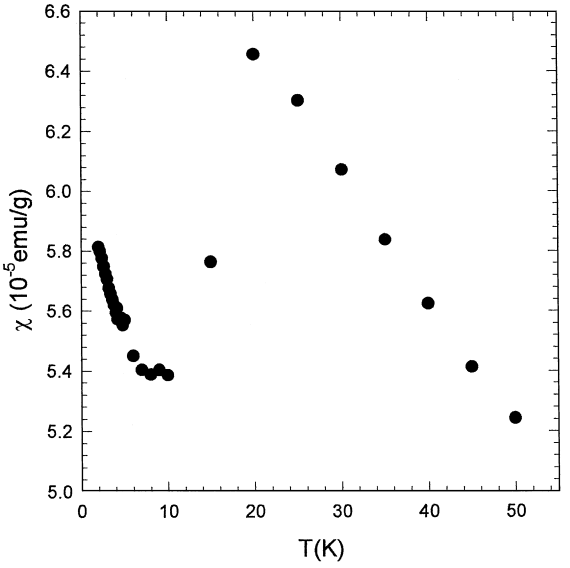

Fig. 1. Variation of magnetic susceptibility χ as a function of temperature T.

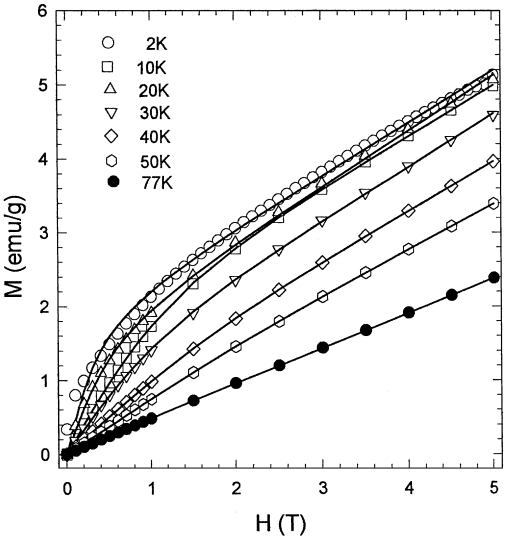

Fig. 3. Variation of magnetisation M as a function of applied field H for a range of temperatures.

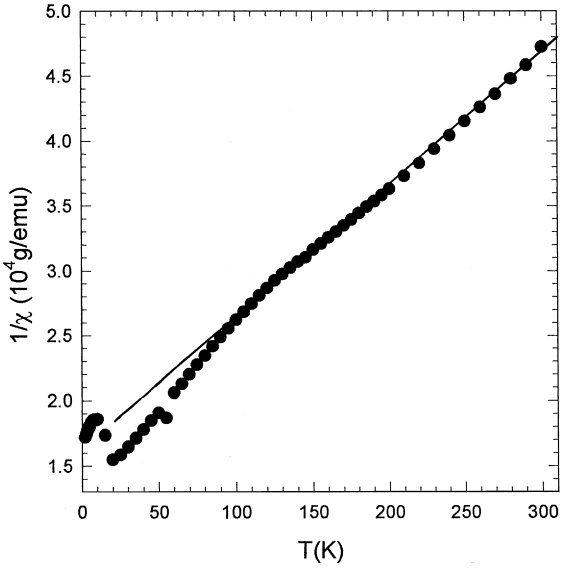

Fig. 2. Variation of inverse susceptibility $1/\chi$ as a function of temperature T.

is seen that magnetic transitions occur at temperatures of about 20 and 8 K, as indicated in the figure. The one at 20 K is typical of an antiferromagnetic transition T_N, while the lower one has the form associated with a ferromagnetic transition. From Fig. 2, it is seen that $1/\chi$ varies fairly linearly with T down to approximately 100 K and extrapolation from this range gives a temperature intercept of -162 K, again corresponding to antiferromagnetic behaviour. Below 100 K, the deviation from linearity indicates the occurrence of another magnetic effect. Below, these results will be correlated with those for the magnetisation measurements.

