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Magnetic spin-flop and magnetic saturation in $Ag_2FeGeSe_4$, $Ag_2FeSiSe_4$ and $Cu_2MnGeSe_4$ semiconductor compounds

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Abstract

Measurements of magnetization (M) at helium temperatures and with pulsed magnetic fields up to 32 T, have been made on polycrystalline samples of the three compounds $Ag_2FeGeSe_4$, $Ag_2FeSiSe_4$ and $Cu_2MnGeSe_4$. All three compounds have orthorhombic symmetry, with the wurtz–stannite structure, and have semiconductor properties. The resulting curves of M versus B have been used to give information on the magnetic spin–flop and magnetic saturation transitions. The observed values of the spin-flop field B_f differ appreciably for the three cases, with mean values of 0.35 T for $Ag_2FeSiSe_4$, 4.0 T for $Cu_2MnGeSe_4$ and 13.5 T for $Ag_2FeGeSe_4$. The saturation behavior is also very different from one compound to another. In the case of $Ag_2FeSiSe_4$, the magnetization curve at low fields (<3 T) is quite different for the cases of pulsed field and steady field measurements. This is attributed to domain effects, with $Ag_2FeSiSe_4$ showing weak ferromagnetic behavior because of crystallographic spin-canting. This effect can also be the cause for the very low value of B_f in this compound.

Keywords: Quaternary magnetic semiconductors; Antiferromagnetic spin-flop; Saturation field

1. Introduction

Quaternary magnetic semiconductors have been investigated recently as possible new materials for semiconductor devices [1]. In part of a current research programme, the magnetic behavior of the compounds $Ag_2FeSiSe_4$ (AFS), $Ag_2FeGeSe_4$ (AFG) and $Cu_2MnGeSe_4$ (CMG) is being investigated. All these compounds have orthorhombic symmetry, with wurtz–stannite structure [2,3], and are basically antiferromagnetic [4]. The samples used in the present work are polycrystalline. Here, the magnetic behavior at high magnetic fields is determined.

Theoretical analysis (e.g. [5,6]) shows that for an antiferromagnetic material, in the field-temperature (B–T) plane of the magnetic phase diagram, three phases can occur: the paramagnetic (P); the antiferromagnetic (AF) and the spin–flop (SF) phases. The analyses have been mainly concerned with uniaxial materials with an easy-axis z, and it is seen that the detail of the diagram depends on the

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orientation of the magnetic field applied along the z direction. Lines of interest in the diagram are the transitions between the phases, i.e. AF–SF, (B_f), the spin-flop field, and AF–P and SF–P, (B_s), the saturation field. In the present work, measurements were made to investigate B_f and B_s at helium temperatures.

2. Samples and measurements

The polycrystalline samples used were prepared by the melt and anneal technique [3]. Measurements of magnetization M as a function of applied field B were made at helium temperatures (a) using the high field pulsed technique (Toulouse) [4] for fields up to 35 T, and (b) using the SQUID steady-field system (Merida) [4] with fields up to 6 T.

3. Results and analysis

Since the present work was done on polycrystalline orthorhombic samples, the theory mentioned above cannot be expected to explain the present data quantitatively. However, it is useful in a qualitative discussion of the results. Figs. 1 (AFG), 2 (AFS) and 3 (CMG) show the variations of M with B obtained for the three compounds with the pulsed system, while Fig. 4 shows the M versus B data obtained for AFS with the steady-field technique.

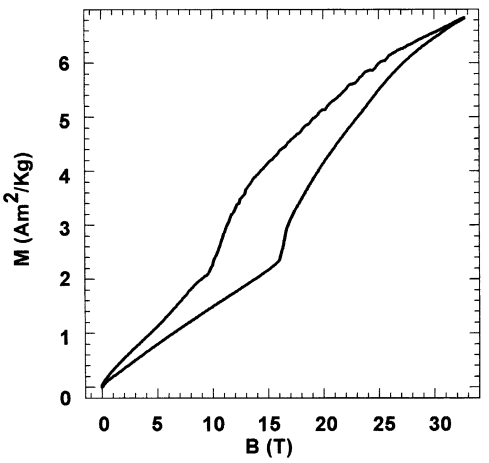

Fig. 1. $Ag_2FeGeSe_4$. Variation of magnetization M with applied magnetic field B showing spin–flop behavior, for measurements using pulsed field system.

