JOURNAL OF MATERIALS SCIENCE 14 (1979) 2241–2248

Electrical transport properties of low-stage AsF_5-intercalated graphite

C. ZELLER, L. A. PENDRYS, F. L. VOGEL
Moore School of Electrical Engineering and Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, PA 19104, USA

The in-plane resistivity of stage 1 and stage 2 AsF_5–graphite intercalation compounds was measured using a contactless r.f. eddy current technique from 1.6 to 290 K. The magnetoresistance of a stage 1 compound was similarly measured from 4.2 K to 290 K. The low temperature stage 2 resistivity data show a well-defined intermediate $\rho \propto T^2$ region in addition to the usual $\rho \propto T$ high temperature region, in qualitative agreement with the Kukkonen theory and indicative of a small, elongated cylindrical Fermi surface. Stage 2 resistivity data also show, for the first time in a graphite-acceptor compound, an apparent low temperature phase transition at ≈ 21 K. Magnetoresistance data were used to determine a stage 1 carrier concentration of $\approx 9 \times 10^{20}$ holes cm^{-3}. Resistive anomalies were observed at ≈ 200 K and ≈ 220 K for stage 1 and stage 2 compounds, respectively.

1. Introduction

Since values of conductivity above that of copper were first reported for compounds of graphite intercalated with strong acid fluorides [1], there has been considerable interest in understanding these compounds. The extreme anisotropy of these materials and the resultant unsuitability of the conventional bridge techniques for making accurate resistivity measurements are now well established and discussed in detail elsewhere [2–4]. This problem had brought into question the basal plane conductivity of some of these compounds, but precise measurements can be made using a contactless r.f. eddy current technique [5]. The original reports of conductivity have been justified using this technique.

In order to understand the electronic nature of these compounds, the mobility and carrier concentration must be determined as a function of temperature. Measurements of the resistivity, magnetoresistance and Hall effect are useful for making these determinations. Some resistivity and magnetoresistivity results are presented for stage 1 and stage 2 AsF_5–graphite intercalation compounds. The stage is defined as the number of contiguous graphite layers separating each intercalant layer in the ordered lamellar structure. In particular, resistivity was measured for both stages from about 1.6 K to 290 K. Magnetoresistance was measured for a stage 1 compound from 4.2 to 290 K.

Stage 1 magnetoresistance data have been used to estimate mobility and carrier concentration as a function of temperature. These are in general agreement with optical results. Detailed resistivity measurements of a stage 2 sample show, in addition to the high temperature $\rho \propto T$ region, a distinct $\rho \propto T^2$ intermediate region. This suggests, according to theory, a very elongated ellipsoidal Fermi surface, in accord with the very high anisotropy in the conductivity. Also, the resistivity plots of stage 1 and stage 2 compounds show several resistive anomalies in the ρ versus T regions. However, a number of questions remain unanswered and these questions are also discussed.

2. Procedure

The intercalated AsF_5–graphite compounds are prepared starting with highly oriented pyrolytic graphite (HOPG). Samples are cut to 5 x 5 mm using an air-abrasive technique, and cleaved to 0.025 cm. Suitable starting material is characterized electrically by a room temperature resistivity of $\approx 40 \pm 2$ $\mu\Omega$ cm and a resistance ratio of $\rho(293\text{ K})/\rho(4.2\text{ K}) \geqslant 15$.

0022–2461/79/092241–08 $02.80/0

Samples of AsF_5–graphite were prepared at ambient temperatures by direct intercalation of AsF_5 vapour with HOPG [3, 4]. The samples were prepared in a 2 × 6 mm flat cross-section pyrex glass tube, having a stop cock and tapered glass which allowed the sample to be separated from the reaction system and sealed for X-ray determination and resistivity measurements without disturbing the ambient. The desired stage was determined by monitoring the c-axis thickness with a microscope equipped with a calibration reticule. Plateaus of c-axis thickness as a function of time were observed. Termination of the reaction near the end of a plateau assured a single homogeneous phase of maximum AsF_5 content [3].

Agreement between X-ray measurements and c-axis thickness change gives a reliable indication of stage. The lack of exfoliation and edge fraying makes stage selection easy. Samples were carefully characterized by using Mo$K\alpha$ radiation X-ray diffraction diagrams to ensure single homogeneous phases. Samples were first examined for constant thickness. The good c-axis alignment of $\approx 1^0$ for HOPG permits good c-axis thickness and a-axis conductivity measurements. For a well-characterized sample, the thickness estimated from X-ray diffraction measurements had to agree with direct visual measurements of the thickness. Also, the weight change upon intercalation has to be consistent with the stage determined by c-axis thickness and had to show maximum concentration of intercalant for the desired stage. The r.f. measurements were performed on well-characterized samples of fixed stage sealed of in pyrex ampoules under ambient conditions.

