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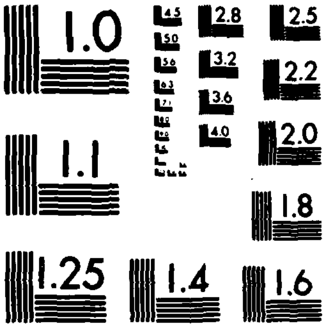

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# INTERCALATION COMPOUNDS: A NEW CLASS OF MATERIALS AS ADVANCED SOLID LUBRICANTS
## (WEAR LIFE STUDIES AND DIFFERENTIAL THERMAL ANALYSIS)

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**8 JANUARY 1983**

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Using graphite as a model host compound the process of intercalation, i.e., the insertion of foreign atoms or molecules between molecular planes of layer-structured solids has been shown to provide new material- with intrinsic lubricating properties substantially more beneficial than those currently available. A synergistic lubricating effect has been uncovered between intercalated metal chloride/graphite species and the non-intercalated metal chloride. A greater than seven-fold increase in endurance life

compared to ordinary graphite has been demonstrated for $CoCl_2$ intercalation compounds using the Falex lubricant tester. Pure intercalation compounds of $CoCl_2$ and $FeCl_3$, i.e., free of non-intercalated metal chloride exhibited a 2.5 fold increase in endurance life. Thermal analyses have shown that these compounds are stable to 325°C in an inert atmosphere. A mechanism has been proposed to explain the lubricating action based on a gradual decomposition of intercalation compounds at metal-to-metal contact junctions where "hot spots" can reach temperatures as high as 1000°C. The intercalated species which comes out of the graphite crystal then reacts with the metal to form a low shear strength solid which prevents further metal-to-metal contact and thus minimizes wear.

# SUMMARY

## INTRODUCTION

Solid lubricants are generally defined as materials which produce lubrication on two relatively moving surfaces under essentially dry conditions as opposed to oil or grease lubrication. Molybdenum disulfide ($MoS_2$) and graphite are probably the best known lubricating solids, the former being used in the majority of applications because of its overall lubricating ability. The use of solids as lubricants encompasses a variety of techniques such as bonded solid films, burnished films, self-lubricated solid composites as well as additives to grease and oil or as a paste. Depending on the application, one form will be more desirable than the others. Solid lubrication is utilized throughout DOD weapons systems where relubrication is impractical or impossible, temperatures exist beyond which oils or greases are stable and where high loads are encountered. Indeed, in some applications, solids are the only means for providing adequate lubrication. The most common usage of solids as lubricants is in the form of bonded films. Typical formulations consist of lubricating pigment ($MoS_2$) incorporating either organic (phenolic, epoxy, polyimide, etc.) or inorganic (silicate, phosphate, etc.) binders. Conventional paint application techniques such as dipping, brushing or spraying are used to deposit films on component surfaces. A film thickness on the order of 0.03 mm has been found to be optimum. Thicker coatings wear rapidly as a result of cohesive forces. Thinner coatings result in only limited durability. At present coatings based on $MoS_2$ have been found to provide the best available lubricating film. The most obvious disadvantage of solid film lubricants is their limited durability. For the most part research efforts to enhance durability have centered on the study of alternate binders and surface pretreatments. Some work has been performed on improving lubricating pigments, but $MoS_2$ still ranks as the best material available today. With this deficiency in mind, an independent research program was initiated at the Naval Air Development Center (NAVAIRDEVCEN) in October 1980 based on studying intercalated solids as advanced solid lubricants. The title of the work unit is "Intercalated Compounds: A New

Class of Materials as Advanced Solid Lubricants", Task Area No. Z02208, Work Unit GC-125.

## RESULTS

The process of intercalation has been shown to provide lamellar solids with enhanced lubricating ability compared to ordinary graphite and $MoS_2$. A synergistic effect between intercalated graphite/$CoCl_2$ species and non-intercalated $CoCl_2$ has been discovered. The pure compounds, i.e., in the absence of non-intercalated metal chloride also exhibit a pronounced lubricating effect. The increase in durability of solid film lubricants formulated with intercalation compounds of $CoCl_2$ and $FeCl_3$ is rapid at concentrations less than 1 mole percent and diminishes above that concentration to a value which is 2.5 times better than ordinary graphite.

Thermal analyses have shown that these compounds are stable to 325°C and decomposte gradually above that temperature. A mechanism of lubricating action based on this decomposition has been proposed. The intercalant exiting the graphite crystal can react with surface "hot-spots" to form low shear strength surface films which prevent wear of the metal substrate.

## CONCLUSION

This research has shown that the process of intercalation can provide a synthesis approach toward the development of solid lubricating materials with properties superior to those currently available.

## FUTURE PLANS

This program is expected to be completed by 1 October 1983. Plans for the final year include:

1. Additional kinetic studies will be performed on the decomposition of graphite/metal chloride intercalation compounds in order to further explore the mechanism of lubrication.
2. The characterization of intercalation compounds will continue employing differential thermal analysis.
3. A comparison of the lubricating properties of metal chloride versus metal intercalation compounds will be made.

# TABLE OF CONTENTS

# LIST OF TABLES

## LIST OF FIGURES

# LIST OF FIGURES

# BACKGROUND

## GENERAL

The ability of graphite to form compounds by intercalation, i.e., the formation of chemical compounds by insertion of atomic or molecular species in the van der Waals gap between carbon layers has been known since 1859. Since that time, a variety of intercalated compounds have been prepared predominately with transition metal chlorides. Several excellent reviews on the subject of intercalation compounds appeared in 1959 and 1960 (1), (2), (3), (4) and a resurgence of interest in the unique properties of these materials in the 1970's (5) led to the first international conference to be held on graphite compounds and the introduction of a new journal titled "Synthetic Metals", integrating research and applications on intercalation compounds of graphite, transition metal compounds, and quasi-dimensional conductors.

Three classes of graphite intercalation compounds have been described, namely;

1. Non-conducting or covalent: Graphite oxide and graphite fluoride are the only known examples. In these compounds, the classic properties of graphite are lost, i.e., the planar structure of the carbon atoms becomes buckled and the materials become non-conductive.

2. Conducting or ionic: Most compounds fall into this class which can be further distinguished by whether the intercalant gives up or receives electrons. For example, alkali metal intercalants are designated donor compounds while metal chloride intercalants are acceptor compounds.

3. Residue compounds: There is some question as to whether these materials are true compounds since the intercalant is retained only at imperfections and peripheral surfaces of the graphite crystal, after decomposition or reduction has taken place.

Since most of the compounds explored in this study fall under the ionic acceptor type classification, a few additional remarks about them are in order. When compounds of this type are analyzed by x-ray diffraction it is found that not all of the layers of the crystal are necessarily intercalated. This observation has led to the use of the term "stage" to describe the extent of intercalation. As shown in Figure 1, a Stage 1 compound is one in which intercalant can be found between every layer of carbon atoms. In Stage 2 compounds, every other layer of carbon atoms is intercalated and so on for Stage 3 and above. No lamellar compound has been found to contain multiple layers of intercalant between adjacent carbon planes (2). As a consequence of intercalation, the interplanar distance between intercalated carbon layers is increased by as much as three-fold. This increased separation should lead to a weakening of the van der Waals forces (i.e., lowering of interplanar binding energy) between planes thus allowing slippage of one plane of atoms over the other more readily. The result of this phenomenon should therefore translate into more effective solid lubrication. It is known that effective lubrication with graphite is dependent on minute quantities of vapor ($O_2$, $H_2O$, etc.) supporting the crystal structure of carbon atoms (6). In vacuum and at elevated temperatures in an inert atmosphere failure of graphite to lubricate has been attributed to collapse of carbon layers as a result of depletion of these vapors. Thus, graphite is not totally an intrinsic lubricant but may be caused to lubricate under certain conditions.

Recent proposals have been made regarding the use of intercalated graphite compounds as organic reagents (7), catalysts (8), battery cathodes (9) and highly conducting materials (10). The obvious application which appears to have been overlooked is as improved lubricating solids. Only one compound, namely; graphite fluoride, one of the nonconducting types, has been thoroughly investigated by the U. S. Army (11), NASA (12) and the U. S. Air Force (13) with the conclusion that while graphite fluoride looked promising as a solid lubricant in applications involving low stress, it was not considered suitable for heavy load requirements. Since this material is not representative of the majority of intercalated graphite compounds, a study was undertaken on a variety of graphite intercalation compounds in order to determine lubricant performance under high loads.

## Mechanism for the Formation of Ionic-Acceptor Type Graphite Interlation Compounds

It is interesting to note the latest mechanistic scheme proposed for the formation and stabilization of ionic-acceptor type graphite intercalation compounds. This may be useful in explaining the lubricating action of these compounds.

The following experimental observations have been made concerning metal halide intercalation compounds of graphite: (14), (15), (16)

1. Chlorinegas does not intercalate graphite at or above room temperature.

2. Electron energy loss measurements on metal halide intercalated graphite have shown a charge transfer of -0.015 electrons per carbon atom.

3. Intercalation will not proceed unless chlorine gas is present in the reaction system. Some metal halides decompose to chlorine gas thus an external source of chlorine is not required for reaction to take place.

4. The activation energy for the intercalation of graphite with metal halides corresponds to the same amount of energy required to vaporize the metal halide.

5. X-ray photoelectron spectroscopy shows evidence of inequivalent chloride atoms in metal halide intercalated graphite. In free metal halides the chlorine atoms are equivalent.

6. From Mossbauer Spectroscopy, no evidence of a change in oxidation state for metal cations is observed. This means that the electrons from graphite are not accepted by the metal cation.

7. The chlorine to metal cation ratio is about 10% greater for the intercalation metal halide than for the free metal halide. For example the stoichiometry for intercalated nickel chloride is $NiCl_{2.13}$ instead of $NiCl_2$.

8. The filling of graphite layers with metal halide reaches about 70% of the theoretical maximum.

9. X-ray analysis has shown that the cohesive length of $NiCl_2$ layers in intercalated graphite is about 100A$^{o}$.

From the above information, it was theorized that the formation of metal halide intercalated graphite commences in three steps:

1. Vaporization of the metal halide and formation of excess halogenated metal halide, e.g., $NiCl_{2.13}$.

2. Nucleation of excess halogenated metal halide islands at the edge of graphite flakes.

3. Diffusion of these islands between carbon layers.

The resultant graphite metal halide intercalation compound is characterized as an ionic-acceptor compound. Electrical charge removed from $\pi$-band in graphite by the metal halide intercalant is localized on chlorine atoms rather than metal atoms. The chlorine acceptor action is made possible by metal ion vacancies produced during the intercalation process by the presence of chlorine gas. The excess halogen on the periphery of metal chloride islands prevents coalescence of these islands. If contact of the islands would occur normal bridging bonds would be reestablished with the expulsion of chlorine and the return of charge to the graphite valence band. Thus excess chlorine stabilizes the metal halide islands.

## Graphite/Transition Metal Intercalants

A review of the literature on graphite/transition metal intercalates reveals a controversy as to their existence. Vol'pin etal (17) claims to have prepared lamellar compounds of Cr, Mo, W. Fe, Co, Ni, Mn and Cu with graphite using various synthetic techniques. Saunders and Fryer (18) reported on the preparation of a graphite iron intercalation compound using graphite-ferric chloride intercalation compound reduced under nitrogen with lithium biphenyl in THF. In two papers Braga etal (19) (20) describe the reaction of ferric chloride graphite intercalate with potassium in THF to form a graphite-iron compound. Other methods reported to produce graphite transition metal intercalates from the corresponding metal halide include: (21)

1. reduction with Na or K in liquid ammonia
2. heating in flowing $H_2$ or $N_2$ or under vacuum
3. reduction with $NaBH_4$ in ethanol, $H_2O$, at room temperature
4. electrochemical reduction.

On the other hand Schafer-Stahl (22) investigated by means of X-ray and Mosshauer methods the products obtained by reduction of graphite ferric chloride according to Braga etal (20) and found "no evidence whatsoever for an ordered compound containing monolayers of ion atoms between carbon layers". Bewer etal (21) also using methods of Braga (20) and Vol'pin (17) "could find no evidence for the formation of ordered layers of iron atoms between graphite layers by reduction of graphite-ferric chloride intercalation compounds". It is considered that the materials formed by reduction of graphite transition metal chloride intercalates are in actuality an intimate mixture of finely divided metal on the surface of graphite. The catalytic activity of such a mixture is more powerful than with a simple physical mixture of the two materials.

The question as to which set of results are to be believed is still open. However, it is postulated from chemical principles that graphite compounds of transition metals are unlikely to exist because transition metals have high ionization-potentials and lattice energies. The formation of two-dimensional intercalated layer would thus be energetically unfavorable (21). It had also been believed from basic chemical principles that inert gasses were not reactive yet many compounds have been produced to date. In the same vain an open mind should be kept as to the question of the existence of graphite transition metal intercalation compounds.