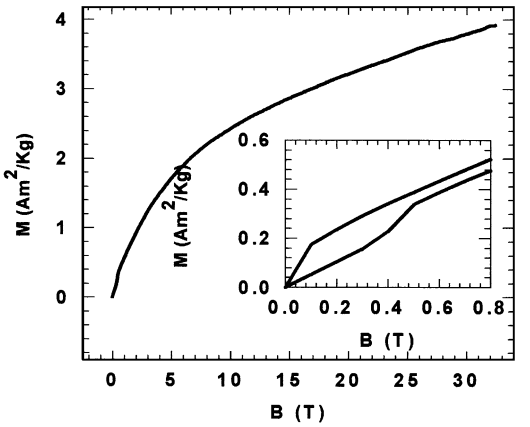

Fig. 2. $Ag_2FeSiSe_4$. Variation of magnetization M with applied magnetic field B, for measurements using pulsed field system. Inset: Expanded version of graph to show spin–flop behavior.

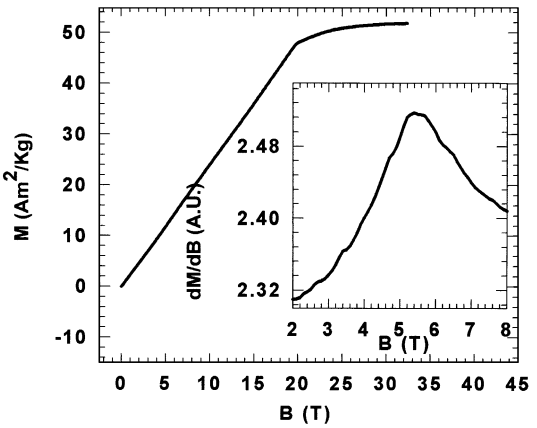

Fig. 3. $Cu_2MnGeSe_4$. Variation of magnetization M with applied magnetic field B showing saturation at 20 T, for measurements using pulsed field system. Inset: Derivative dM/dB curve to show the spin–flop transition.

Considering first the spin-flop behavior, in Fig. 1 the B_f transition for AFG is clearly seen. It is observed that an appreciable hysteresis is present, with B_f having a value of 16.2 T with increasing B and approximately 10 T for decreasing B. The theoretical analysis in Ref. [6] indicated that

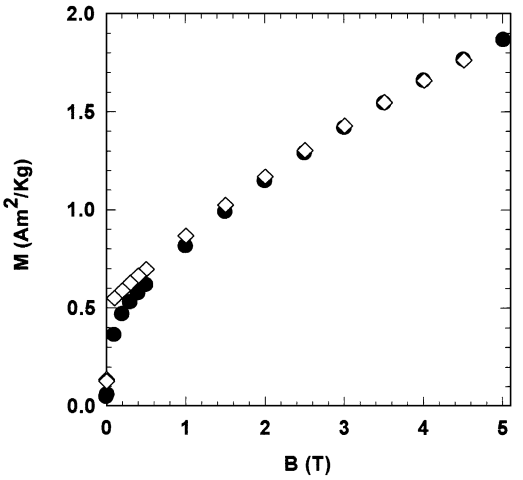

Fig. 4. $Ag_2FeSiSe_4$. Variation of magnetization M with applied magnetic field B, for measurements using a steady field system.

hysteresis should occur, but it was not observed in that work on single crystal $GdAlO_3$. For the AFS and CMG data, no such large B_f effect was observed. However, in Fig. 2, the amplified curve in the inset shows a small B_f transition at relatively very low values of B, with B_f values of 0.4 and 0.2 T for the up and down cases. Similarly, in the CMG data, no B_f transition is easily seen, but the inset in Fig. 3 gives a derivative dM/dB curve for the up run, which shows a small transition, the temperature behavior of which shows spin-flop form, with a B_f of approximately 5 T. A corresponding value of $\cong 4$ T is obtained for the down run.

