Electron-phonon scattering in $HgBr_2$ and IBr graphite intercalation compounds

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Abstract.   The Hall coefficient and the dc resistivity in the basal plane and along the c axis of stage-2 IBr and stage-3 HgBr$_2$ graphite intercalation compounds (GICs) were measured between 4.2 and 370 K. The resistivity of the IBr GIC indicates a metallic-like behaviour and a structural phase transition at 175 K. The Hall coefficient above 300 K of the HgBr$_2$ GIC indicates deintercalation from an irreversible reduction of the carrier concentration. A study of the temperature dependence of the resistivity and Hall coefficient of the stage-2 IBr GIC above room temperature shows that the electron–out-of-plane phonon scattering plays a major role in this compound. The Hall coefficients are temperature independent below room temperature. The one-carrier model gives a value of 8.1×10^{26} m^{-3} for the IBr and a value of 7.9×10^{26} m^{-3} for the HgBr$_2$ GIC for the carrier concentrations.

1. Introduction

Graphite intercalation compounds (GICs) formed with halogen molecules are considered to be a class within the large family of acceptor-type GICs [1]. Although a number of studies has been made of the electronic properties of donor compounds containing the alkali metals [2], a systematic knowledge of the transport properties of the acceptor GICs, especially with halogen molecules, is limited. Among these investigations the study of the resistivity of the AsF$_5$ GIC [3, 4] and a wide range of studies of different stages of the SbCl$_5$ GIC [5, 6], the electronic properties and structural phase transitions of the low stages of the ICl GICs [7, 8] and the recent study of the Hall effect in the low stages of different chloride GICs [9] are mentioned here. To our knowledge, a rather small amount of work on the electronic properties of the bromide GICs has been reported. The de Haas–van Alphen (dHvA) effect of the stage-2 IBr GIC has been studied to reveal a superlattice formation and zone folding at low temperature [10].

Two GICs are studied for a number of reasons. The IBr GIC should have interesting properties similar to those observed in the ICl [7, 8] GIC. In addition, the effect of deintercalation on the resistivity and Hall effect of a GIC is reported for the first time. The HgBr$_2$ GIC is investigated because no one has studied its properties previously.

The low stages of GICs have a metallic-like behaviour below room temperature with a relatively high anisotropic character. The temperature dependence of the resistivity of most low stages of graphite intercalation compounds below room temperature can be described by

$$\rho = \rho_0 + AT + BT^2. \tag{1}$$

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The parameters *A* and *B* depend on the intercalated compound, the stage number and the direction of the current through the sample and in general are much smaller for acceptor than for donor compounds. The constant term ρ_0 represents the residual resistivity; the linear term is consistent with the electron–phonon scattering mechanism. The quadratic term has been ascribed to carrier–carrier scattering. However the origin of this term has been a matter of conjecture for a long time. Although the carrier–carrier mechanism as well as the scattering of carriers by acoustic phonons in the case of elongated Fermi surfaces treated by Gantmakher and Dolgopolov [11] and Kukkonen [12], known as the (GDK) theory, results in a quadratic term for the resistivity, the first mechanism is too small in the case of acceptor GICs and the second mechanism, which is a suitable theory for describing the temperature dependence of the resistivity of semimetals, is inapplicable for compounds with a relatively large, two-dimensional Fermi surface. According to Sugihara [13], the carriers of the GICs are scattered by two distinct modes of vibration from out-of-plane and in-plane phonon modes. As a result, the resistivity of these compounds can be written in two parts with different temperature dependences and magnitudes. It can be shown that the scattering of the carriers by the out-of-plane mode phonons has a dominant contribution to the resistivity over a significant range of temperature. One of the interesting features of this component of the resistivity is that it is almost independent of carrier concentration.

The main purpose of the present work is to study the temperature dependence of the resistivity of the stage-2 IBr and stage-3 $HgBr_2$ GICs to understand more about the major scattering processes which are dominant in these compounds and also to observe the manifestations in the resistivity of the structural phase transitions in these compounds. In order to obtain the carrier concentration and to see the effect of this parameter on the resistivity, the temperature dependence of the Hall coefficients was also studied over a wide range of temperature.