For the magnetisation measurements, in all cases the M versus H data showed the general form expected when BMPs are present in the compound, and a set of M versus H results, for values of H up to 5 T, are shown in Fig. 3. Here, the experimental points are shown with curves determined by fitting to Eq. (1) as discussed below. In the initial work, carried out on the pulsed magnetic field system at Toulouse, measurements were made in fields up to ~ 35 T at 2 K and no magnetic saturation was observed up to the maximum value (Fig. 5 of Ref. [8]), so that the maximum of 5 T used here was considered sufficient for the present work. In Fig. 3, it is seen that for 20 K and above, the spacing and shape of the curves are of the same regular form given previously [5] for other compounds showing

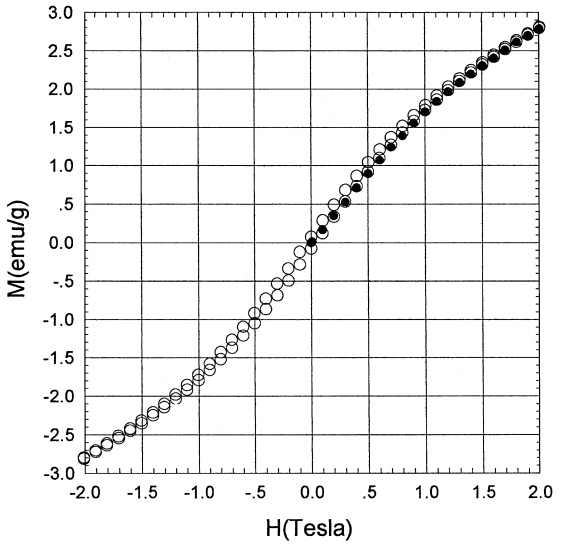

Fig. 4. Variation of magnetisation M with applied field H at 5 K, showing hysteresis behaviour.

BMP effects. Below 20 K, the curves are close together and some overlap occurs (hence for the purpose of clarity, the curves for 5 and 16 K have been omitted from Fig. 3). As indicated below, this behaviour can be attributed to effects of anisotropy at low temperatures. In the case of the 2 and 5 K data, a further effect was observed, in that a small amount of hysteresis was present, as shown in Fig. 4, where the data for 5 K is plotted. Here, the applied magnetic field was cycled between the limits $+6$ and -6 T, and the resulting M values are shown in Fig. 4 (limited to a 2 T range for clarity). For the hysteresis loop, the difference between the up and down curves is small but can be clearly observed, while the initial magnetisation curve shows some deviation from the hysteresis form. At all other temperatures of measurement, the curves appeared completely reversible.

These results are discussed below.

4. Analysis and discussion

From the form of the M versus H curves in Fig. 3, it is seen that the magnitude of the BMP resultant moment falls with increased temperature, becoming practically zero at 77 K, where the linear form of the graph corresponds to normal paramagnetic behaviour. This could account for the form of the $1/\chi$ in the range $20 < T < 100$ K. Thus it is seen that with decreasing temperature, four different magnetic ranges are observed. At high temperatures, the compound shows normal paramagnetic form, but in the vicinity of 80 K, BMPs are observed in a paramagnetic matrix. As seen from the χ versus T curve, a transition to antiferromagnetic form occurs at the Néel temperature $T_N = 20$ K and below this the BMPs occur in this antiferromagnetic matrix. Finally, below 8 K, the BMPs are present, but a weak ferromagnetic behaviour also occurs.