In order to overcome the difficulties encountered in using the conventional 4-point bridge method on extremely anisotropic materials, an r.f. induction technique was used for making electrical transport measurements. This technique measures conductivity only along the basal plane and is therefore insensitive to the degree of anisotropy. The r.f. eddy current technique also does not require contacts. The nature of the lamellar compounds studied restricts the sample geometries to small thin square plates, for which this technique is well suited. The 100 kHz technique, which employed a ferrite core for room temperature measurements, was reported earlier [2]. The frequency has been changed to 1 kHz to overcome scatter due to the small skin depth at high frequencies and problems with hysteresis loss, edge defects and variation of sample placement.

An electromagnet with programmable sweep control was used to obtain magnetic fields up to 20 kG. Examination of the field between the pole pieces showed that the magnetic field was extremely homogeneous over the volume of the sample. A calibrated Hall probe was used to measure the field. By sweeping on both sides of zero, it was possible to determine the zero very accurately and to measure fields to within a few gauss.

Low temperature measurements were performed from 1.6 K to room temperature using standard cyrogenic techniques. Fixed points were obtained using liquid nitrogen and helium baths. Temperatures from 4.2 to 77 K were obtained either by allowing the probe to warm slowly from 4.2 K, or by passing a steady flow of cold He gas through the sample space. A heater was used to elevate the probe temperature above the ambient value of 77 K. Also, the ferrite core has been eliminated in order to permit low temperature measurements.

Electrical conductivity of a sample is determined by measuring the change in mutual inductance between a pair of co-axial coils upon introduction of the sample between the coils. A second identical pair of balance coils in series opposition are positioned parallel to the first as shown in Figs. 1a and b. After nulling, insertion of the sample results in a net signal due only to the change in mutual inductance of the first pair of coils. A phase-sensitive detector is used to select the phase of the signal corresponding to the conductivity of the sample. According to the semi-empirical theory [2], the voltage change of the phase due to the resistive component of a sample in the non-skin depth limited regime is given by

$$\Delta V = \frac{kes^2}{\rho}$$

where e = thickness, s^2 = surface area, ρ = resistivity, and k = a constant determined empirically. Numerous calibration data show this equation to be correct within the parameter ranges of interest, and provide a value for k. The effect of varying the excitation frequency was studied to ensure that transport data were obtained only in the non-skin depth limited regime.

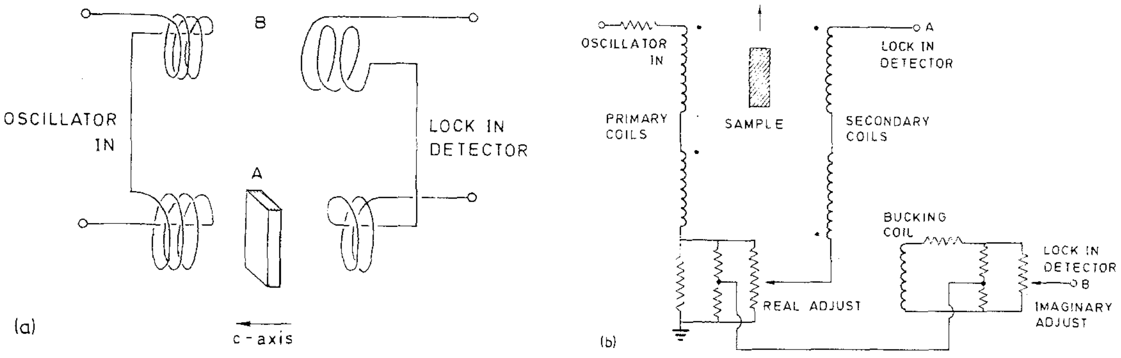

Figure 1 (a) Air-coil r.f. induction for resistivity versus temperature measurements. (b) Schematic of r.f. induction probe electronics.