2. Experimental method

Highly oriented pyrolytic graphite (HOPG) was used in the preparation of the intercalation compounds. The HOPG was cleaved into pieces with a thickness of approximately 0.3 mm and a surface area of 2 mm $\times$ 3 mm. These pieces were washed in acetone, ultrasonically cleaned and dried under vacuum at an elevated temperature. The high reactivity of IBr used for intercalation required handling in an atmosphere that was free of water vapour and oxygen. Therefore, most of the handling was done in a dry box filled with argon. The stage-2 IBr GIC was produced by placing HOPG and IBr in a sealed reaction tube and heating it to a temperature of 50–55 °C with the graphite and intercalant at the same temperature. At this temperature IBr is a dark-red liquid. The reaction lasted 15 days. The composition $C_{20.8}IBr$ was determined by the change in weight during intercalation. The stage-2 IBr GIC was characterized by (00*l*) x-ray diffraction as shown previously with a spectrum revealing a pure staged sample with no diffraction peaks from mixed stages [10] with a period scale I_c of 10.5 Å. The stage-3 $HgBr_2$ GIC samples were prepared by reacting $HgBr_2$ with HOPG in a Br atmosphere at a pressure of 2 atm at a temperature of 200 °C for 9 weeks. They were determined to be in stage 3 with a *c*-axis repeat distance $I_c = 16.8$ Å from (00*l*) x-ray diffraction as shown in figure 1. There were no traces of other stages. A stage-3 $HgBr_2$ GIC had been reported earlier [14] with a repeat distance I_c of 16.84 Å. No experimental conditions were given.

Electrical contacts to the sample were made with silver paste. The (00*l*) plane resistivity was measured with the standard four probe method. The potential probes were on opposite edges and current was along the length of the sample. For the measurement of the resistivity along the *c* axis, the current contacts in the shape of a ring were on opposite cleaved surfaces of
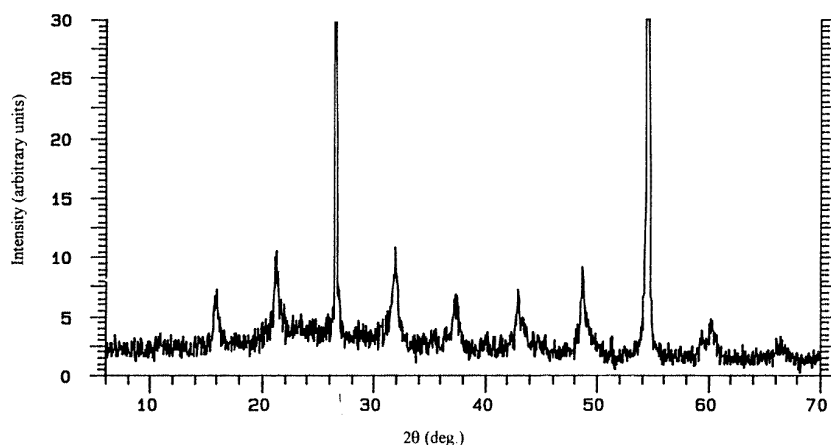
Figure 1. The x-ray (00*l*) diffraction of the stage-3 HgBr$_2$ GIC.

the sample. The Hall voltage was determined from transverse voltage probes with the magnetic field perpendicular to the current direction and parallel to the *c* axis. The sample was rotated 180° and the odd component with respect to the field direction was determined in order to cancel the voltage caused by a small misalignment of the probes. The rotation was done with a computer programed stepping motor mounted on the top of the sample holder.

3. Results

The resistivities ρ_a and ρ_c of the stage-2 IBr and the stage-3 HgBr$_2$ GICs were measured with the current perpendicular and parallel to the *c* axis, respectively. The temperature dependence of ρ_c in the range of 4.2–300 K for both compounds is presented in figure 2. For the stage-3 HgBr$_2$, ρ_c has a value of 0.33 Ω cm at 4.2 K and increases with increasing temperature. The slope of the resistivity changes at 175 K. This was observed during cooling and warming. At this temperature ρ_c has a value of 1.1 Ω cm and increases to 1.7 Ω cm at room temperature. The resistivity, ρ_c, of the stage-2 IBr GIC has a value of 0.70 Ω cm at 4.2 K and 2.4 Ω cm at 300 K.

