Synthetic Metals, *12* (1985) 91–96

THERMAL TRANSPORT PROPERTIES OF $SbCl_5$-GRAPHITE AND OF HOPG IN THE c-DIRECTION

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ABSTRACT

We report measurements of the c-axis thermal conductivity and thermoelectric power of $SbCl_5$-GIC's. Thermal conduction is dominated by the lattice, with defects being the dominant scatterers. The thermopower is in good agreement with theoretical predictions for GICs. Finally, results for the very low temperature thermal conductivity of pure graphite in the c-direction are presented and discussed.

INTRODUCTION

The unique structural configuration of graphite intercalation compounds (GICs) affects all of their physical properties, the transport phenomena in particular. The already high anisotropy of the graphite matrix is further enhanced by intercalation, and this leads, in many cases, to a creation of essentially quasi-2d compounds. Motivated by this unusually high structural anisotropy, several investigations have been carried out over the past few years on a variety of compounds of different stage index and over a wide range of temperatures in order to ascertain the nature of the charge carrier scattering under the conditions of this extreme anisotropy.

Recently, an emphasis has been placed also on the thermal transport behavior of these interesting layered materials. In particular, the temperature and stage dependence of the in-plane thermal conductivity and thermopower were two topics researched in some detail by both experimentalists [1-3] and theorists [4]. The results indicate that both the electronic and phonon contributions to the thermal conductivity of graphite are drastically altered by intercalation. While the carrier thermal conductivity is enhanced by as much as an order of magnitude due to the higher free carrier density, the lattice conductivity is significantly degraded by higher rates of

0379-6779/85/$3.30

phonon scattering on the structural defects originating in the intercalation process. However, in the liquid helium temperature range, the lattice thermal conductivity of low stage compounds is comparable to, and in some cases even exceeds, the phonon contribution in pure graphite; this suggests that the low-frequency lattice modes of the intercalant play a significant role in this temperature regime.

As in the case of the electrical resistivity, structural anisotropy of GICs is expected to lead to anisotropy in the thermal transport properties. Currently, there is very little information available on the c-axis thermal transport behavior of GICs; only one report dealing with the thermal conductivity of a stage 2 acceptor-type $FeCl_3$-graphite and a stage 5 donor-type K-graphite has been published so far [5].

In this paper we present the results of our measurements on the thermal conductivity and thermopower of a series of stages of the acceptor-type compound $SbCl_5$-graphite [6]. We have chosen this system not only for its unusually high air-stability but, primarily, for the wealth of information which has already been collected regarding its structural and transport properties.

EXPERIMENTAL

Thermopower and thermal conductivity were determined by a steady-state technique. Samples in the form of discs of typically 8mm diameter and 0.5-0.75mm thickness were prepared by the standard two-zone method in vapor from Union Carbide HOPG and high-purity $SbCl_5$. All samples investigated are pure stages as confirmed by (00ℓ) X-ray scans made on several different regions of each sample.

Samples were sandwiched between an oxygen-free-high-conductivity (OFHC) copper plate serving as a heat sink and a copper disk. Both were provided with holders for small carbon-glass thermometers and heaters and through both a small hole was drilled in the center to allow the attachment of thermopower probes directly on the sample. A thin film of Apiezon M grease was applied to provide not only excellent thermal contact between the sample and the OFHC surfaces, but also to prevent the corrosive attack of $SbCl_5$ on copper. We have chosen resistance thermometry over thermocouples because of its higher sensitivity, particularly at low temperatures. Since the c-axis thermal resistance of graphite and GICs is high, the thermal resistance of the copper-sample interface is, in this case, insignificant. We have confirmed this assertion in independent tests. To minimize heat loss, all electrical connections to thermometers and heaters were made with 0.07mm diameter Evanohm wire.

Thermopower was measured using 0.1 mm diameter Pb wires which were attached (through the holes in the OFHC copper plate and disk) directly to the sample with a silver paint. Voltages were detected with a Keithley nanovoltmeter. Since the thermal conductance of Pb wires at low temperatures is as much as 5% of the sample conductance, to avoid error in the thermal conductivity data we have made thermopower measurements separately.