As has been shown previously [5], the M versus H curves for BMPs can be very well fitted to an equation of the form

$$M = M_0 L(X) + \chi_m H, \tag{1}$$

where the Langevin term $L(X)\,(= \coth x - 1/x)$ represents the contribution of BMPs and the term $\chi_m H$ the contribution of the matrix. Here, $M_0 = N m_s$ and $x = m_{eff} H/k_B T$ where N is the number of BMPs involved, m_s and m_{eff} are, respectively, the true and effective spontaneous moments per BMP. In the Langevin function, the effective moment m_{eff} determines how quickly the true moment aligns along H. Because of the effects of interaction between the BMPs, Wolff (quoted in Ref. [5]) has proposed that $m_{eff} = m_s T/(T + T')$, where T' represents the interaction. With T' relatively small, at the higher temperatures investigated, to a good approximation $m_{eff} = m_s$. As shown by McCabe et al. [5], for temperatures lower than ~ 20 K, anisotropic behaviour is observed, because of the interaction of the BMPs with the tetragonally anisotropic matrix. Thus at a given T, the values of M are different for H parallel and H perpendicular to the symmetry axis c. However, for temperatures above about 20 K, anisotropy effects were found to be negligible, and in this range $m_{eff} = m_s$.

In the present work using polycrystalline samples, the values of the various parameters in Eq. (1) will be mean values over a random arrangement of small crystallites. As shown above, for $Cu_2FeGeSe_4$, the Néel temperature T_N is 20 K,

and so the effects of anisotropy will be important only in the antiferromagnetic range. The hysteresis effects observed at 2 and 5 K can also probably be attributed to this anisotropy, since, in this range, the thermal effects are small enough for the anisotropy to influence the spin directions when the applied field is zero or small. With a polycrystalline sample, the various crystallites can act in a way formally similar to domains and produce hysteresis effects.

From the form of the M versus H curves at 5 K (Fig. 4), it is seen that the magnitude of this hysteresis effect is relatively small. Thus, bearing in mind the limitations described above, for a good approximation, the M versus H data at all temperatures, even 2 and 5 K, can be analyzed in terms of Eq. (1), with M_0, m_{eff} and χ_{m} used as fitting parameters. As indicated above, the fitted curves are shown in Fig. 3, where it is seen that in most cases a very good fit was obtained. The rather poor fit to the 2 K (and 5 K) data at low values of H is due to the hysteresis effects present in that range. Values of the fitting parameters were thus determined as a function of temperature, and these are plotted against T in Figs. 5–7.

As indicated by McCabe et al. [5], in the range where $m_{\mathrm{s}} = m_{\mathrm{eff}}$, values for N can be obtained from the ratio M_0/m_{eff}. In Fig. 8, values are shown for M_0/m_{eff} ($= N$) as a function of T. It is seen that in the range $20 < T < 70$ K, this value is almost constant with a mean value of 0.011/g, i.e. N is almost constant with a mean value in this temperature range of $0.011/\mu_{\mathrm{B}}/\mathrm{g} = 1.19 \times 10^{18}/\mathrm{g}$. This gives a value of N and hence a concentration of non-ionised acceptors of $6.55 \times 10^{18}/\mathrm{cm}^3$. This value is smaller than that reported previously [8], but those measurements and the present ones were made on two separately prepared samples. With these values of N and the activation energy of 42 meV quoted above, the concentration of holes and hence of ionised acceptors at 50 K is less than $10^{16}/\mathrm{cm}^3$. Thus the change in N in the range 2–50 K is negligible, giving N constant as obtained above.

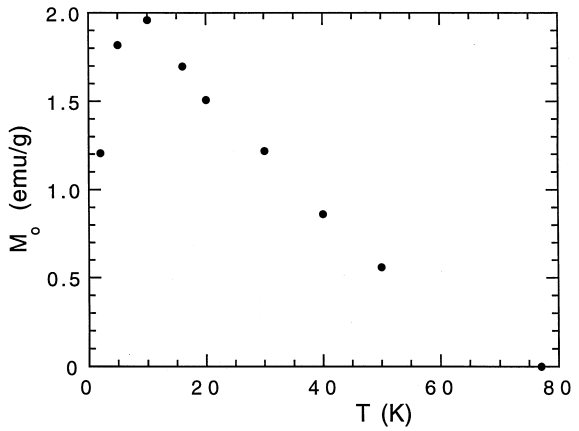

Fig. 5. Variation of total BMP magnetisation M_0 ($= Nm_{\mathrm{s}}$) with temperature T.