The resistivity of both compounds was also measured with the current perpendicular to the *c* axis in the range of 4.2–300 K as shown in figure 3. At 4.2 K. ρ_a has a value of 0.52×10^{-4} Ω cm for the stage-2 IBr GIC and a value of 1.8×10^{-4} Ω cm for the stage-3 HgBr$_2$ GIC. The resistivity of both compounds increases with increasing temperature so that at room temperature ρ_a is 2.0×10^{-4} Ω cm for the IBr and 2.3×10^{-4} Ω cm for the HgBr$_2$ compound. It is interesting to note that the percentage change of ρ_c and ρ_a for the stage-2 IBr and stage-3 HgBr$_2$ GICs between 4.2 and 300 K is almost the same and equal to 30% but the ratio of ρ_c/ρ_a for the IBr GIC is approximately two times larger.

The resistivity of the low stages of most graphite intercalation compounds can be fitted to equation (1) below room temperature. The best-fit parameters for ρ_a and ρ_c for both compounds are presented in table 1. The fitting was performed in the range of 4.2–300 K. except for ρ_c of the HgBr$_2$ GIC which was done between 4.2 nd 175 K.

In order to observe the structural phase transition in the stage-2 IBr GIC, its resistivity was measured above room temperature. The experimental results are presented in figure 4.
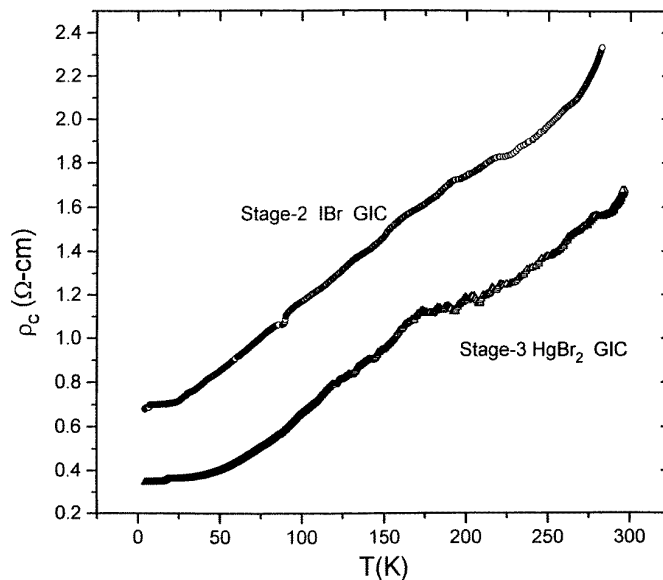
Figure 2. Resistivity of the stage-2 IBr and the stage-3 HgBr$_2$ GICs against temperature with the current parallel to the c axis.

Table 1. The best-fit parameters ρ_0, A and B for ρ_a and ρ_c for the stage-2 IBr and stage-3 HgBr$_2$ GICs. The fitting was performed between 4.2 and 300 K except for ρ_c of the stage-3 HgBr$_2$ GIC which was done between 4.2 and 175 K.

	ρ_c			ρ_a		
GIC	ρ_0 (Ω cm)	A (Ω cm K^{-1})	B (Ω cm K^{-2})	ρ_0 (Ω cm $\times 10^{-4}$)	A (Ω cm $\times 10^{-4}$)	B (Ω cm $\times 10^{-4}$)
stage-3 HgBr$_2$	0.321	8.4×10^{-4}	2.3×10^{-5}	1.76	3.0×10^{-4}	6.0×10^{-6}
stage-2 IBr	0.6	5×10^{-3}	4.4×10^{-6}	0.51	1.84×10^{-3}	6.5×10^{-6}

The experiment with a newly prepared sample was begun by warming it from room temperature by means of an electric heater mounted on the sample holder. The sample was heated to 370 K and then cooled to helium temperature. ρ_c increases with increasing temperature with a high rate, such that it reaches a value four times larger than its room temperature value at 370 K. When the sample was cooled to room temperature, the resistivity follows the same path except around 350 K where there is hysteresis. As the sample was cooled to 4.2 K, the resistivity increases to a value that is 1.6 times larger than its room temperature value. This experiment was also performed on ρ_a of the stage-2 IBr GIC and a similar behaviour was observed.