3. Results and discussion

Three stage 1 intercalated AsF_5–graphite samples measured at room temperature, had resistivities in the range 2.7 to 3.3 $\mu\Omega$ cm. These values are higher than the best value of 2 $\mu\Omega$ cm reported for a stage 1 sample by Foley *et al.* [3]. However, the reproducibility of some properties of compounds of graphite intercalated with Lewis acids is known to be affected by several factors. These factors are: (1) the purity and crystal perfection of the graphite, (2) the kinetics of the intercalation process and (3) the purity of the reagent. Unfortunately, the conduction mechanism for acceptor compounds is not known well enough to determine the precise influence of these factors on the resistivity. The resistivity of a stage 1 AsF_5–graphite sample for temperatures ranging from 1.5 to 293 K is plotted in Fig. 2. The resistivity ratio between 293 and 4.2 K is ≈ 6.8. Three resistivity regions are evident. The regions from 50 to 200 K and 200 to 300 K are clearly linear. The change in slope at 200 K is indicative of an electronic transformation of the intercalant. Weinberger *et al.* [6] have interpreted the motional narrowing of their NMR results beginning at 220 K for stage 1 AsF_5–graphite as the onset of ordering of the AsF_5 intercalant. According to their interpretation, this ordering apparently continued to increase as the temperature was decreased and was not complete at 136 K, the lowest temperature measured. Khanna *et al.* [7] have studied conduction electron spin resonance and have drawn a similar conclusion about gradual ordering between ≈ 200 and ≈ 150 K. However, it is only evident, from our results and the results of others, that there is an electronic transformation of the intercalant.

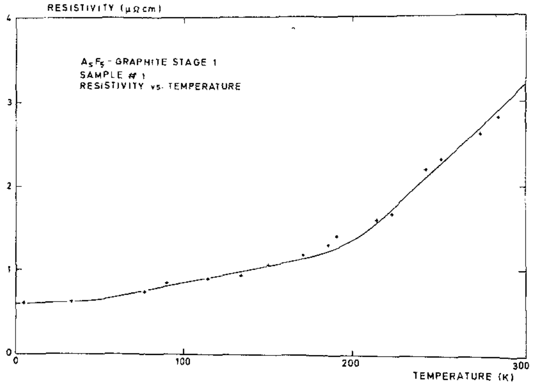

Figure 2 Resistivity versus temperature of a stage 1 AsF_5–graphite intercalation compound.

Magnetoresistance data were obtained for a second stage 1 sample of intercalated AsF_5–graphite. The resistance ratio of this sample between 293 and 4.2 K was ≈ 14. At room temperature it was observed that $\Delta\rho/\rho = \mu_M^2 H^2$, where H is the applied magnetic field and $\Delta\rho/\rho$ is the fractional change in resistivity at applied fields H up to about 20 kG. Fig. 3 shows a plot of $\Delta\rho/\rho$ versus H^2 at room temperature. This plot was used to determine a value of 1990 cm^2 V^{-1} sec^{-1} for the magnetoresistance coefficient μ_M. At low temperatures, it is found empirically that

$$\left(\frac{\Delta\rho}{\rho}\right)_{\text{low field}} = \mu_M^2 H^2 - \alpha^4 H^4$$

where μ_M and α are determined by experiment. For high fields, it is observed empirically that

$$\frac{\rho}{\Delta\rho} = \left(\frac{\rho}{\Delta\rho}\right)_{\text{sat.}} + \frac{1}{\beta^2 H^2} - \frac{1}{\gamma^2 H^4}$$

where $(\rho/\Delta\rho)_{\text{sat.}}$ = the saturation value of $\rho/\Delta\rho$ at very high magnetic fields, and β and γ are constants

TABLE I Magnetoresistance data of a stage 1 AsF_5–graphite intercalation compound

Parameter	Temperature		
	4.2 K	77 K	293 K
μ_M	46 700 $cm^2 V^{-1} sec^{-1}$	14 000 $cm^2 V^{-1} sec^{-1}$	1990 $cm^2 V^{-1} sec^{-1}$
α	$3.36 \times 10^{-6} G^{-1}$	$1.19 \times 10^{-4} G^{-1}$	–
β	$1.95 \times 10^{-4} G^{-1}$	$1.89 \times 10^{-5} G^{-1}$	–
γ	$3.66 \times 10^{-4} G^{-1}$	$5.36 \times 10^{-5} G^{-1}$	–
$\left(\frac{\Delta\rho}{\rho}\right)_{sat.}$	0.461	Undefined	–

to be determined experimentally. Plots of $\Delta\rho/\rho$ versus H^2 and $\rho/\Delta\rho$ versus $1/H^2$ at 4.2 K are shown respectively in Figs. 4 and 5. Note that at 4.2 K, the parabolic region is limited to a few hundred gauss. A plot of $\Delta\rho/\rho$ versus H^2 measured at 77 K is shown in Fig. 6. At high fields, an extrapolation of $\rho/\Delta\rho$ versus $1/H^2$ in the limit of $1/H^2$ approaching zero yields a value for $(\Delta\rho/\rho)_{sat.}$ Values for the mobility μ_M, and the higher order terms α, β, γ, and $(\Delta\rho/\rho)_{sat.}$ at 4.2, 77 and 293 K are listed in Table I.