RESULTS AND DISCUSSION

Figure 1 shows the c-axis thermal conductivity of five different GICs as well as pure HOPG between 2-300K. It is seen that near room temperature the thermal conductivity of the intercalated graphites, while not showing any obvious stage dependence, is at least an order of magnitude smaller than HOPG. On the basis of our previous c-axis resistivity studies [7] in conjunction with the Wiedemann-Franz law, we estimate that conduction via carriers along the c-axis is less than 0.1% of the total thermal conductivity for all stages throughout the temperature range. Therefore, we attribute the degradation of

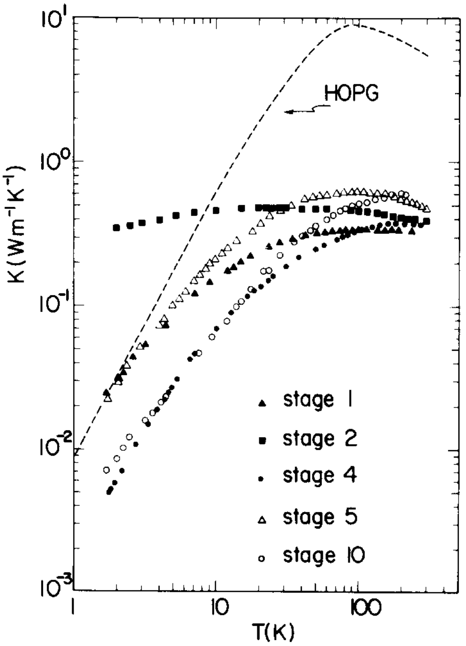

Fig. 1. Temperature dependence of the c-axis thermal conductivity of $SbCl_5$-graphite. Dashed curve indicates the data for a sample of HOPG.

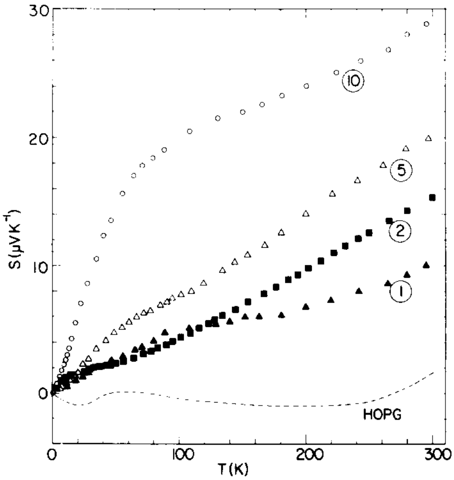

Fig. 2. Temperature dependence of the c-axis thermopower of $SbCl_5$-graphite. Stage index is indicated by encircled numbers. Dashed curve represents a sample of HOPG.

the thermal conductivity of the GICs with respect to pure graphite to a strong scattering of phonons by defects originating in the intercalation process, combined with a softening of the out-of-plane phonon modes in the intercalation compounds. At lower temperatures, the dominant phonon wavelength increases and the effect of both point and extended defect scattering is correspondingly weaker. As a consequence the thermal conductivity of the GICs approaches that of HOPG. A special case, however, is the stage 2 sample which displays a nearly temperature independent thermal conductivity; below about 8K the thermal conductivity of this compound exceeds that of pure graphite. This sample was produced by directly immersing HOPG in $SbCl_5$ liquid (as opposed to two-stage vapor growth); we therefore tentatively ascribe the enhanced thermal conductivity to the presence of poorly correlated islands of $SbCl_3$ [8]. It has been shown [9] that below the commensurate-incommensurate phase transition (near 230K) the specific heat of stage 2 compounds grown by direct immersion is nearly constant, a feature which is reflected in the thermal conductivity.