## EXPERIMENTAL

Intercalated graphite compounds were either obtained from a commercial source (23) or prepared in-house. The commercially prepared compounds were ground in a mortar and pestle and only that portion which passed through a 150-micron sieve utilized. In-house preparations of graphite-metal halide intercalates consisted of thoroughly mixing graphite powder (44 micron, used as received) and the anhydrous metal halide in a 1 to 3 ratio, respectively and sealing the mixture in evacuated carius tubes. The tubes were heated at 300 to 400°C for extended periods. After cooling to room temperature, the tubes were broken and the recovered powder weighed. The reaction product was washed with copious quantities of water or .5N HCl to remove unreacted metal halide followed by washing with acetone. After drying at 66°C, the powder was then weighed again. Knowing the initial concentration of graphite and the differences in weight between the unwashed and washed powder, an estimate of the degree of intercalation could be obtained. In order to verify the presence of intercalated metal halide, a small sample of intercalated graphite (50 mg) was placed in a crucible and heated at 649°C for 30 minutes in air. The presence of intercalated species is evident from the characteristic color of the metal oxide residue found. This residue was found with samples of initial reaction mixture which had been washed free of metal halide. Thus, the metal oxide formed was the decomposition of metal halide which had been intercalated in the graphite structure.

The powders were formulated into solid film lubricants and investigated as a lubricating source on the Falex lubricant tester. A simple formulation using only lubricating solids and MIL-R-3043 phenolic resin as a binder was employed. A formulation based on 33 wt. percent $MoS_2$ (MIL-M-7866) and 67 wt. percent MIL-R-3043 (34 wt. percent solids) was used as a standard. All other formulations were prepared using the same volume of lubricating solids as $MoS_2$. This was calculated using the apparent density which was determined by a procedure similar to that previously reported (24). The lubricating film was formed by spraying the solid lubricant formulation on the test specimens providing a coating with a film thickness in the range of 0.03 mm. The test specimens were then treated at 149°C for one hour.

The Falex lubricant tester which was used to study the lubricating properties of the resultant films has been previously described (25). Essentially, a 6.35 mm diameter cylindrical pin (AISI 3135 steel) is rotated at 290 rpm against two stationary V-blocks (AISI-1137 steel) under load. Two properties of the solid film lubricant were determined, i.e., endurance life and load-carrying capacity (ASTM D2625). Surface preparation of the test specimens consisted of grit blasting with 120 steel grit which produced a surface roughness of 50-60 rms. The results reported are averages of at least four determinations.

Thermal analyses of materials were obtained on a DuPont 910 differential scanning calorimeter under the following conditions:

| | |
|---|---|
| Temperature Range: | 40 to 500°C |
| Heating Rate: | 20°C/Min. |
| Atmosphere: | 3.4 MPa He |
| Sample Size: | 5 to 8 mg |

Kinetic studies were performed on 250 mg samples sealed in pyrex ampules heated to 425 ± 5°C. At specific times the ampules were taken from the furnace, cooled to room temperature and weighed to see if the seal remained closed. The ampule was then broken and the sample washed with water until free of any trace of chloride ion. The water washings were then placed in a weighed beaker and heated at 150°C overnight to dryness. The weight of the residue was taken as the amount of anhydrous $CoCl_2$ that decomposed from the graphite/$CoCl_2$ compound.

## RESULTS

Initial results obtained during the first year of this study are reported in references (26) and (27). These results are summarized in Tables 1 and 2 along with some recent data generated on compounds not previously studied. As shown in Tables 1 and 2, a substantial improvement in the durability of solid film lubricants formulated with some of the commercially prepared intercalated graphite compounds was obtained. An analytical examination of the graphite/metal chloride compounds revealed the presence of non-intercalated metal chloride. This observation was somewhat surprising since it is standard procedure to wash the compounds after reaction to rid them of the free metal chloride. The effect of this free metal chloride on the Falex endurance life results previously obtained was then studied.

### ENDURANCE LIFE

Starting with the graphite/19.8 Wt. % $CoCl_2$ intercalation compound, the material with the longest endurance life, an extraction with water was performed and the amount of $CoCl_2$ dissolved in the water determined. As shown in Table 3, 4.6 wt. % of the graphite/19.8 wt. % $CoCl_2$ intercalate was found to be free $CoCl_2$.

The endurance life of the remaining intercalate compound was observed to be reduced considerably from 390 minutes to 119 minutes. Therefore, it appears that the presence of free metal chloride has a profound effect on increasing endurance life with intercalated species. In order to further verify this finding, anhydrous $CoCl_2$ was added to the extracted intercalate in the same concentration as found in the original sample. The endurance life was then found to approach that of the original composition (346 min. vs. 390 min.). The slight decrease in endurance life is probably due to inadequate physical mixing of the two components. The addition of $CoCl_2$ to unintercalated graphite was found to produce only a slight increase in endurance life over graphite (68 min. vs. 51 min.). These results demonstrate that there exists a synergistic effect between the graphite/$CoCl_2$ intercalate and free $CoCl_2$ for obtaining enhanced durability with these solid lubricant systems.

Similar results were obtained for $FeCl_2$ and $YCl_3$ intercalation compounds as shown in Table 4. All of these compounds contained some non-intercalated metal chloride which when extracted reduced the endurance life of the resultant solid film lubricant. For $YCl_3$, the extracted product contained so small a concentration of intercalate (1.7 wt. %) that this solid film lubricant gave essentially the same results obtained for ordinary graphite.

A series of tests were than performed on graphite intercalation compounds of $CoCl_2$ and $FeCl_3$ at various concentration levels insuring that the materials were free of non-intercalated metal chloride. Figure 2 shows the interesting results obtained in this study. The mole percent concentration of intercalant in graphite is plotted vs. the average Falex endurance life in minutes. It can be observed that the endurance life rapidly increases relative to graphite at low concentrations of intercalant and remains relatively constant at higher concentrations. At concentrations greater than 1.0 mole percent intercalant no appreciable increase in endurance life is achieved. The limiting value obtained for endurance life of approximately 125 minutes is 2.5 fold greater than graphite and 1.8 fold greater than $MoS_2$.

## THERMAL ANALYSIS

The use of differential scanning calorimetry (DSC) to characterize materials has been well documented. Basically if a sample of material and an inert reference medium are heated at a known rate in a controlled environment the increase in temperature of the material and reference medium will be approximately the same. When a heat-related change takes place in the material a temperature difference exists between the two reference points.

If the material evolves heat it is said to be an exothermic reaction and the temperature of the sample will be higher than that of the reference medium. Conversely, if the material absorbs heat it is said to be an endothermic reaction and the temperature of the sample will be lower than the reference medium. The difference in temperature which results between the material under study and the reference medium from such heat related changes is directly related to the differential heat flow between the two reference points. This differential heat flow can be quantitatively measured and plotted on a X-Y,Y recorder as a function of the sample temperature. Such plots are referred to as thermograms.

Figures 3 to 19 show DSC thermograms obtained on graphite and a variety of graphite intercalation compounds. Figure 3 shows the thermogram obtained for ordinary graphite. As expected no heat changes occur under an inert atmosphere in the temperature range 40 to 500°C. This thermogram is presented as a baseline for comparison with the other thermograms to be presented. Figure 4 is a thermogram of graphite/19.8 wt. % $CoCl_2$ intercalation compound as received. The two endotherms starting at 97°C and 139°C respectively are representative of the dehydration of a small amount ($<$ 0.2 wt. %) hydrous cobalt chloride ($CoCl_2.2H_2O$). Figure 5 is a thermogram of a known sample of $CoCl_2.2H_2O$ which confirms this observation. In Figure 4 another endotherm is observed at 325°C. Since no endotherms occur at this temperature for ordinary graphite (Figure 3) or $CoCl_2.2H_2O$ (Figure 5) it is concluded that this endotherm is characteristic of the intercalation compound. At present, it is believed that this endotherm is associated with the initial decomposition of the intercalation compound, i.e., graphite/$CoCl_2$ going to graphite and free $CoCl_2$. Whether it is a total or partial decomposition remained to be determined (See section on kinetic study).

Figure 6 is a thermogram of the graphite/19.8 wt. % $CoCl_2$ which has been washed with water to remove both hydrous and anhydrous free cobalt chloride. As can be observed the endotherms for the dehydration of hydrous $CoCl_2$ have disappeared and the endotherm at 325°C is still present. Figure 7 is a thermogram taken on the same sample shown in Figure 6 after being exposed to a temperature of 500°C. The endotherm at 325°C has disappeared.

Figures 8 and 9 are thermograms of graphite/38.4 wt. % $CoCl_2$ and graphite/43.9 wt. % $CoCl_2$ intercalation compounds respectively. No free hydrous or anhydrous $CoCl_2$ is present in these materials. Again the endotherm at 325°C can be observed for both of these compounds.

Figure 10 shows the thermogram obtained on graphite/8.2 wt. % $FeCl_3$ intercalation compound as received. The shallow endotherm starting at 100°C is indicative of the decomposition of hydrated $FeCl_3$. Unlike the hydrous $CoCl_2$ which dehydrates to anhydrous $CoCl_2$. $FeCl_3.XH_2O$ decomposes to $Fe(OH)_3$. An endotherm at 325°C similar to that found with intercalated $CoCl_2$ is also observed. On washing the graphite/8.2 wt. % $FeCl_3$ intercalation the thermogram shown in Figure 11 was obtained. The endotherm for the decomposition of $FeCl_3$. $XH_2O$ at 100°C has disappeared. The endotherm at 325°C is still present. As with the $CoCl_2$ intercalation compound, it is believed that this endotherm is representative of the initial decomposition of graphite/$FeCl_3$ intercalation compound.

Figures 12 and 13 are thermograms of graphite/15.1 wt. % $FeCl_3$ and graphite/26.5 wt. % $FeCl_3$ intercalation compounds, respectively. The endotherm at 325°C is visible from both compounds. In addition, a smaller endotherm at 260°C is also present.

Figure 14 is a thermogram of graphite/19.3 wt. % $NiCl_2$ intercalation compound. The endotherm starting at 150°C is due to the dehydration of hydrous $NiCl_2$. An endotherm at 310°C is attributed to the initial decomposition of $NiCl_2$ intercalation compound. On washing the graphite/19.3 wt. % $NiCl_2$ compound the thermogram shown in Figure 15 was obtained. The endotherm for dehydration of free hydrous $NiCl_2$ has disappeared but the decomposition endotherm at 310°C is still present.

The next series of thermograms were obtained for as received graphite/metal intercalation compounds. The compounds were prepared by exposing the corresponding graphite/metal halide intercalation compound to hydrogen at elevated temperature. As seen in Figures 16 to 19, no metal halide hydrates are present. Basically, one endotherm was found for each compound studied. This endotherm corresponds to a decomposition of the graphite intercalate. As shown in Figures 16 and 17, this endotherm occurs at 240°C for both 10 wt. % and 21.2 wt. % Co. For 4.0 wt. % Fe (Figure 18), the endotherm occurs at 300°C while with 14.0 wt. % Ni the endotherm is observed at 215°C (Figure 19). Table 5 summarizes the results of intial onset temperatures of decomposition and the heat evolved for the decomposition endotherm of the various compounds studied.

## KINETIC STUDY

It was of interest to determine if the endotherm at 325°C for the graphite/$CoCl_2$ intercalation compounds, represented a total or partial decomposition of the compound. As shown in Table 6, only 3.6 wt. % of the $CoCl_2$ intercalate (0.58 wt. % of the compound) was found to decompose after 1 hour at 425°C which is 100°C higher than the onset temperature of the endotherm. Clearly then the endotherm at 325°C represents only a partial decomposition of the intercalated species. Further kinetic studies in this area of investigation are currently in progress.

## DISCUSSION

The study of intercalation compounds as improved solid lubricants centered on the fact that an increase in layer separation of the host material would provide a path for lower shear rate solids. Indeed initial data reported in references (26) and (27) did suggest that the wear life improvement of graphite intercalated solid lubricants was dependent on concentration of intercalant and the separation distance between graphite layers. However, thermal and "wet" chemical analysis of the graphite/metal chloride intercalation compounds revealed the presence of metal chloride that was not intercalated. Extraction of this "free" metal chloride yielded the "pure" intercalation compound of the particular metal chloride. The study of endurance life for the "pure" intercalation compound using $CoCl_2$ and $FeCl_3$ showed that the endurance life increased rapidly at low concentration of intercalant and leveled-off above 1 mole %, being about 2.5 fold higher than "ordinary" graphite. This new data suggested a different mechanism of action than that previously postulated.

The Falex wear test configuration used in these studies is a highly loaded device used to screen solid lubricant materials under extreme conditions of stress. Under these conditions, solids outperform oils and greases which are not able to maintain a film of lubricant between mating surfaces.

Because of this high stress, temperatures generated at contact junctions can be as high as 1000°C. Even though the test is run at ambient temperature these so called "hot spots" are short-lived (approximately .001 second) but can cause chemical breakdown of material in the contact zone. This is a recognized mechanism for conventional anti-wear and extreme-pressure lubricant additives. In such a mechanism the lubricant additive is stable at low temperatures but decomposes at high temperature to form surface films at "hot spots" on the surface. For example, clorinated organic compounds have been observed to react with steel surface at elevated temperature to provide a film of iron chloride which provides for easier shear and thus lessens the wearing process of the metal.

For the metal intercalates, the question as to their existence has already been discussed in the background section of this report. Freeman etal (28) have analyzed samples of graphite-metal intercalates obtained from the same source (23) as those investigated in this program. Using a 600 KV high resolution microscope they found that all samples contained small particles, typically 2-10 nm which were either metal or one of its oxides. For the iron compound lattice images and electron diffraction revealed the presence of $Fe_3O_4$. All visible particles appeared to be located on the surface of the graphite powder and not inside the graphite lattice.