The higher order terms at 293 K could not be determined from these measurements which were limited to a maximum field of 20 kG. At present, there is no model sufficiently detailed to interpret the expansion terms α, β and γ, and the saturation properties.

A resistivity versus temperature plot is shown for a third stage 1 AsF_5 graphite sample in Fig. 7. The behaviour is quite similar to that of the first sample with linear regions extending from 50 to 200 K and 200 to 300 K. Again, a change in slope at 200 K is observed indicating an electronic transformation. For this sample, unlike the first, data was taken while changing temperature quickly (<10 min per data point). As a result, thermal hysteresis of resistivity values is evident in the region from 50 to 200 K, and, to a lesser extent,

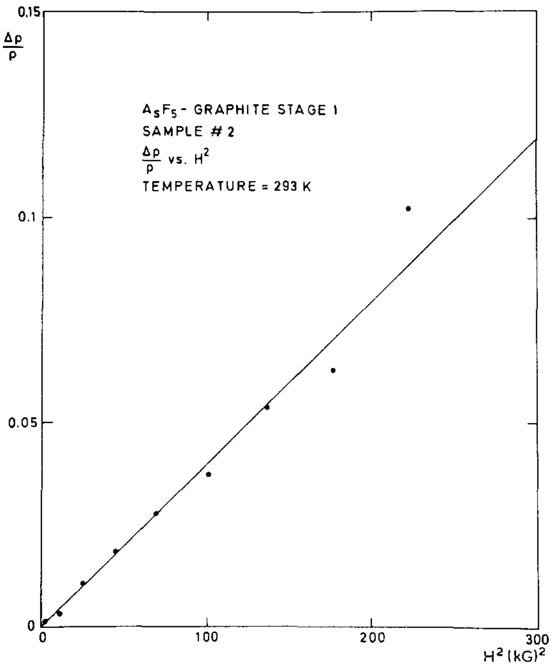

Figure 3 $\Delta\rho/\rho$ versus H^2 for a second sample of stage 1 AsF_5–graphite. Temperature = 293 K.

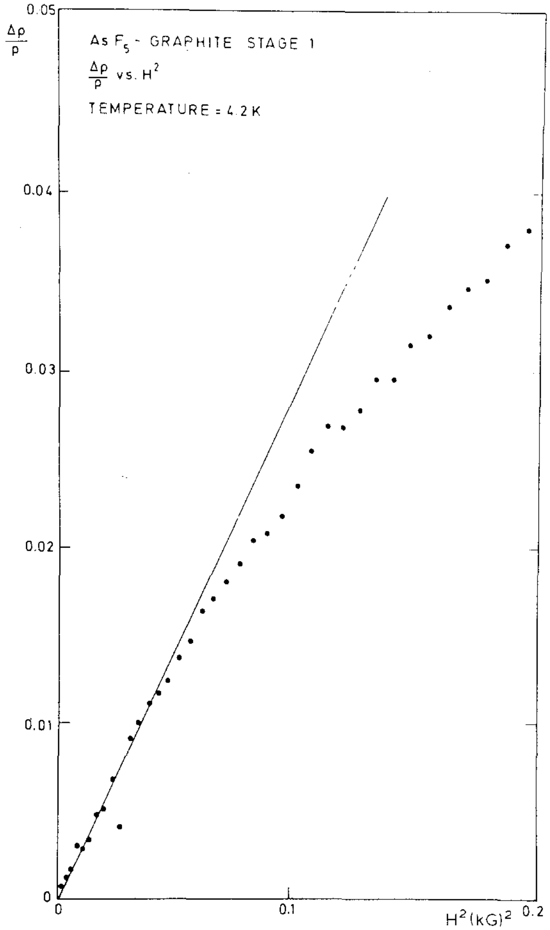

Figure 4 $\Delta\rho/\rho$ versus H^2 for a second sample of stage 1 AsF_5–graphite. Temperature = 4.2 K.