The temperature dependence of the Hall coefficient, R_H, in a magnetic field of 1 T along the c axis and with a current of 20 mA perpendicular to the c axis was studied in both compounds. The experimental results are presented in figure 5. The Hall coefficient is independent of temperature in the range of 4.2–300 K for both compounds. R_H has a value of $(7.2 \pm 0.3) \times 10^{-9}$ m^3 C^{-1} for the stage-3 HgBr$_2$ GIC and a value of $(7.6 \pm 0.1) \times 10^{-9}$ m^3 C^{-1} for the stage-2 IBr GIC. The experiments were also performed with different currents and magnetic fields. No significant change was observed in the Hall coefficients.
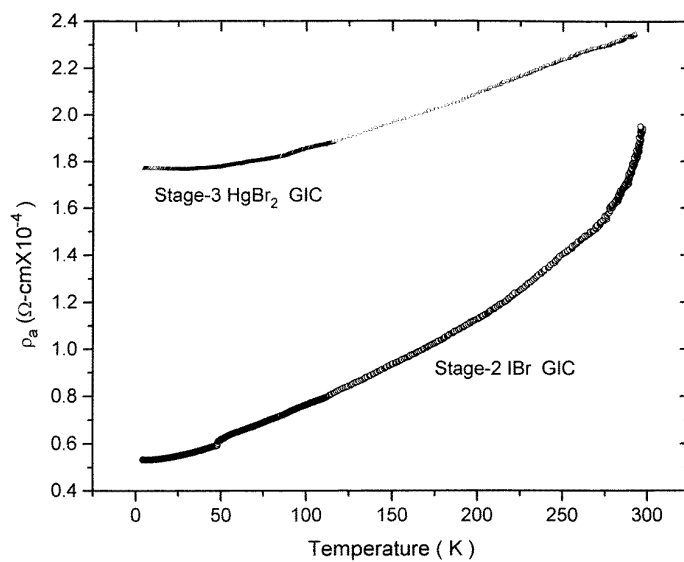
Figure 3. Temperature dependence of the in-plane resistivity of the stage-2 IBr and the stage-3 HgBr$_2$ GICs.
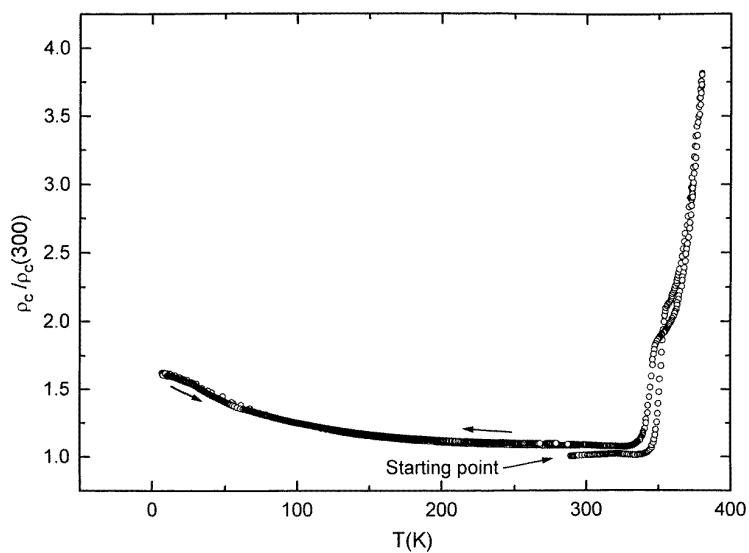

Figure 4. Temperature dependence of the ratio $\rho_c/\rho_c(300)$ of the stage-2 IBr GIC between 4.2 and 370 K. $\rho_c(300)$ is the resistivity at 300 K. The warming of the sample started at room temperature.