The cobalt sample showed similar results indicative of the presence of $Co_3O_4$. For the platinum compound electron diffraction revealed only graphite. However, micrographs show the presence of small particles which subsequent analysis revealed to be metallic platinum and not the oxide. The nickel compound also showed the presence of metallic nickel rather than the oxide. An irregular graphite layer spacing was often present which was attributed to some of the metal remaining intercalated.

Analyses of these compounds are underway in the light of the fact that appreciable endurance lives have been obtained (See Table 2) with some of these compounds and an entirely different mechanism may be operative.

## ACKNOWLEDGEMENT

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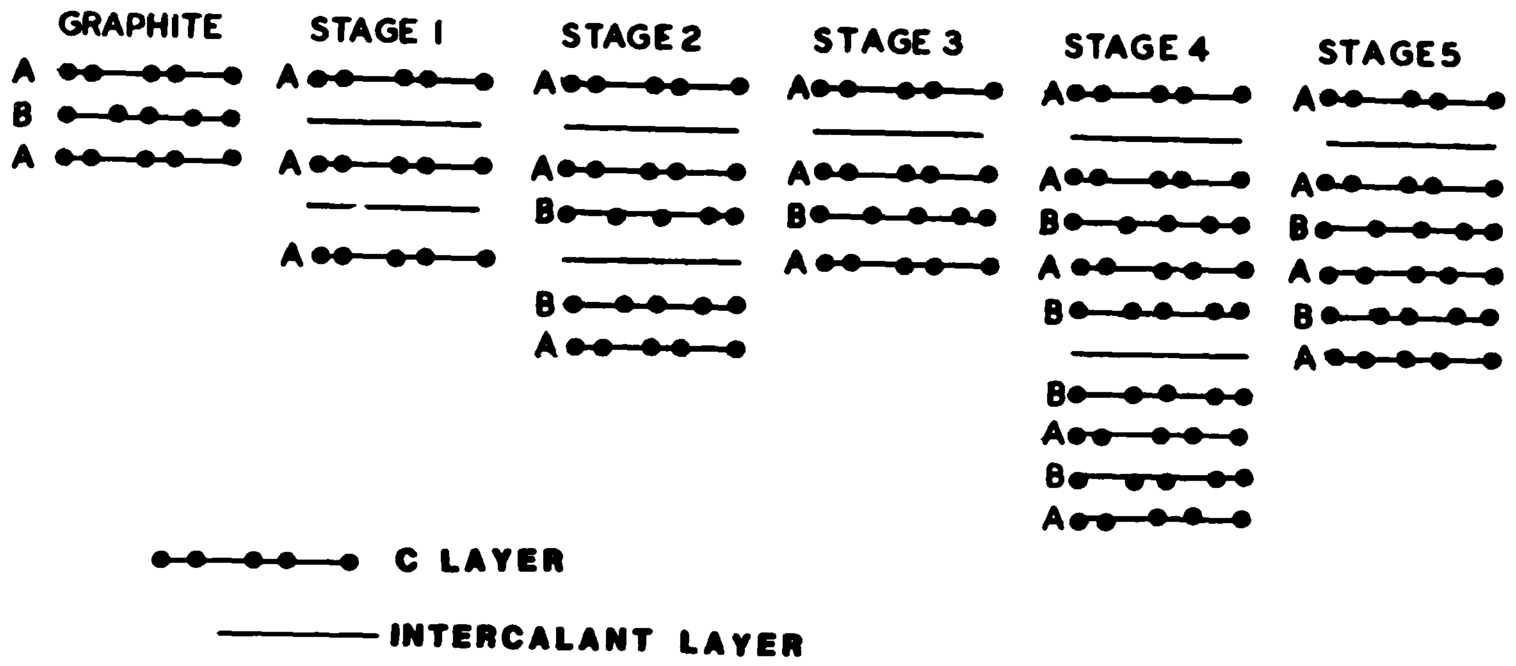

Figure 1. Representation of Stages in Graphite Intercalation Compounds

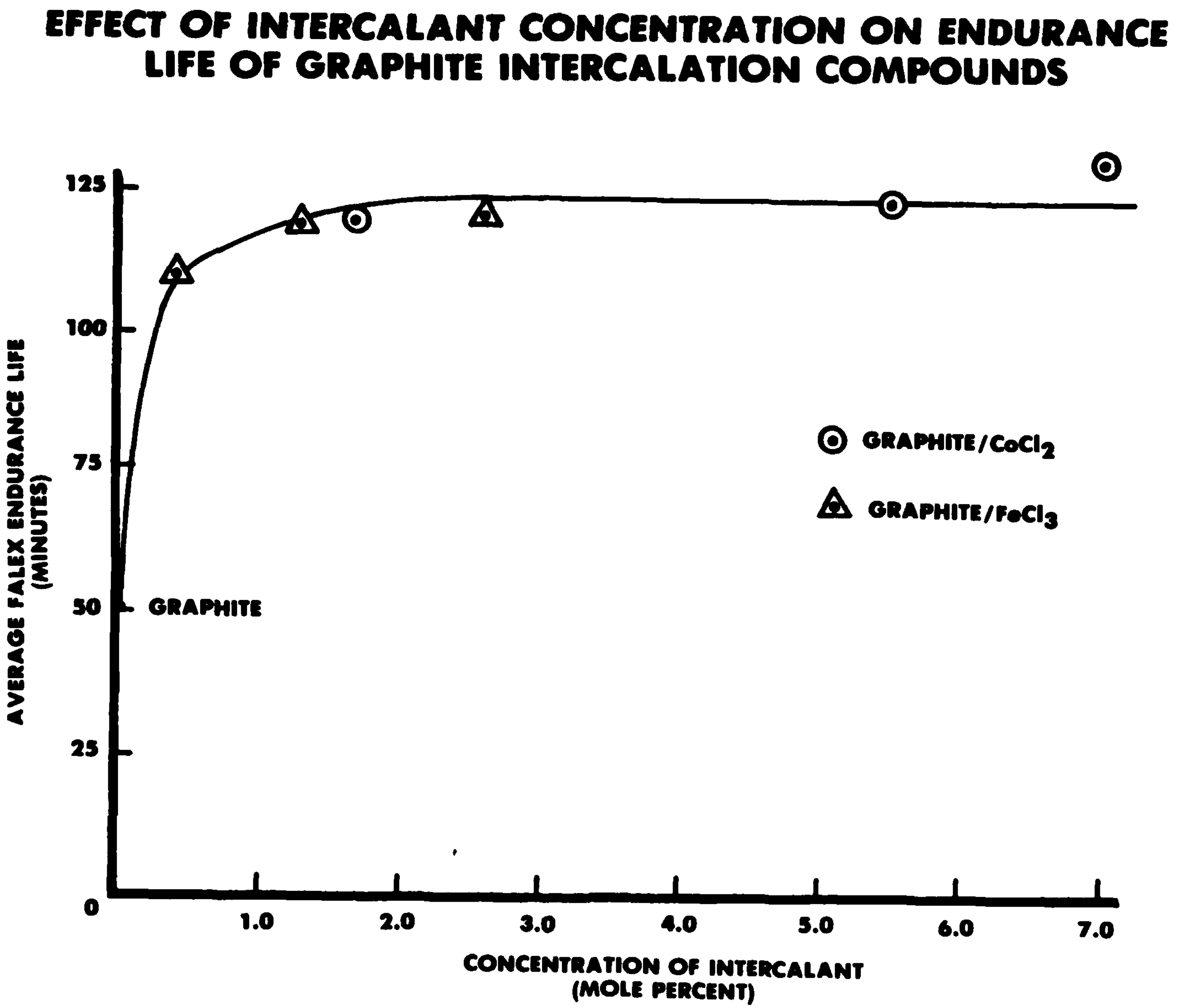

Figure 2. Effect of Intercalant Concentration on Endurance Life of Graphite Intercalation Compounds