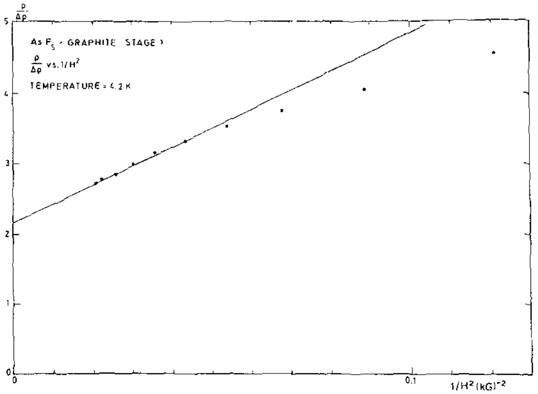

Figure 5 $\rho/\Delta\rho$ versus $1/H^2$ for a second sample of stage 1 AsF_5–graphite. Temperature = 4.2 K.

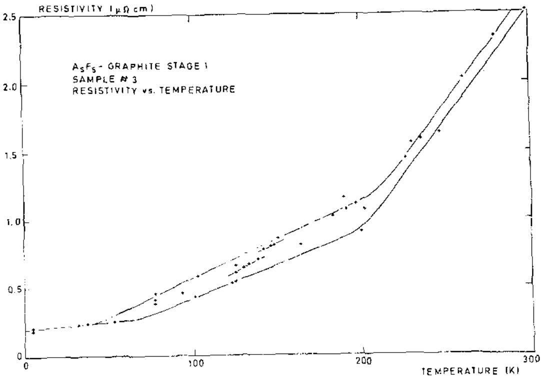

Figure 7 Resistivity versus temperature of a third sample of stage 1 AsF_5–graphite. Lines enclose data scatter due to hysteresis.

above 200 K. This hysteresis was not observed for the first sample in Fig. 2 where the data was taken slowly (several hours between data points).

The magnetoresistivity has also been measured as a function of temperature for a third sample. Calculated values of the magnetoresistance coefficient versus temperature are shown as a function of temperature on Fig. 8. Values of the magnetoresistance coefficient μ_M were calculated assuming $\Delta\rho/\rho = \mu_M^2 H^2$ and using values of $\Delta\rho/\rho$ obtained at 5 kG. The curve is linear from 4.2 to 50 K. A single carrier hole model appears to be adequate to explain optical data on acceptor compounds [8]. The assumption that carriers are predominately holes are based on the chemistry of the intercalant, AsF_5, a strong electron acceptor [1], which upon intercalation in semimetallic graphite increases p-type conductivity. The simplest model consistent with magnetoresistance results requires two kinds of holes with differing mobilities.

If a single average mobility is assumed, it is possible to determine an approximate value of the carrier density using $n = 1/e\mu\rho$ where n = carrier density, μ = drift mobility and ρ = resistivity.

In order to determine the carrier density it is necessary to know μ, the drift mobility. The actual quantity measured, the magnetoresistance coefficient μ_M, is related to the drift mobility as follows:

$$\mu_M^2 = \frac{\langle\mu\rangle\langle\mu^3\rangle - \langle\mu^2\rangle^2}{\langle\mu\rangle^2},$$

where $\langle\mu\rangle$ = drift mobility.

To evaluate $\mu_M/\langle\mu\rangle$, the moments of $\langle\mu\rangle$ or the relaxation time τ (since $\tau(E) \propto \mu(E)$) must be calculated over all energies. The calculation of

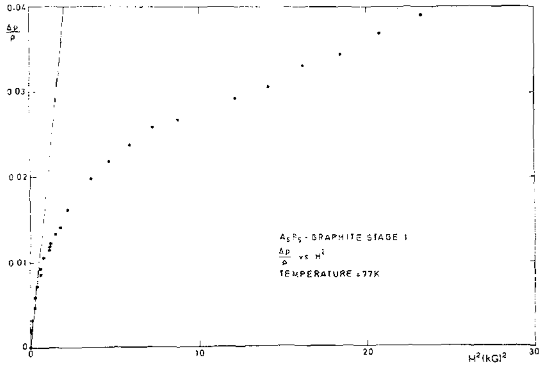

Figure 6 $\Delta\rho/\rho$ versus H^2 for a second sample of stage 1 AsF_5–graphite. Temperature = 77 K.