The Hall coefficient of the stage-2 IBr GIC was also measured above room temperature up to 370 K. The experimental results are shown in figure 6. R_H increases with increasing temperature and has a value of 8.8×10^{-9} m^3 C^{-1} at 370 K. When the sample is cooled to room
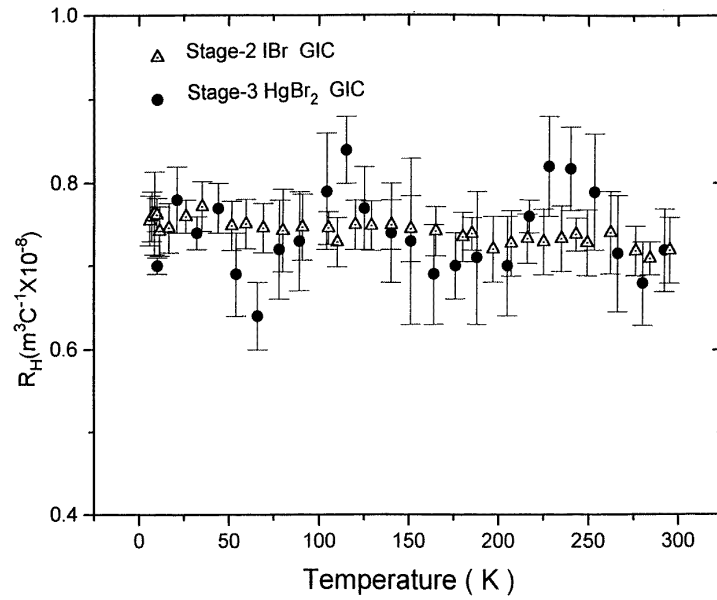
Figure 5. Temperature dependence of the Hall coefficients of the stage-2 IBr and the stage-3 $HgBr_2$ GICs. The error bars are the standard deviations of the points in each 10 K interval.
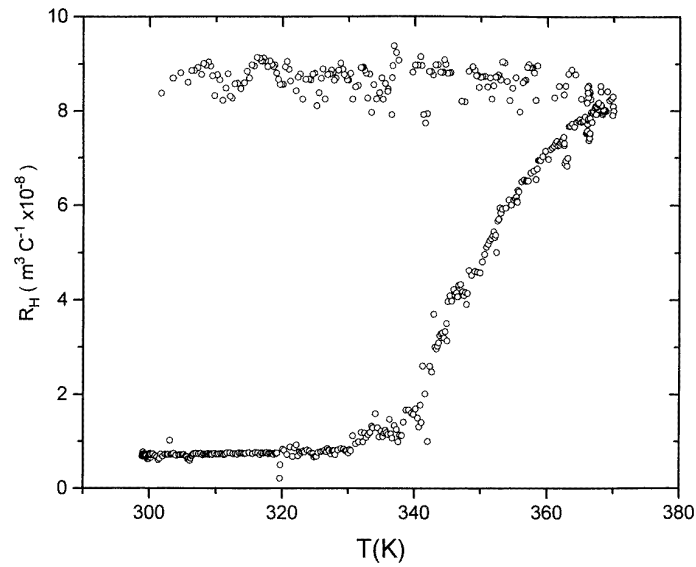

Figure 6. Temperature dependence of the Hall coefficient of the stage-2 IBr GIC between 300 and 370 K. The warming of the sample started at 300 K.

temperature, R_H does not follow the same path and remains at its 370 K value. Experiments were also done with other samples which had not been heated above 300 K previously.

The temperature was also increased from 300 K and stopped at different temperatures between 340 K and 360 K. In each case R_H followed the dependence in figure 6 up to the chosen upper temperature limit. It stayed at the value of this temperature when the temperature was reduced to and below 300 K. Thus any change in R_H is permanently established and is irreversible.

4. Discussion

According to Sugihara [13] the electron–phonon scattering is a major contribution to the temperature dependence of the resistivity of the lower stage GICs. The interaction can be written in two parts as the scattering of electrons by the in-plane and the out-of-plane phonons has different characteristics. The two components are ρ_{in} and ρ_{out}.