When the results from the steady-field measurements on AFG and AFS were compared with the pulse field data (in the range $0 < B < 6$ T), it was found that for AFG the data were in reasonable agreement. However, for AFS the two M versus B curves were very different (Figs. 2 and 4). The steady-field data at low B is typical of weak ferromagnetic behavior, and is attributed to the canting of the mainly AF spins resulting in a small ferromagnetic component. The curve of magnetic susceptibility versus temperature shows agreement with this [7]. From the data, the canting angle δ is estimated to be between 1 and 2°. This behavior is not seen in the pulsed field data because the ferromagnetic domain relaxation time is too long for the effect to be observed in the rapid rise-time of the pulse.

This weak ferromagnetic component can also explain the very low value of B_f for AFS. An approximate analysis of the AF spin–flop behavior [5] indicates that $B_f^2 = \{2K/(\chi_2 - \chi_1)\}$, where χ_1 and χ_2 are the susceptibility with B parallel and perpendicular to z, respectively. If a small ferromagnetic component is added to the analysis, the modified relation becomes $B_f^2 = [2K/\{(\chi_2 - \chi_1)\cos\delta + \chi_m \sin\delta\}]$, where χ_m is the ferromagnetic susceptibility. Since χ_m will be much larger than χ_1 or χ_2, even a small value of δ will result in a large reduction in B_f compared with the purely AF case.

With regard to the saturation field B_s, a transition is clearly observed only in the case of CMG (Fig. 3), where the transition is seen at 20.0 T. With AFG and AFS (Figs. 1 and 2), for fields above B_f, in both cases the M versus B graph shows continuous curvature up to the highest value of B observed. This behavior is due to the polycrystalline nature of the orthorhombic samples, which results in all possible values of θ, the angle between B and z, being present in each sample. Theoretical analysis [8] shows that the spin–flop transition is discontinuous at B_f when $\theta = 0°$ but, as θ increases, becomes a smooth curve extending over a range of B that increases as θ increases, with M versus B becoming a straight line at $\theta = 90°$. It is also found [6] that the value of B_s varies with θ, B_s increasing as θ increases. On this basis, Fig. 5a shows a schematic diagram of typical forms to be expected for the M versus B curves for different values of θ. Fig. 5b shows the form to be expected from a summation over all values of θ, which corresponds to the results observed for AFG and AFS. A tangent through the origin to this curved part of the graph, as in Fig. 5b, gives an estimate of where the SF–P saturation transition starts to occur. Thus for AFG (Fig. 1), B_s starts at about 27 T and continues above 35 T. In the case of AFS (Fig. 2), the onset of the saturation transition occurs at about 1 T. However, it appears that the B_f and B_s transitions overlap appreciably, so that it is difficult to make any estimates of range. Again, the very low values for B_s are probably due to the effects of spin canting. For CMG (Fig. 3), the behavior is very different, with B_s extending over a small range, 20–23 T.

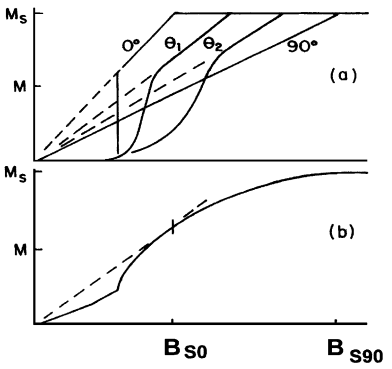

Fig. 5. (a) Schematic diagram to show the variation of magnetization M with applied field B for various values of θ, the angle between B and the easy direction of magnetization z. (b) Expected variation of M with B obtained by summing over all values of θ occurring in a polycrystalline sample. B_{s_0} and $B_{s_{90}}$ are the values of B_s for θ of 0° and 90°, respectively.

4. Conclusions

All three compounds show the expected magnetic phase diagram form with both B_f and B_s present and hysteresis in the B_f values. In each case, both B_f and B_s are observed over a range of B values because of the polycrystalline nature of the samples. However, the overall magnetic behavior is very different in the three cases. With AFG and AFS, the difference is mainly due to the fact that AFG is purely AF, while AFS shows weak ferromagnetic form due to crystallographic spin canting. Previous crystallographic work has indicated that the detailed structure of CMG is probably different from AFG and AFS [3,9], which could account for the differences in the magnetic behavior.

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