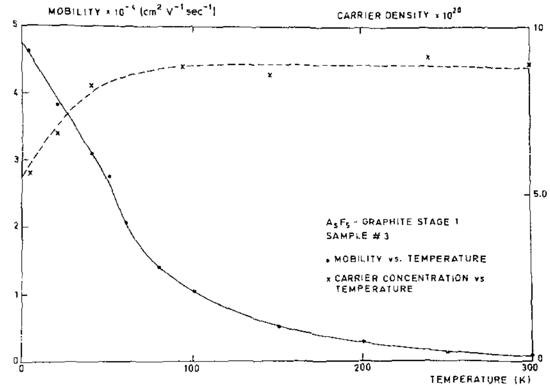

Figure 8 Estimated mobility and carrier concentration versus temperature for the third sample of stage 1 AsF_5–graphite; • mobility versus temperature; x carrier concentration versus temperature.

$\langle \tau^n \rangle$ for the isotropic case is straightforward. In three dimensions,

$$\langle \tau^n \rangle = \frac{\int_0^\infty \tau^n\, v^4 \exp(-m^* v^2/2kT)\mathrm{d}v}{\int_0^\infty v^4 \exp(-m^* v^2/2kT)\mathrm{d}v}$$

using the assumption that $E \propto \frac{1}{2}\, m^* v^2$ and the classical Boltzman distribution. Moments of τ evaluated from this equation and from a similar equation for two dimensions are used to determine $\mu_\mathrm{M}/\langle\mu\rangle$ from the following expression:

$$\frac{\mu_\mathrm{M}}{\langle\mu\rangle} = \frac{\sqrt{(\langle\tau\rangle\langle\tau^3\rangle - \langle\tau^2\rangle^2)}}{\langle\tau\rangle^2}$$

where $\langle\mu\rangle$ = drift mobility defined from $\sigma = e\, n\, \langle\mu\rangle$. The calculated ratios are $\mu_\mathrm{M}/\langle\mu\rangle$ (2D) = 0.961, $\mu_\mathrm{M}/\langle\mu\rangle$ (3D) = 0.616 for two and three dimensions, respectively. Although it is not known how to account for anisotropy, it is necessary that $\mu_\mathrm{M}/\langle\mu\rangle < 1$ if the conductivity is due predominately to one kind of carrier (e.g., in this case, a hole-like carrier). Therefore, it may be assumed (without total justification) that the calculated ratios provide reasonable physical bounds for the realistic intermediate case and that $\mu_\mathrm{M}/\langle\mu\rangle \lesssim 1$.

If the drift mobility is assumed to equal the magnetoresistance coefficient μ_M, the carrier density determined in this manner is then given as a function of temperature in Fig. 8. Above 50 K, the carrier concentration assumes a constant value of $\approx 9 \times 10^{20}\,\mathrm{cm}^{-3}$.

The density of stage 1 $\mathrm{AsF_5}$ intercalant is $5.9 \times 10^{21}\,\mathrm{cm}^{-3}$. Therefore, the fractional ionization, f, defined as the carrier concentration over the concentration of intercalant molecules equals 0.15. This is somewhat more than the value of 0.05 determined by optical means [8]. The value from optical measurements was calculated from the experimental value for the plasma frequency and a value of effective mass, $m^* = 0.039\, m_\mathrm{e}$, that is, the effective mass for pure graphite [9]. This value is probably lower in low stage intercalated compounds by a factor of 3 to 5 in the basal plane, so the value of f determined from optics may be somewhat low. Since $\mu_\mathrm{M} \leqslant \mu$, μ may be underestimated to a certain extent, and so the carrier concentration, n, may be overestimated. A correction for this overestimate of n obtained from magnetoresistance measurements would also bring the value of carrier concentration due to the two approaches into close agreement. More recent measurements by Weinberger *et al.* [10] of magnetic spin susceptibility yield a value of $f = 0.24$ for stage 1 material, in reasonable agreement with the value presented here.

The room temperature resistivity of three stage 2 intercalated $\mathrm{AsF_5}$–graphite samples was determined to be in the range 1.8 to 2.4 $\mu\Omega$ cm. A plot of resistivity versus temperature for one sample is shown in Fig. 9. The resistivity ratio for this sample between 293 and 4.2 K is ≈ 4.5. Fig. 9 shows several resistivity regions listed in Table II. The changes in slope at 165 and 225 K are due to electronic transformations of the intercalant. Fig. 10 displays a plot of resistivity versus temperature in regions I and II of Fig. 9 on an expanded scale. Khanna *et al.* [7] have attributed conduction electron spin resonance results to an onset of ordering at ≈ 200 to 220 K.