The results of our thermopower measurements are shown in Fig. 2. S(T) is positive for all stages, approximately linear in temperature above 77K, and shows a systematic increase with the stage index from about 10 $\mu V\ K^{-1}$ for stage 1 to 28 μVK^{-1} for a stage 10 sample at room temperature. This behavior is quantitatively consistent with the theory of Sugihara [10] which predicts that the c-axis thermopower will be nearly metallic, taking the form

$$S_c(T) \approx \frac{\pi^2 k_B{}^2 T}{3e\ E_F} \frac{2\sum_s (E_F - \Delta_s)^2}{\sum_s (1 - \Delta_s/E_F)(E_F - \Delta_s)^2} \qquad (1)$$

where Δ_s is the energy of band s at k=0. This model predicts $S_c(300K)=18\ \mu VK^{-1}$ for a stage 2 $SbCl_5$ compound, which is in quite good agreement with the observed value. Alternatively, fitting the formula (1) to our thermopower data for stages 1 and 2 yields Fermi energies of 1.96 eV and 0.8 eV respectively. While the inverse dependence of $S_c(T)$ on the Fermi energy is qualitatively verified for all stages investigated, it is difficult to estimate numerically the Fermi energy for stages higher than 2 due to the multivalley nature of these compounds and the uncertainties in the k=0 band energies.

Figure 3 exhibits the result of our measurements of $K_c(T)$ on pure HOPG at very low temperatures. We see that $K_c \sim T$ with n increasing from 2 to 3 as temperature is lowered below 2K. This is to be contrasted with our recent results for the in-plane conduction in HOPG [11], in which the power dependence of the lattice thermal conductivity decreased at lower temperatures. Those results were explained by a model in which both in-plane and out-of-plane phonons contribute to the in-plane thermal conductivity. It has been shown that the specific heat of the out-of-plane modes crosses over from T^2 to T^3 below 4K whereas for the in-plane modes the specific heat is proportional to T below 4K [12]. Therefore in view of the temperature dependence of $K_c(T)$ it appears that the c-axis thermal conduction is dominated by the out-of-plane phonons, with in-plane phonons playing little, if any, role. From the magnitude of the T^3 term we estimate that the mean free path of these phonons is about 1μ below 1K. This indicates that these phonons are scattered mainly by stacking faults, the average spacing of which is on the order of this mean free path.

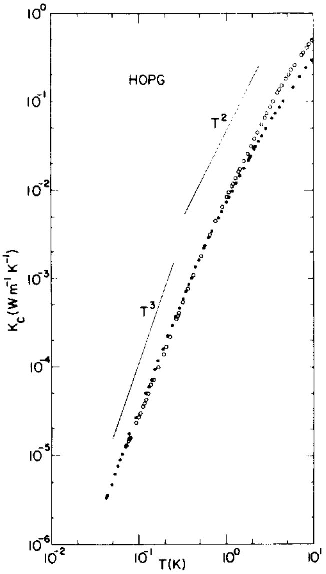

Fig. 3. C-axis thermal conductivity of two samples of HOPG at very low temperatures.

CONCLUSION

We have measured the c-axis thermal conductivity of HOPG down to 70mK, and the c-axis thermopower and thermal conductivity of stages 1,2,4,5 and 10 of $SbCl_5$-graphite down to 2K. The results for the intercalates indicate that the thermal conduction, which is nearly all of lattice origin, is significantly degraded by scattering of phonons on defects. A special case is a stage 2 sample, the thermal conductivity of which exceeds that of pure graphite below 8K. This behavior, which mirrors that of the specific heat, is believed to arise from poorly correlated intercalant islands. The thermopower of all samples is positive, linear above 77K, and inversely proportional to the stage index, all of which is in agreement with the theoretical predictions of Sugihara. Finally, the very low temperature thermal conductivity of pure graphite is proportional to T^n with n increasing from 2 to 3 as $T \to 0$. This is consistent with the temperature dependence of the specific heat of out-of-plane phonons in this material. The magnitude of the T^3 term below 1K indicates that stacking faults are predominantly responsible for the lattice thermal resistance.

ACKNOWLEDGMENTS

We would like to acknowledge useful conversations with Professor J.-P. Issi regarding the thermal transport in GICs. We thank Professor R. Clarke for fruitful discussions of the structural aspects of GICs and for a critical reading of the manuscript. The work was supported by the National Science Foundation, Low Temperature Physics Grant DMR-83-04356.

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