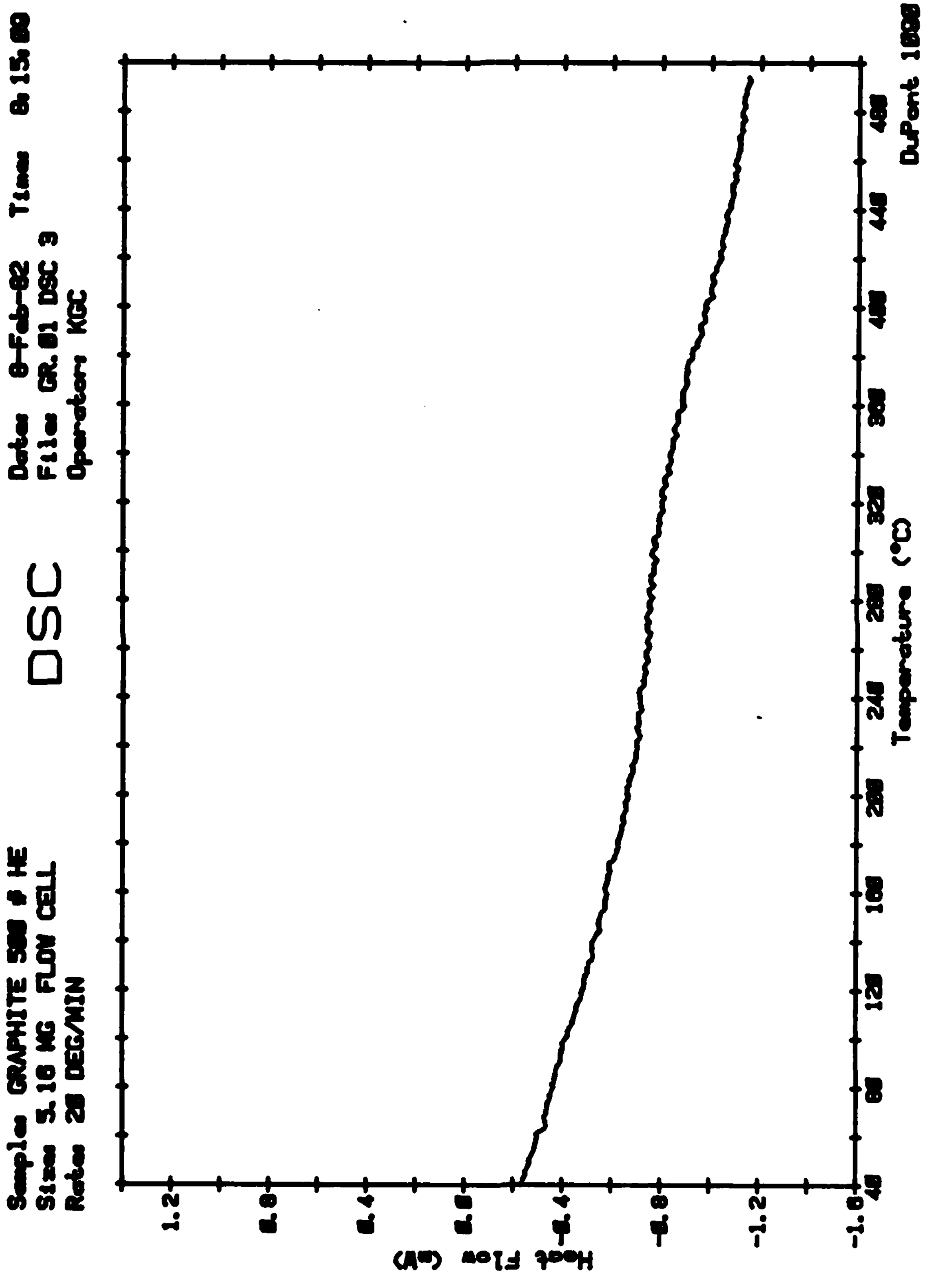

Figure 3. DSC Thermogram of Graphite

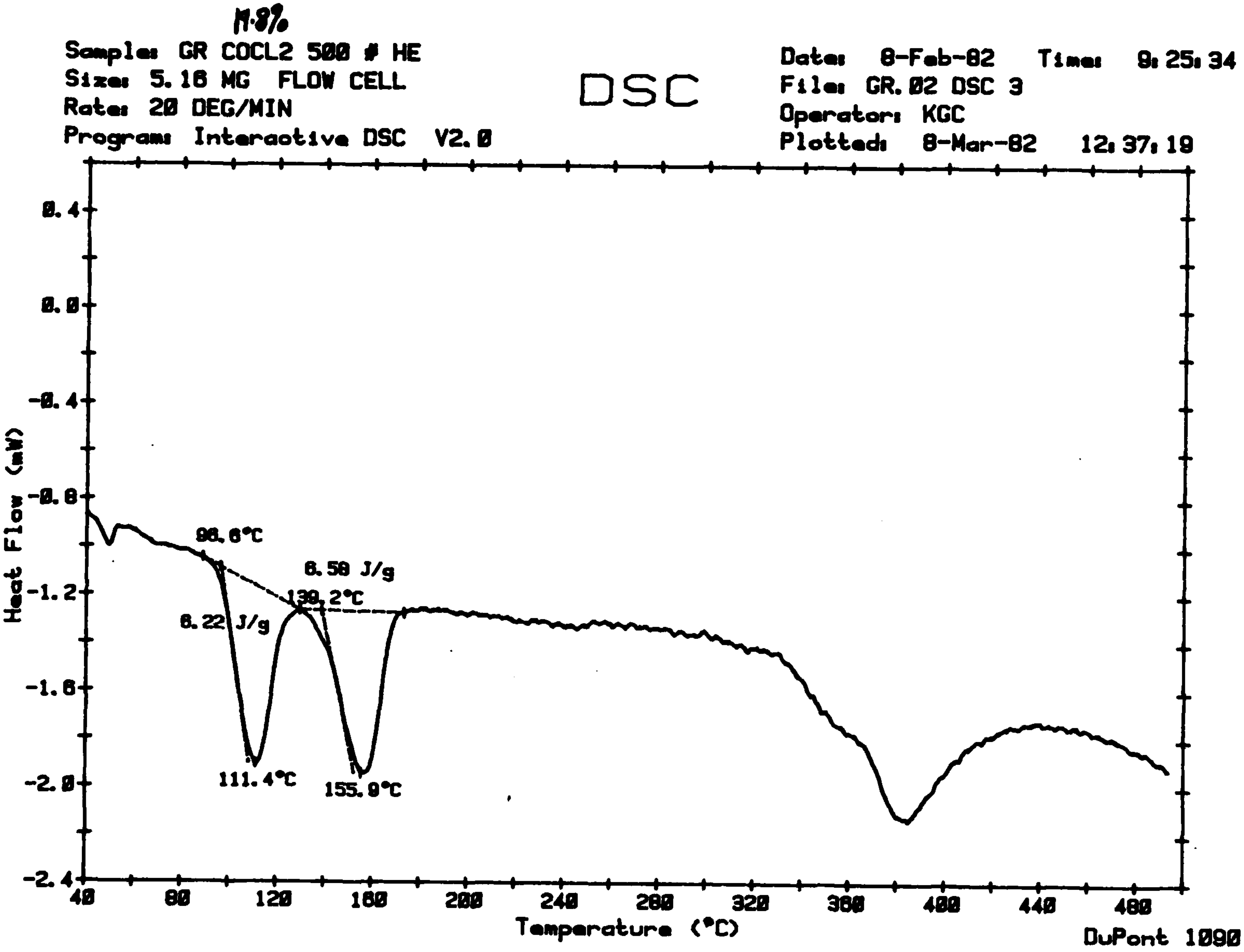

Figure 4. DSC Thermogram of Graphite/19.8 wt. % $CoCl_2$ Intercalation Compound, As Received

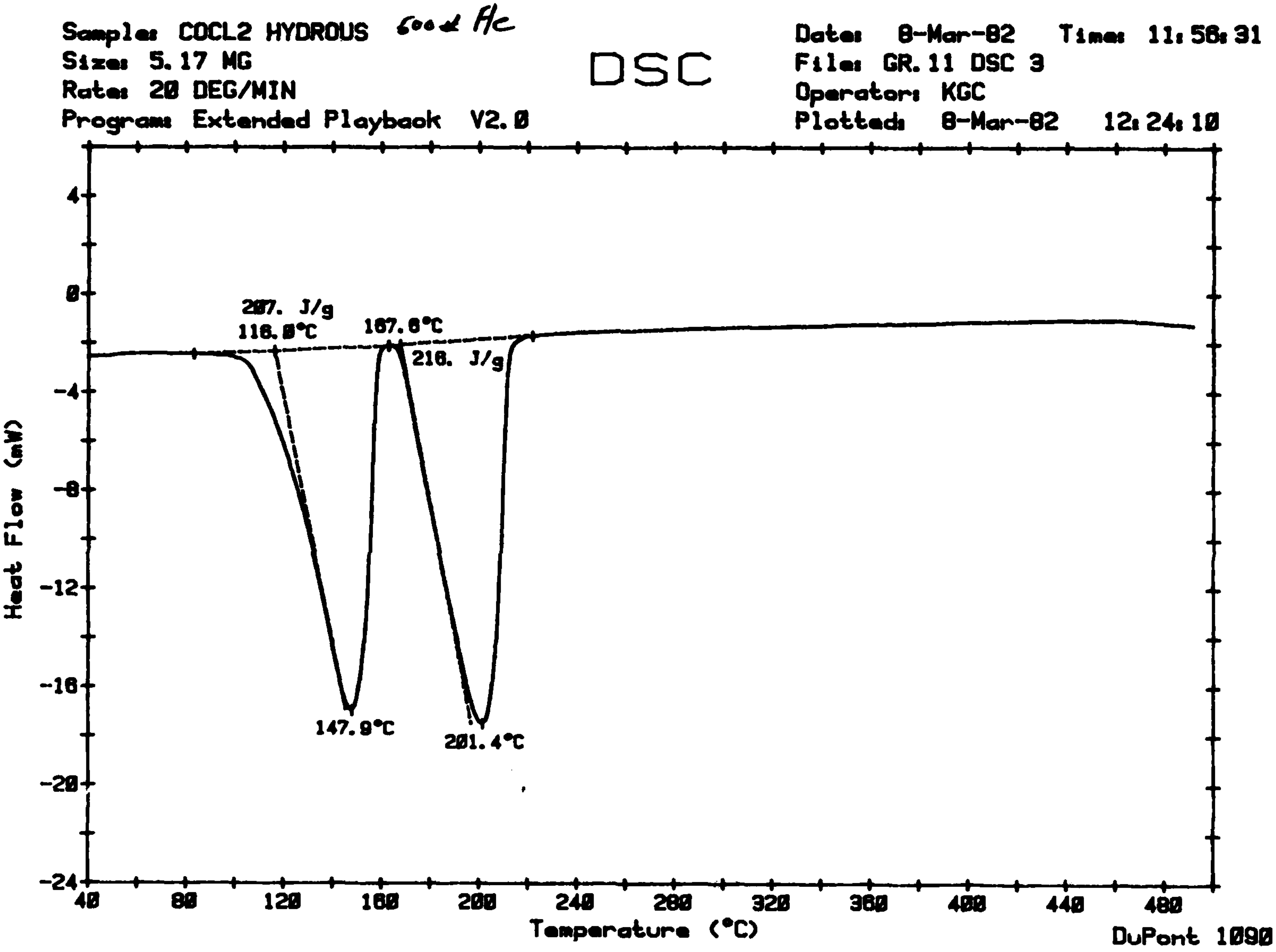

Figure 5. DSC Thermogram of Hydrous $CoCl_2$

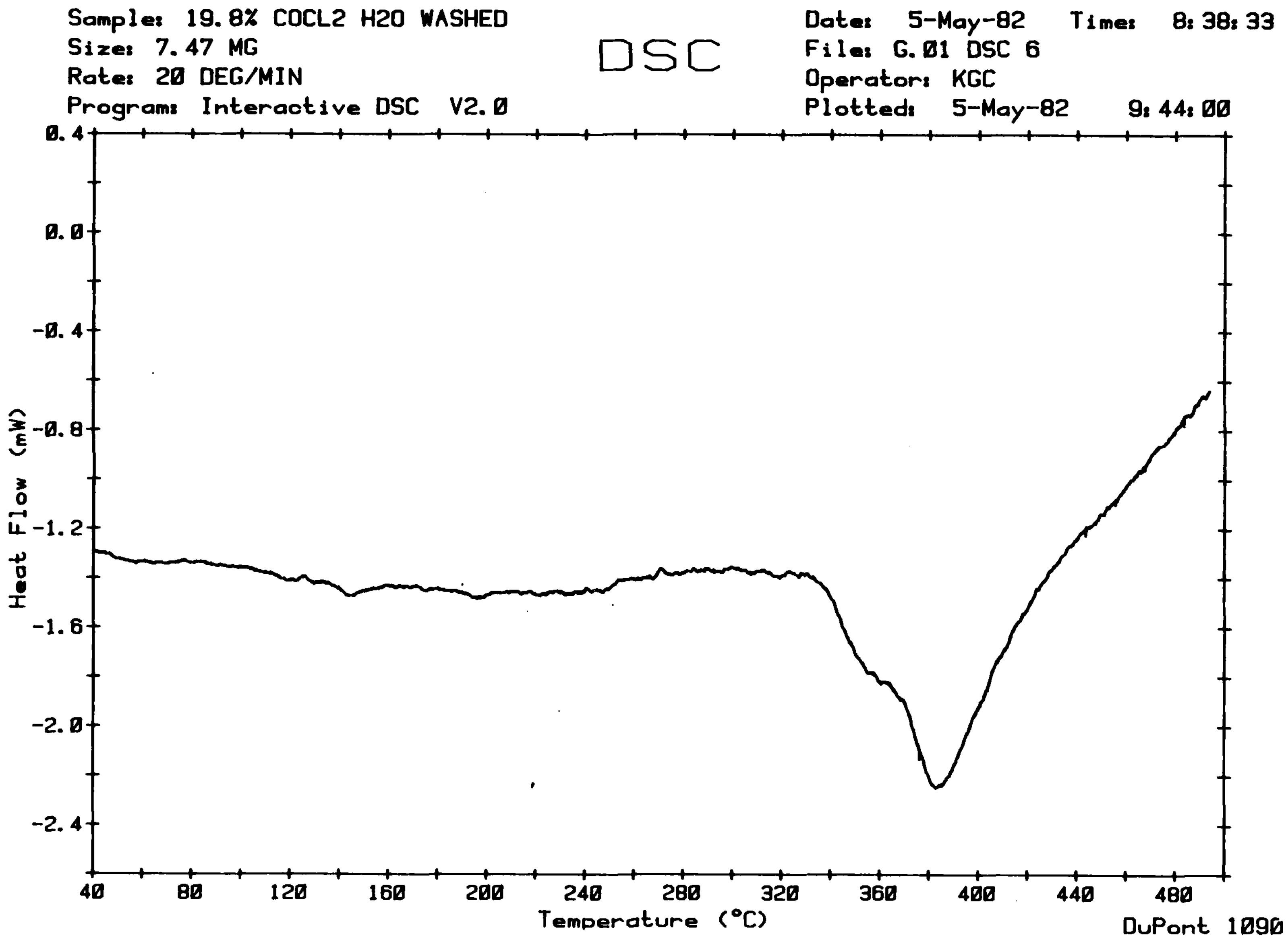

Figure 6. DSC Thermogram of Graphite, 19.8 wt. % $CoCl_2$ Intercalation Compound Washed with Water

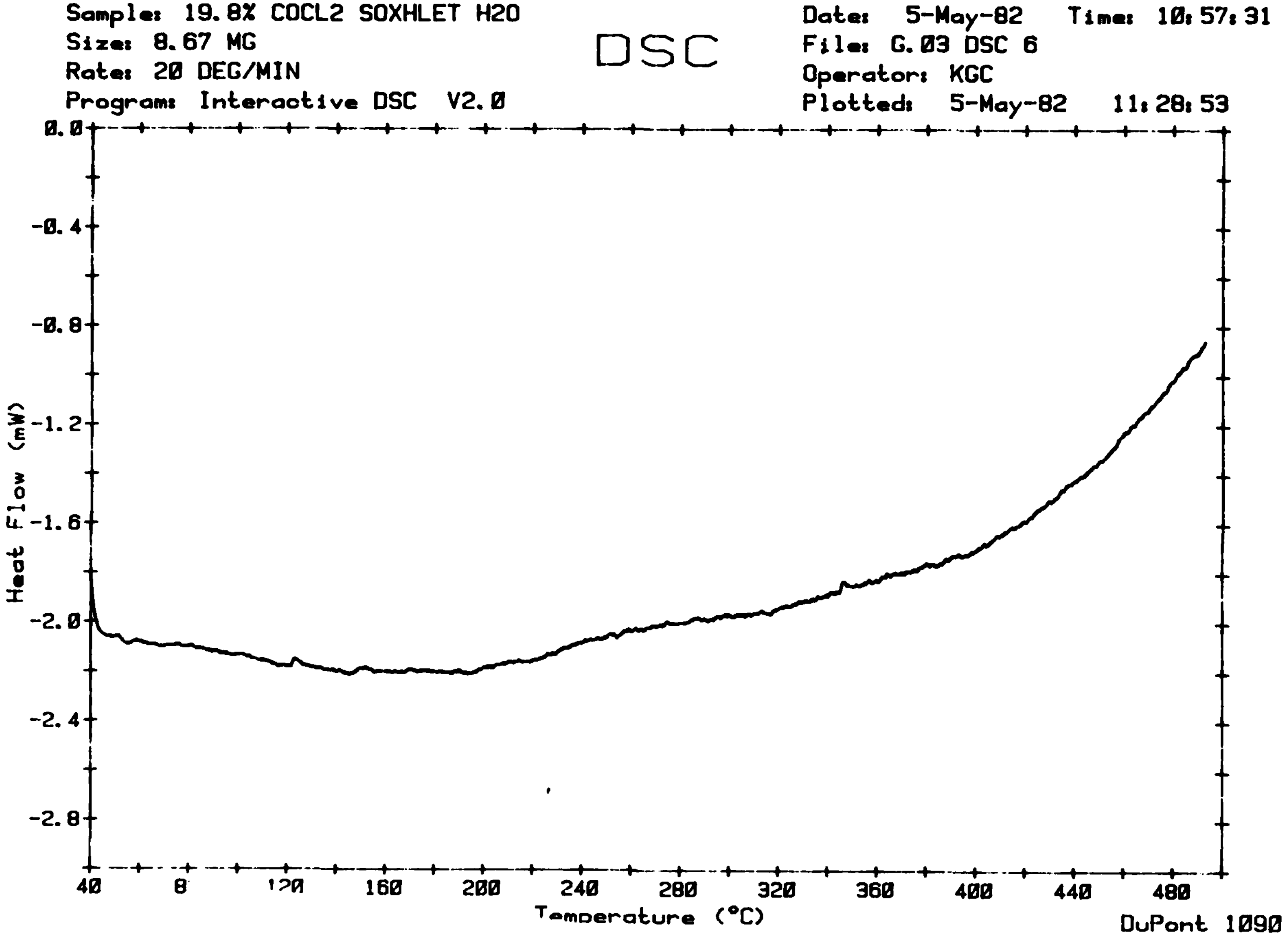

Figure 7. DSC Thermogram of Graphite/19.8 wt. % $CoCl_2$ Intercalation Compound Washed with Water and Heated to 500°C