A linear dependence of T is expected for electrical resistivity of metals due to acoustical-phonon scattering at high temperatures. The Bloch formula for the resistivity of metals having a spherical Fermi surface and an isotropic phonon spectrum yields a T^5 dependence at low temperatures which changes gradually to a T dependence at high temperatures [11]. Kukkonen [12] has extended the theory to a semi-metal with a small cylindrical Fermi surface. This theory predicts, in addition to the low temperature T^5 region and the high temperature T region, a well-defined T^2 region. A T^2 region is clearly observed on the resistivity versus temperature plot of intercalated $\mathrm{AsF_5}$–graphite presented here. It is tempting to interpret the resistivity below 21 K as a T^5 region, but the transition from T^5 to T^2 behaviour should be very smooth. The observed transition at 21 K is believed

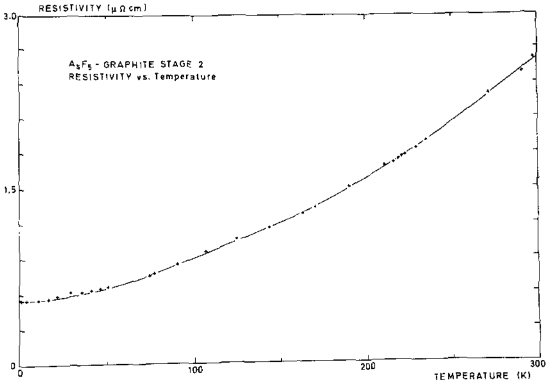

Figure 9 Resistivity versus temperature of a stage 2 $\mathrm{AsF_5}$–graphite intercalation compound.

TABLE II Resistivity regions of stage 2 AsF_5–graphite

Region	Temperature range	Behaviour
I	0–21 K	–
II	21–60 K	T^2
III	60–165 K	T
IV	165–220 K	T
V	220–300 K	T

to be instead a newly observed phase transition that is not now understood. Nevertheless, the T^2 region above 21 K is well defined. The Fermi surface is realistically likely to be a very elongated ellipsoid, which is closely approximated by the cylinder used in the theory. Such a Fermi surface is consistent with the extreme anisotropy of conductivity of $\sigma_a/\sigma_c \approx 10^6$ confirmed earlier [3].

The qualitative agreement of the resistivity data of the stage 2 compound with the Kukkonen theory supports the model of a highly anisotropic Fermi surface, which for theoretical purposes is approximated by a long cylinder. This is consistent with the established anisotropy data. For a given number of carriers, a high anisotropy results in a low k_F in the basal plane, thus giving a partial explanation to the high mobility in the a-plane relative to mobility in the c-axis direction. However, the scattering time varies inversely as the scattering matrix element and depends on the phonon dispersion relation [13]. These are also likely to be anisotropic, but it is not possible from the data presently available to distinguish the degree of contribution from each of these sources to the anisotropy of the conductivity. Nor is it possible to determine mobility using the Kukkonen theory and assuming an elongated cylinder of finite length.

An upper limit of $\approx 9 \times 10^{20} cm^{-3}$ can be established for the carrier density. The actual value is probably not less than half this upper limit. For a cylinder of finite length, it would be useful to relate exactly the magnetoresistance coefficient μ_M, to the drift mobility, μ. All of the data leads to the plausibility of a predominately hole carrier with a necessary spread in the mobility as a function of energy. It is not known how or to what extent the anisotropy determines the spread in mobility necessary to account for magnetoresistance data.

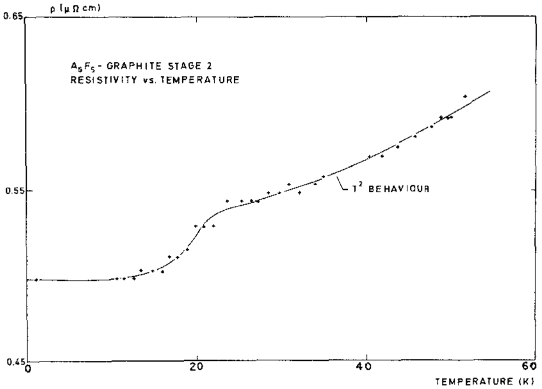

Figure 10 Detailed resistivity versus temperature of stage 2 AsF_5–graphite at very low temperatures.