Interesting features of Sugihara's results for ρ_{in} and ρ_{out} are that (a) the ratio ρ_{in}/ρ_{out} is quite small at low temperatures and still is less than $1/20$ at room temperature. Therefore the carrier scattering by the out-of-plane phonon modes predominates the scattering by the in-plane phonons. (b) ρ_{out} is almost independent of the carrier concentration. These results are used in the analysis although a calculated fit between theoretical and experimental results was not attempted.

The increase in R_H shown in figure 6 must result in a decrease in the carrier concentration. The decrease is permanent since R_H does not change with decreasing temperature. This indicates that there is deintercalation of the sample which permanently reduces the carrier concentration. It is plausible that this can occur because it starts at a temperature close to the temperature used to prepare the GIC. Also after deintercalation the semiconducting nature of the resistivity below 300 K in figure 4 indicates a low carrier concentration. However, in spite of a relatively large change in the carrier concentration (80%), the dependences of the resistivity for increasing and decreasing temperature changes agree from 370 K to room temperature. This is expected for ρ_{out} which is independent of the carrier concentration. Thus, ρ_{out} is the dominant resistivity. As the sample was cooled to helium temperature after it had been heated to 370 K. the resistivity increased with a semiconducting behaviour. A similar temperature dependence has been reported for the higher stages of some other graphite intercalation compounds [17]. It is likely that deintercalation of the sample resulted in the production of higher stages with properties of a semiconductor.

The x-ray diffraction and absorption spectroscopy studies [18, 19] of the stage-2 IBr GIC established that the IBr molecules form a commensurate superlattice with lattice parameters of ($\sqrt{183}R26.33° \times 2\sqrt{3}R0°$) with respect to the graphite lattice vectors. The existence of a superlattice was also established in a study of the dHvA spectrum where the large number of dHvA frequencies was explained by the overlapping of the Fermi surfaces by the zone folding effect [10]. The formation of the superlattice is expected to have an effect on the temperature dependence of the resistivity. However, the only change is the change of the slope in ρ_c and ρ_a of the IBr GIC at 275 K in figures 2 and 3 during warming and cooling. It is not possible to attribute this smooth change to a transition since there is usually a more abrupt change as in the InCl$_3$ GIC [20].

The stage-3 HgBr$_2$ GIC has a metallic characteristic. However, there is a noticeable change in the slope of the resistivity ρ_c at 175 K during both cooling and warming processes. This might also be the manifestation of a structural phase transition. A recent study of the dHvA effect of the stage-3 HgBr$_2$ GIC exhibits a complicated spectrum which may be explained by the presence of a commensurate supperlattice at low temperatures.

The Hall coefficients of the two compounds in the range of 4.2–300 K are temperature independent. The positive value indicates hole conduction. The one-carrier model with $R_H = 1/ne$ is appropriate to calculate the number of carriers per unit volume, where n is

the number of carriers per unit volume and e is the electron charge. For the stage-2 IBr $n = 8.1 \times 10^{26}$ m^{-3} and for stage-3 HgBr$_2$ $n = 7.9 \times 10^{26}$ m^{-3}. These values are within the range of values 6.8×10^{26} m^{-3} to 8.5×10^{26} m^{-3} which has been reported for the low stages of chloride compounds [9].

5. Conclusions

The stage-2 IBr and stage-3 HgBr$_2$ GICs have metallic-like behaviour between 4.2 and 300 K when the samples have never been heated above 300 K. After the IBr GIC is heated to 370 K. the resistivity is semiconducting below 300 K. There is an indication of a structural phase transition at 175 K for HgBr$_2$. The temperature dependence of the resistivity and the Hall coefficient of the stage-2 IBr GIC above room temperature shows that the Sugihara mechanism of scattering dominates the resistivity behaviour of the stage-2 GIC and indicates that the resistivity of this compound is by scattering by out-of-plane phonon modes of vibrations. The Hall coefficients of the stage-2 IBr and stage-3 HgBr$_2$ GICs are temperature independent between 4.2 and 300 K and indicate a net carrier concentration of 8.1×10^{26} m^{-3} for the IBr and 7.9×10^{26} m^{-3} for the HgBr$_2$ compound. These values are in the range reported for most acceptor GICs, especially for the chloride compounds.

Acknowledgments

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