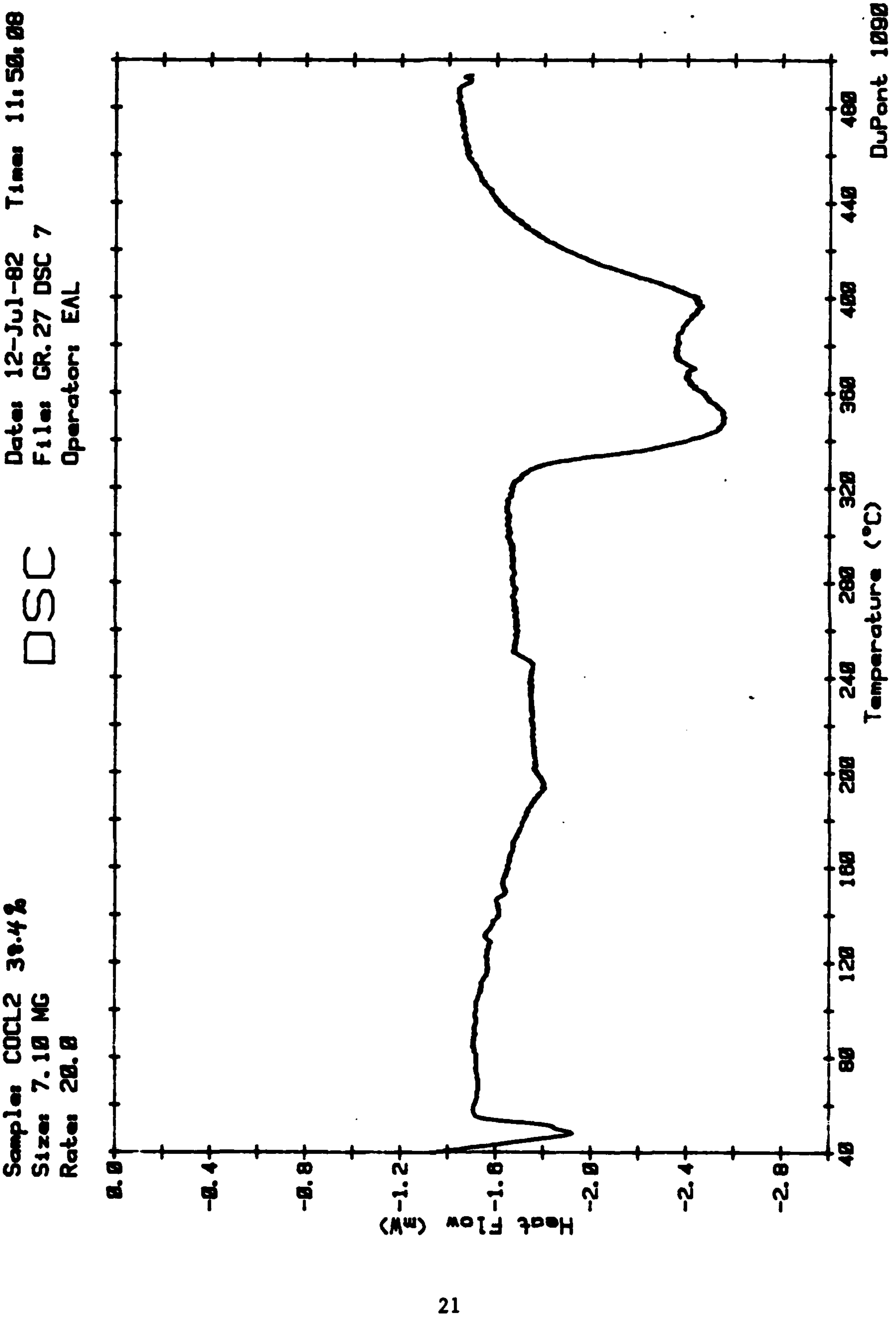

Figure 8. DSC Thermogram of Graphite/38.4 Wt. % $CoCl_2$ Intercalation Compound

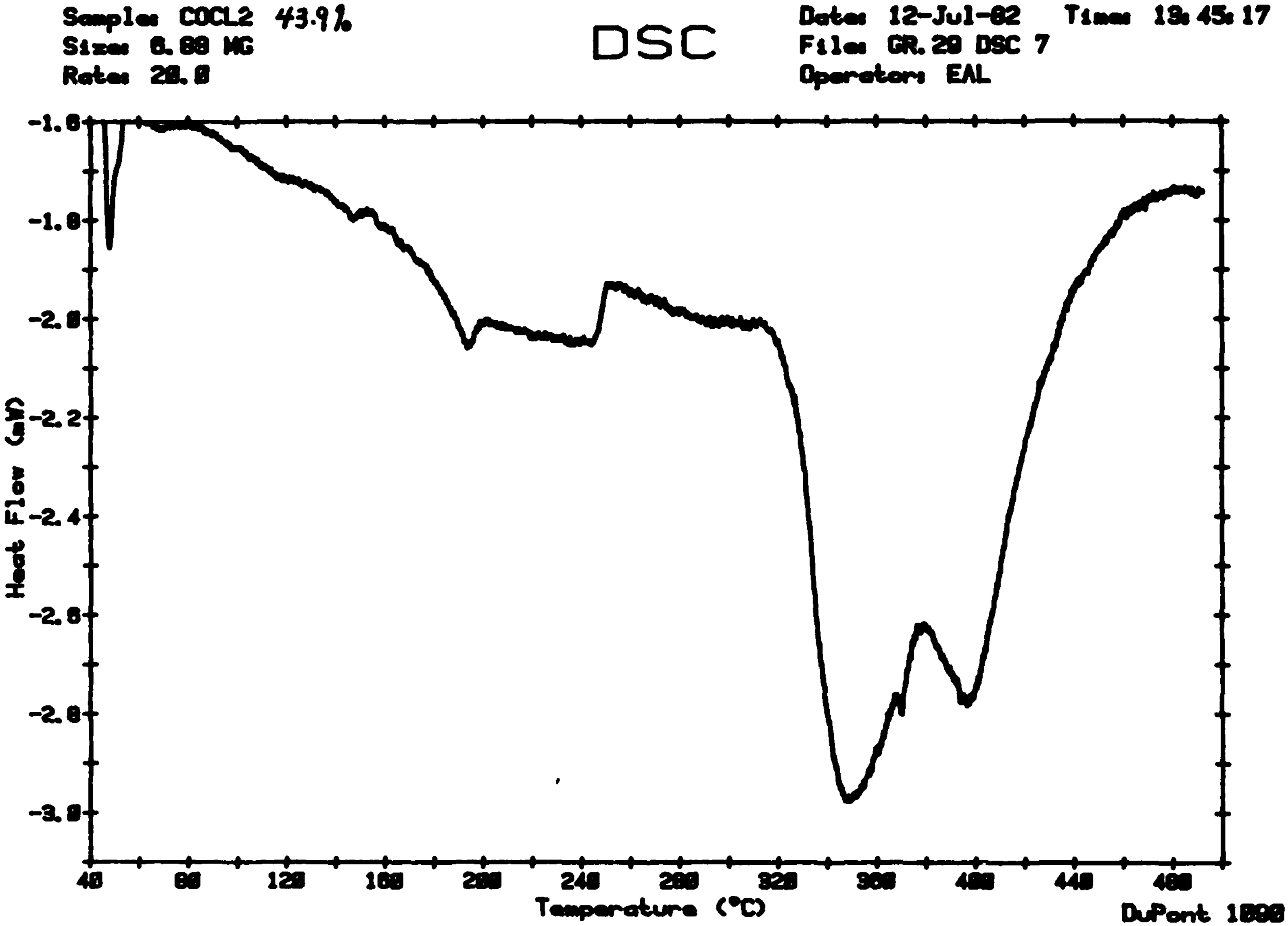

Figure 9. DSC Thermogram of Graphite/43.9 Wt. % $CoCl_2$ Intercalation Compound

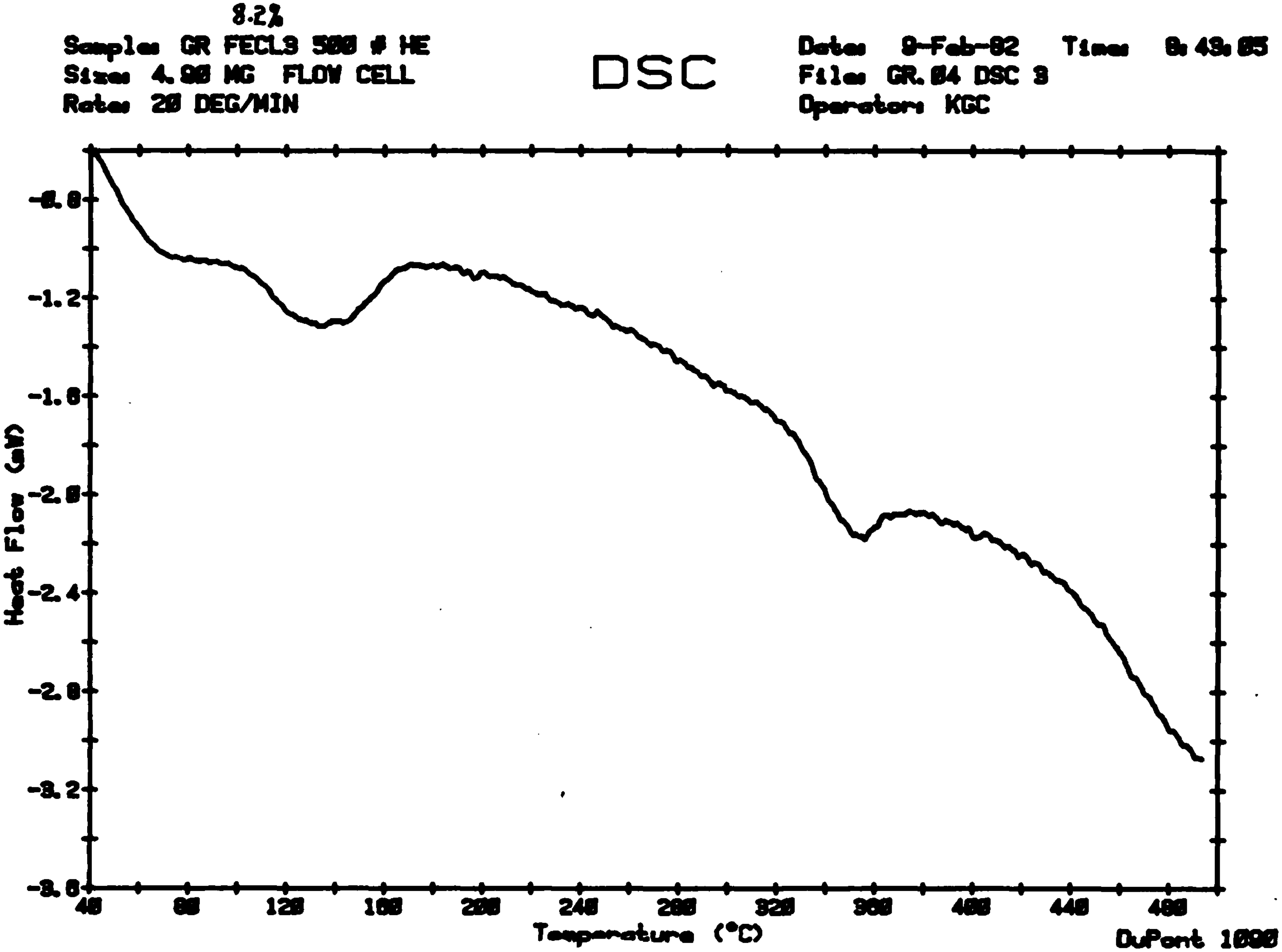

Figure 10. DSC Thermogram of Graphite/8.2 Wt. % $FeCl_3$ Intercalation Compound, As Received