Another question which remains unanswered concerns the nature of the material. Is low stage AsF_5–graphite a metal? Or is it a very heavily doped semi-metal? The carrier concentrations of known semi-metals fall in a range from about 10^{17} to $10^{21} cm^{-3}$. Metals have carrier densities within a rather limited range from about 10^{22} to $10^{23} cm^{-3}$. Also, semi-metals have an equal number of electrons and fairly well-defined holes, due to the small band overlap responsible for conduction. The estimated value of 10^{21} cm^{-3} hole carriers for AsF_5–graphite is intermediate. The picture obtained from these data, optical results [6] and our knowledge of the chemistry of the intercalated electron acceptor compounds, as discussed above, is one of conduction due predominately to hole carriers. If the material is a metal, then it is necessary to understand "metallic" behaviour due to a rather large number of holes. For the present, it is considered best to think of these materials as heavily doped semi-metals (HOPG, the starting material, is a semi-metal), but it is not known if the holes are degenerate. It may be necessary to treat these highly anisotropic conductors as an entirely new class of materials.

4. Conclusions

Resistivity measurements using a contactless r.f. eddy current technique of carefully characterized stage 1 and stage 2 AsF_5–graphite intercalated compounds show electronic transformations at $\approx$ 200 K for stage 1 and at $\approx$ 220 K for stage 2 in the higher temperature $\rho \propto T$ region. These temperatures are believed to mark the onset of an electronic transformation in the intercalant where considerable thermal hysteresis is evident. The existence of a $\rho \propto T^2$ region in the resistivity curve of a stage 2 sample in qualitative agreement with the Kukkonen theory provides evidence of an elongated ellipsoidal Fermi surface. The degree of contribution of this and other factors such as phonon scattering to the high anisotropy of the conductivity has yet to be determined. A low temperature phase transition was observed at 21 K for a stage 2 compound. This is believed to be the first transition of this kind reported for a graphite-acceptor intercalation compound and is not currently explained.

Magnetoresistance measurements of a stage 1 sample show that the hole carrier concentration, $n = 9 \times 10^{20} \text{cm}^{-3}$, is mostly independent of temperature and represents a fractional ionization of 0.15 in agreement with other experiments. These results support, therefore, the contention that the intercalant contribution to the carrier concentration is fairly low and that the unusually high mobility must be explained to account for the high conductivity observed for these acceptor compounds.

Acknowledgements

We are grateful to Dr A. W. Moore of Union Carbide for provision of HOPG. Support for this program was given by National Science Foundation under a Materials Division grant (No. DMR 75-04954) and through the Laboratory for Research on the Structure of Matter (MRL grant No. DMR 76-80994).

References

1. F. L. VOGEL, *J. Mater. Sci.* **12** (1977) 982.
2. C. ZELLER, G. M. T. FOLEY, E. R. FALARDEAU and F. L. VOGEL, *Mater. Sci. Eng.* **31** (1977) 255.
3. G. M. T. FOLEY, C. ZELLER, E. R. FALARDEAU and F. L. VOGEL, *Solid State Comm.* **24** (1977) 371.
4. E. R. FALARDEAU, G. M. T. FOLEY, C. ZELLER and F. L. VOGEL, *J. C. S. Chem. Comm.* (1977) 389.
5. C. ZELLER, A. DENENSTEIN and G. M. T. FOLEY, *Rev. Sci. Instr.* **50** (1979) 602.
6. B. R. WEINBERGER, J. KAUFER, A. J. HEEGER, E. R. FALARDEAU and J. E. FISCHER, *Solid State Comm.* **27** (1978) 163.
7. S. K. KHANNA, E. R. FALARDEAU, A. J. HEEGER and J. E. FISCHER, *ibid.* **25** (1978) 1059.
8. L. R. HANLON, E. R. FALARDEAU and J. E. FISCHER, *ibid.* **24** (1977) 377.
9. I. L. SPAIN, *Chem. and Phys. of Carbon* 8 (1973) 1.
10. B. R. WEINBERGER, J. KAUFER, A. J. HEEGER, J. E. FISCHER, M. MORAN and N. A. W. HOLZWARTH, *Phys. Rev. Lett.* **41** (1978) 1417.
11. J. M. ZIMAN in "Electrons and Phonons" (Oxford University Press, Oxford, 1960) Ch. 9.
12. C. A. KUKKONEN, *Phys. Rev.* **B18** (1978) 1849.
13. P. R. AIGRAIN in "Electronic Processes in Solids" (Technology Press of M. I. T. and John Wiley & Sons, Inc., New York and London, 1960) Ch. 12.

Received 12 and accepted 26 January 1979.