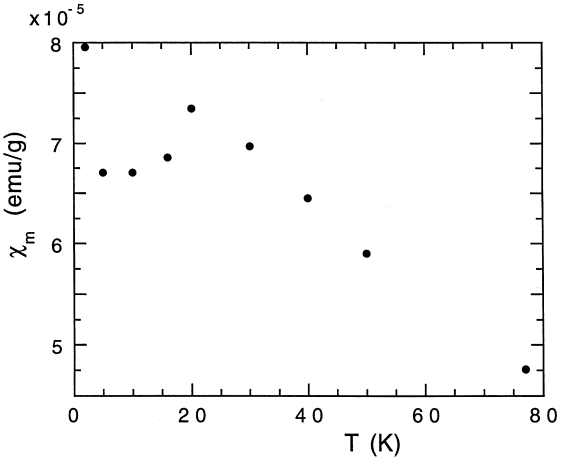

Fig. 6. Variation of the matrix susceptibility χ_{m}, with temperature T.

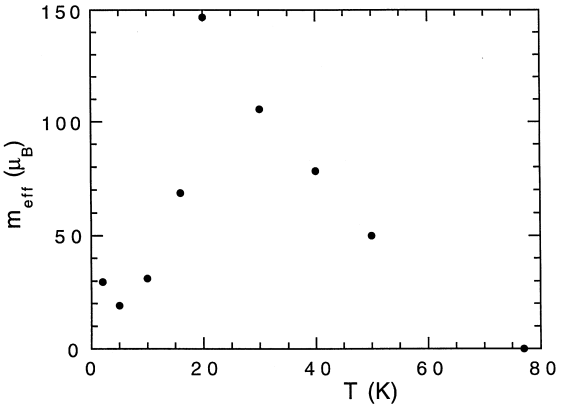

Fig. 7. Variation of m_{eff}, the effective spontaneous moment per BMP, with temperature.

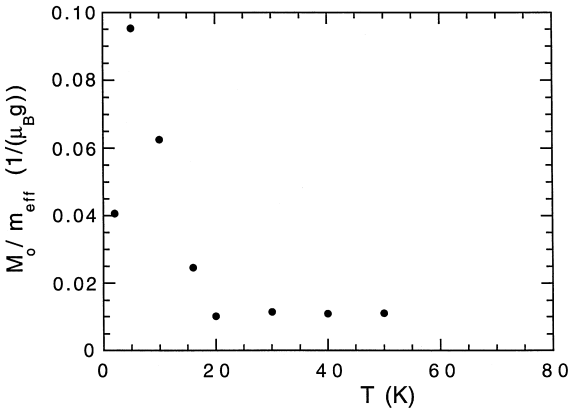

Fig. 8. Variation of the number of BMPs $N\ (=M_0/m_{\mathrm{eff}})$ with temperature T.

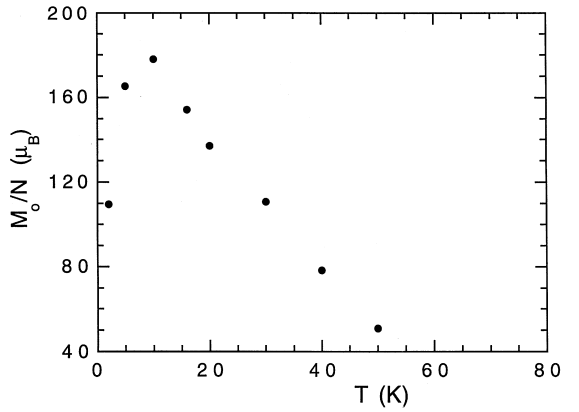

Fig. 9. Variation of the true spontaneous moment of a BMP $m_{\mathrm{s}}\ (=M_0/N)$ with temperature T.