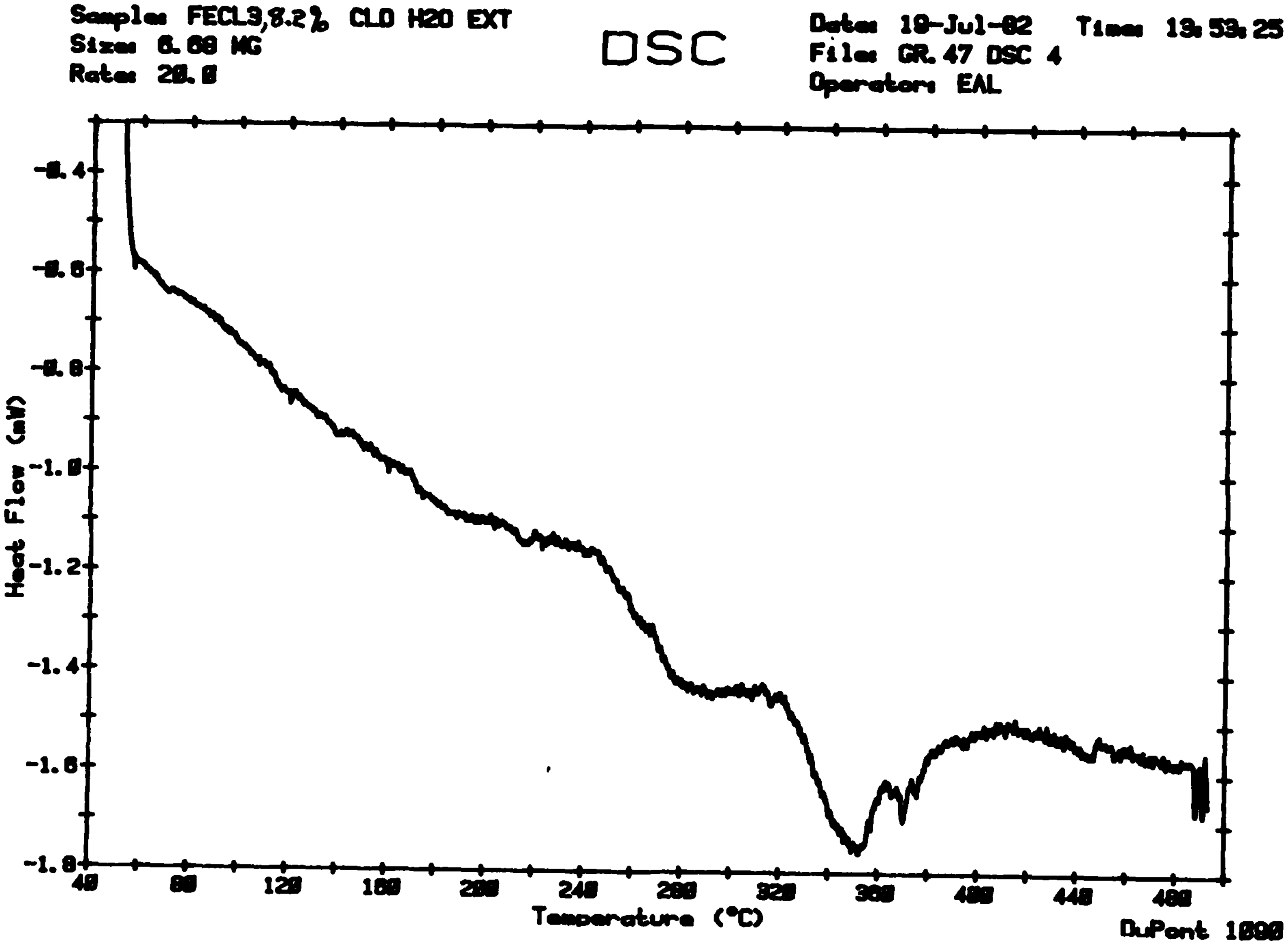

Figure 11. DSC Thermogram of Graphite/8.2 Wt. % $FeCl_3$ Intercalation Compound Washed with Water

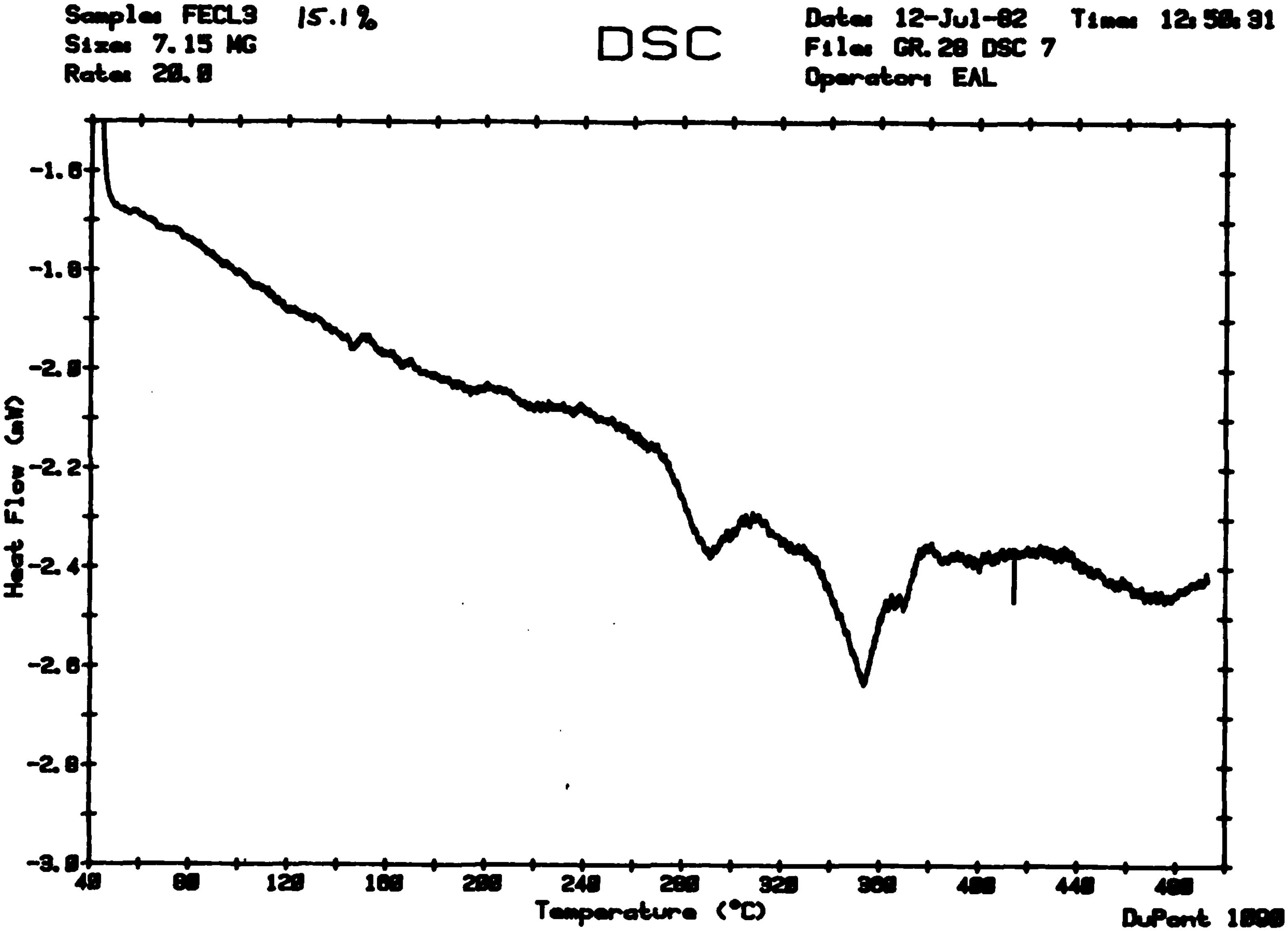

Figure 12. DSC Thermogram of Graphite/15.1 Wt. % $FeCl_3$ Intercalation Compound

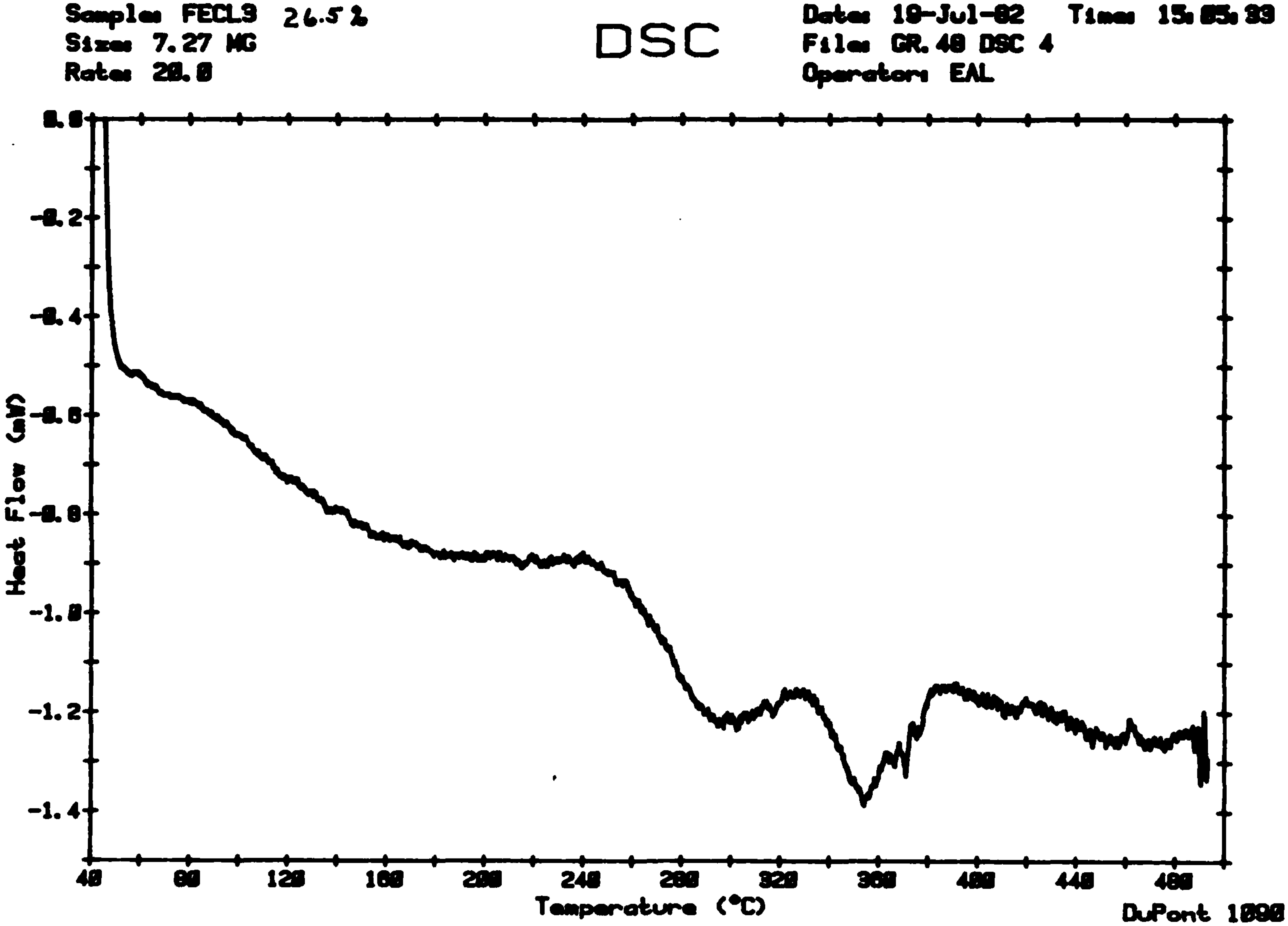

Figure 13. FSC Thermogram of Graphite/20.5 Wt. % $FeCl_3$ Intercalation

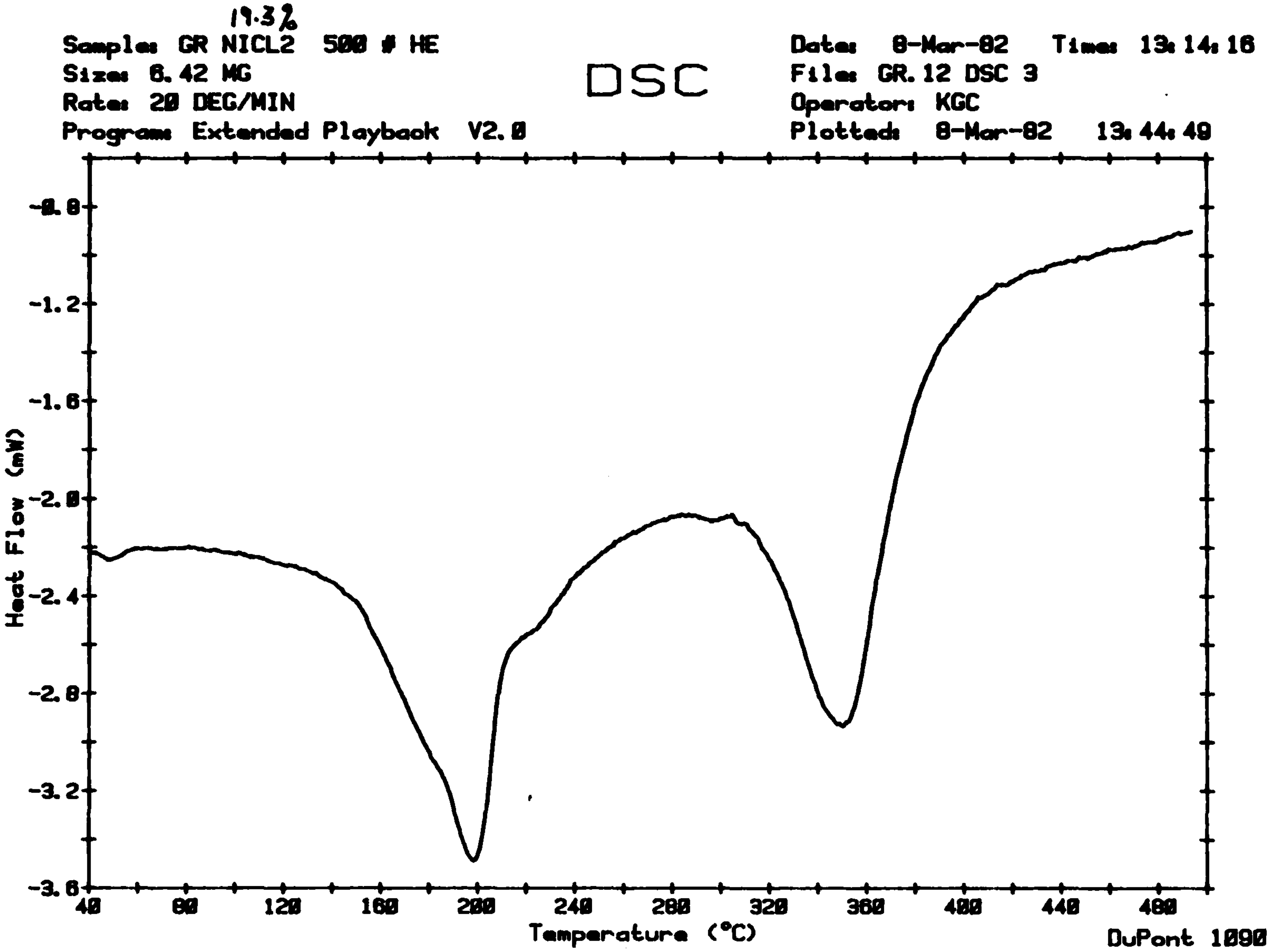

Figure 14. DSC Thermogram of Graphite/19.3 Wt. % $NiCl_2$ Intercalation Compound, As Received

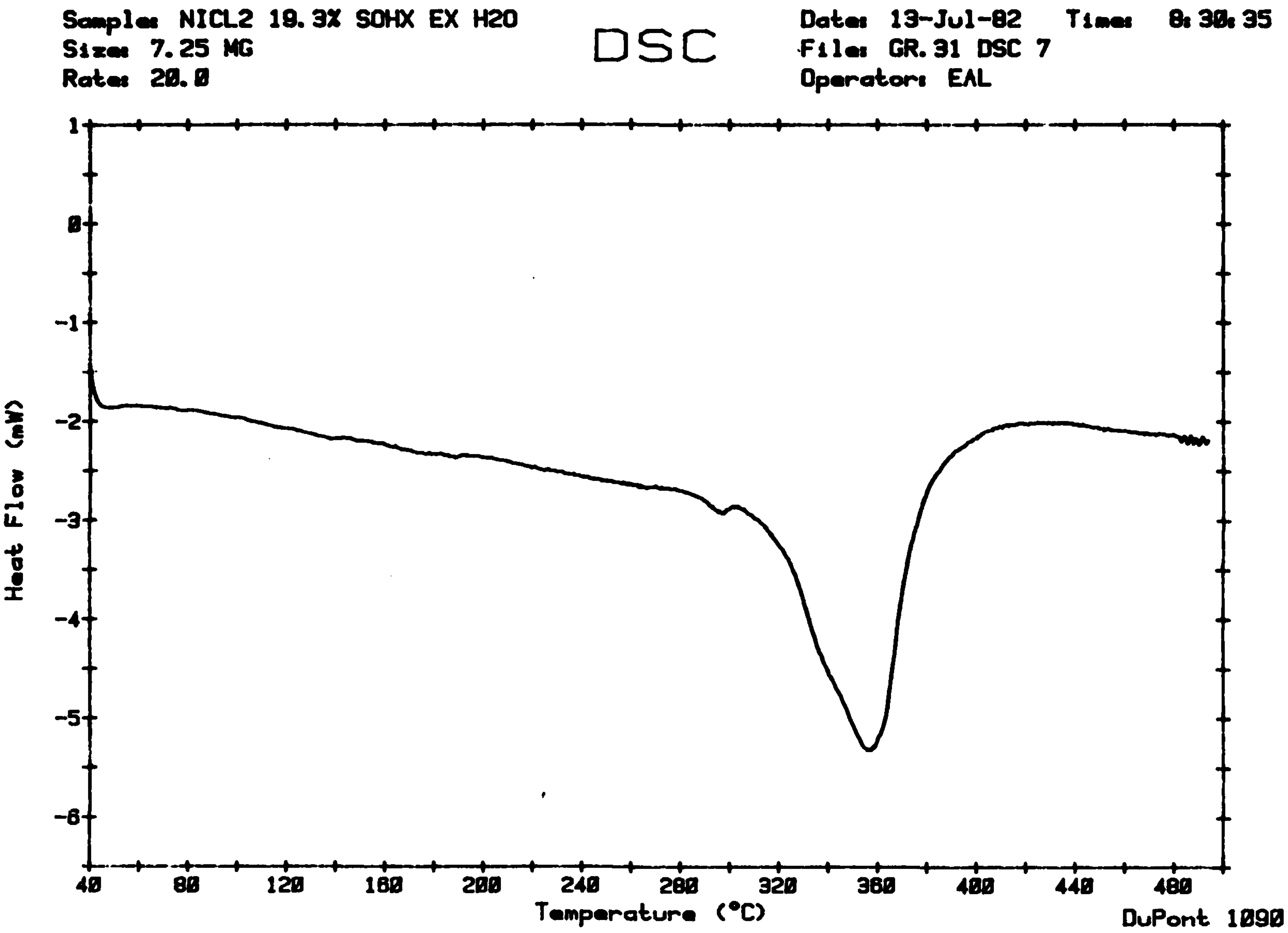

Figure 15. DSC Thermogram of Graphite/19.3 Wt. % $NiCl_2$ Intercalation Compound, Washed with Water

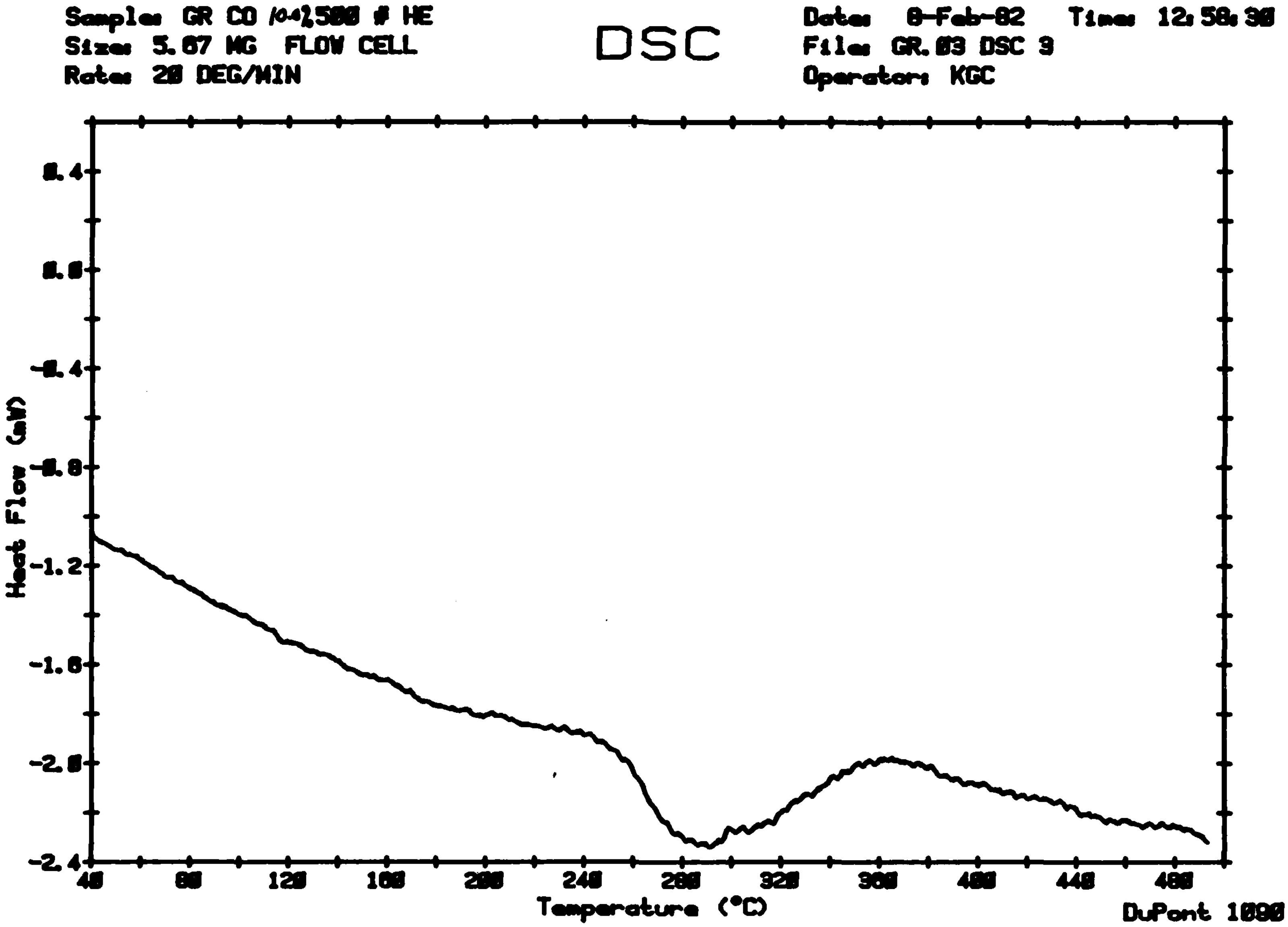

Figure 16. DSC Thermogram of Graphite/Wt. % Co. As Received

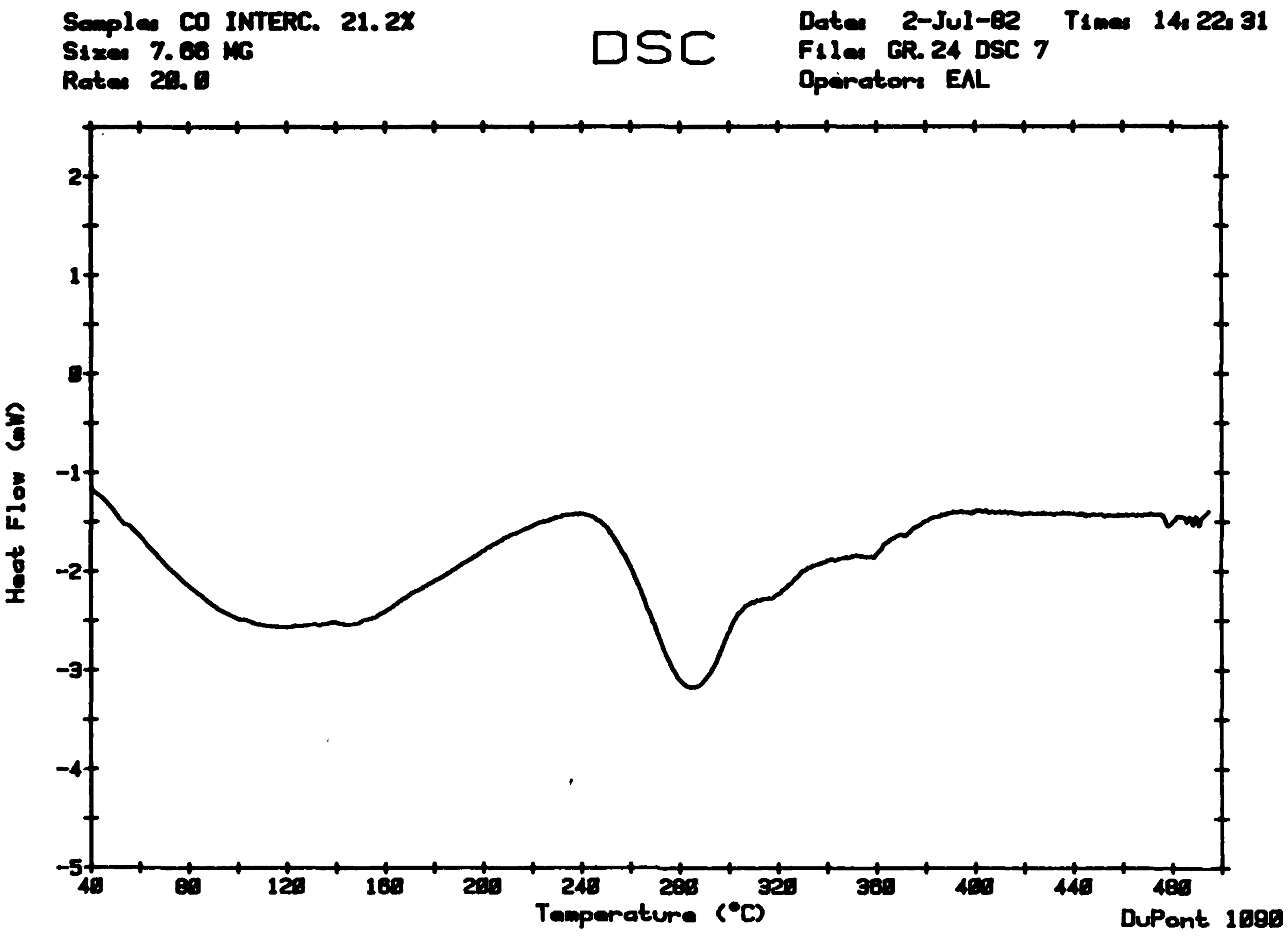

Figure 17. DSC Thermogram of Graphite/21.2 Wt. % Co, Intercalation Compound, as Received