With this value for N, values for m_{s} can be obtained from the M_0 values and the variation of m_{s} with T is shown in Fig. 9. It is seen that for 10 K and above, the variation of m_{s} with T is practically linear, and extrapolates to a value of 212 μ_{B}/BMP at $T=0$. Taking the atomic moment for Fe^{2+} as 5 μ_{B} gives the mean number of Fe atoms in each BMP as 42.4. This is to be compared with the value of 28.6 Mn ions per BMP obtained by McCabe et al. [5] for p-type $Cu_2Mn_{0.9}Zn_{0.1}SnS_4$. The assumption, that in a very simple model all Fe ions inside a spherical BMP are aligned and that none outside contribute, gives the radius of the BMP to be 12.0 Å, which is a reasonable number for an acceptor Bohr radius in such a material. These values indicate the fraction of Fe ions inside the BMPs to be approximately 5%.

5. Conclusions

Measurements of χ versus T indicate that in $Cu_2FeGeSe_4$, magnetic transitions occur at 20 and 8 K, the former being an antiferromagnetic transition and the latter a transition to weak ferromagnetic form. From the measurements of M versus H, it is seen that BMPs occur at all temperatures below ~ 70 K. Analysis of the M versus H curves by fitting to a Langevin-type of equation gave values for the number of BMPs, the average magnetic moment and hence the average size of a BMP. These values were found to be consistent with previously published data. For temperatures below 8 K, the B versus H curves showed magnetic hysteresis.

It has been suggested above that this hysteresis behaviour can be attributed to the effects of uniaxial anisotropy of the matrix, which seems most probable. However, two other possible mechanisms that could produce this effect were considered:

(a) Canting of the antiferromagnetic aligned spins, giving a small resultant spin component in the matrix. In the corresponding compounds, $Ag_2FeGeSe_4$, $Ag_2FeSiSe_4$ and $Ag_2FeSnSe_4$, which have the orthorhombic wurtz-stannite structure, much more pronounced hysteresis effects are observed, extending to a temperature of above 200 K. These results are attributed to spin canting (to be published).

(b) Interaction between the spontaneous spins of the BMPs producing ferromagnetic alignment and a resultant spin in the absence of an applied magnetic field. This will be discussed further at a later date when detailed results on more of these quaternary compounds are obtained.

Acknowledgements

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References

[1] J.C. Woolley, S.F. Chehab, T. Donofrio, S. Manhas, G. Lamarche, A. Manoogian, J. Magn. Magn. Mater. 61 (1986) 13.
[2] T. Dietl, J. Spalek, Phys. Rev. Lett. 48 (1982) 355.
[3] D. Helman, P.A. Wolff, J. Warnock, Phys. Rev. B 27 (1983) 4848.
[4] P.A. Wolff, Diluted magnetic semiconductors, in: J.K. Furdyna, J. Kossur (Eds.), Semiconductors and Semimetals, Vol. 25, Academic Press, New York, 1988.
[5] G.H. McCabe, T. Fries, M.T. Liu, Y. Shapira, L.R. Ram-Mohan, R. Kershaw, A. Wold, C. Fau, M. Averous, E.J. McNiff Jr., Phys. Rev. B 56 (1997) 6673.
[6] L. Guen, W.S. Glaunsinger, J. Solid State Chem. 35 (1980) 10.
[7] M. Quintero, A. Barreto, P. Grima, R. Tovar, E. Quintero, G. Sánchez-Porras, J. Ruiz, J.C. Woolley, G. Lamarche, A.-M. Lamarche, Mater. Res. Bull. 34 (14) (1999), in press.
[8] M. Quintero, R. Tovar, A. Barreto, E. Quintero, A. Rivero, J. Gonzalez, G. Sanchez-Porras, J. Ruiz, P. Bocaranda, J.M. Broto, H. Rakoto, R. Barbaste, Phys. Stat. Sol. (b) 209 (1998) 135.