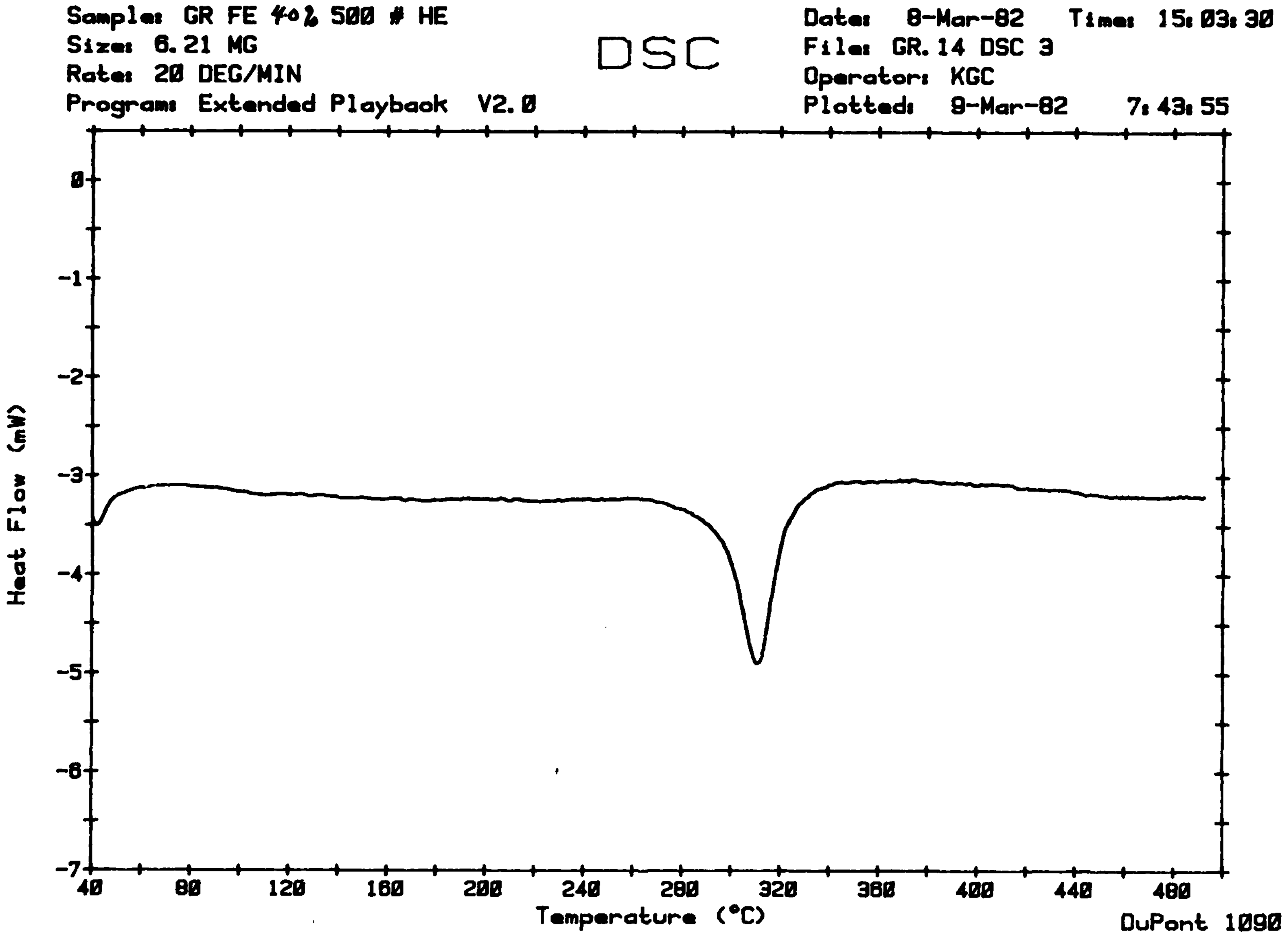

Figure 18. DSC Thermogram of Graphite/4.0 Wt. % Fe Intercalation Compound, As Received

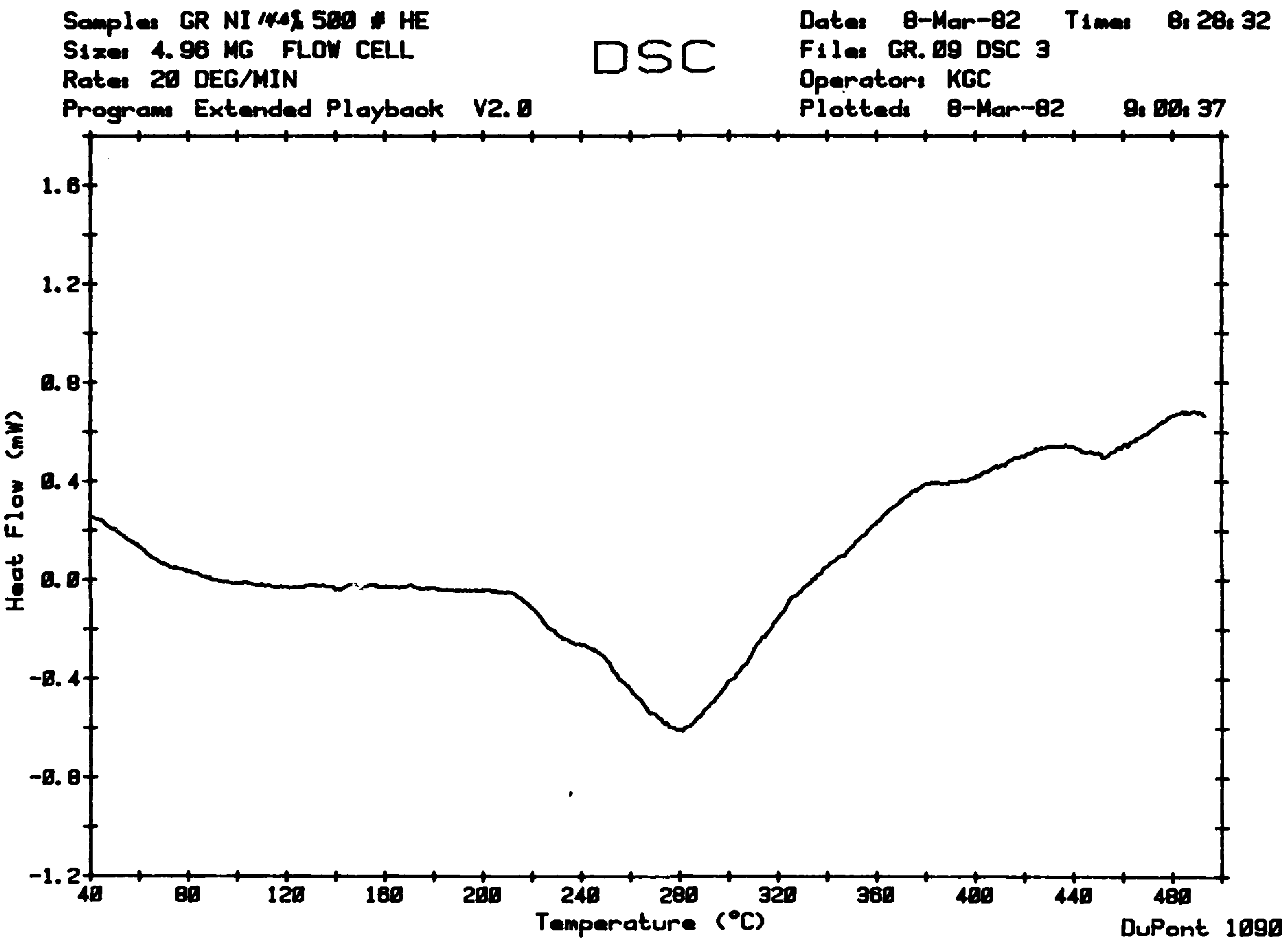

Figure 19. DSC Thermogram of Graphite/14.0 Wt. % Ni Intercalation Compound, As Received

## TABLE 1. FALEX TEST RESULTS

| Solid Film Lubricant | Average Endurance Life (4448N Gage Load) (Minutes) | Load Carrying Capacity (Newtons) |
|---|---|---|
| $MoS_2$ | 68 ± 10 | 14,457 |
| Graphite | 51 ± 8 | 6,672 |
| Graphite¢8.2 wt. % $FeCl_3$ (Intercalate) | 187 ± 24 | 11,121 |
| Graphite-8.2 wt. % $Fe\ Cl_3$ (Physical Mixture) | 90 ± 14 | 6,672 |

## TABLE 2. FALEX ENDURANCE LIFE TEST RESULTS

| Wt % | Solid Film Lubricant | Mole % | Average Endurance Life (4448N Gage Load) (Minutes) | Endurance Life Ratio (Graphite Intercalate to Graphite |
|---|---|---|---|---|
| | **Graphite/Metal Chlorides** | | | |
| 19.8 | $CoCl_2$ | 2.2 | 390 ± 65 | 7.6 |
| 13.7 | $CuCl_2$ | 1.4 | 258 ± 30 | 5.1 |
| 11.6 | $InCl_3$ | 0.71 | 188 ± 50 | 3.7 |
| 8.2 | $FeCl_3$ | 0.66 | 187 ± 24 | 3.7 |
| 5.0 | $YCl_3$ | 0.32 | 116 ± 22 | 2.3 |
| 12.3 | $ZrCl_4$ | 0.72 | 105 ± 24 | 2.1 |
| 17.0 | $NbCl_5$ | 0.90 | 98 ± 9 | 1.9 |
| 5.0 | $SmCl_3$ | 0.25 | 85 ± 8 | 1.7 |
| 12.2 | $MoCl_5$ | 0.61 | 81 ± 5 | 1.6 |
| 7.7 | $WCl_6$ | 0.25 | 61 ± 5 | 1.2 |
| 33.0 | $SbCl_5$ | 1.94 | 58 ± 5 | 1.1 |
| 19.3 | $NiCl_2$ | 2.2 | 45 ± 8 | 0.88 |
| 4.3 | $RuCl_3$ | 0.26 | 45 ± 8 | 0.88 |
| 1.2 | $PdCl_2$ | 0.08 | 35 ± 12 | 0.69 |
| 7.3 | $CrCl_3$ | 0.59 | 27 ± 10 | 0.53 |
| 1.2 | $PtCl_3$ | 0.09 | 15 ± 4 | 0.29 |
| 5.1 | $GaCl_3$ | 0.37 | 13 ± 10 | 0.25 |
| 37.0 | $AlCl_3$ | 5.0 | 7 ± 3 | 0.14 |
| 6.4 | $BiCl_3$ | 0.23 | 3 ± 0 | 0.06 |
| | **Graphite/Metals** | | | |
| 10.0 | Co | 2.7 | 163 ± 32 | 3.2 |
| 4.0 | Re | 0.89 | 161 ± 22 | 3.2 |
| 5.1 | Cu | 1.0 | 78 ± 8 | 1.5 |
| 14.0 | Ni | 3.2 | 43 ± 8 | 0.84 |
| 2.3 | Rh | 0.27 | 30 ± 13 | 0.59 |
| 1.6 | Ru | 0.19 | 7 ± 4 | 0.14 |
| 1.7 | Pd | 0.20 | 7 ± 3 | 0.14 |
| 2.2 | Pt | 0.14 | 7 ± 3 | 0.14 |
| | **Graphite/Miscellaneous** | | | |
| | Oxide *62.2 wt. % C) | | 37 ± 10 | 0.73 |
| | 47.8 wt. % $SbF_5$ | | 30 ± 8 | 0.59 |
| | Fluoride $(CF_x)_n$ x >1 | | 10 ± 4 | 0.20 |
| | 58.2 wt. % $CrO_3$ | | 0 ± 0 | 0 |

TABLE 3. COMPOSITION AND ENDURANCE LIFE OF $CoCl_2$ CONTAINING SOLID LUBRICANT MATERIALS

| | Wt. % | | | |
|---|---|---|---|---|
| Material | Non-Intercalated $CoCl_2$ | Intercalated $CoCl_2$ | Graphite | Falex Endurance Life (min) |
| 19.8 wt. % $CoCl_2$ As Received | 4.6 | 15.2 | 79.6 | 390 ± 65 |
| After Extraction with $H_2O$ | 0 | 16.0 | 84.0 | 119 ± 18 |
| $CoCl_2$ Added | 4.6 | 15.2 | 79.6 | 346 ± 40 |
| Graphite - $CoCl_2$ (Physical Mixture) | 4.6 | 0 | 95.4 | 68 ± 4 |
| Graphite Only | 0 | 9 | 100.0 | 51 ± 8 |

TABLE 4. COMPOSITION AND ENDURANCE LIFE OF "AS RECEIVED" AND WATER EXTRACTED INTERCALATION COMPOUNDS

| Material | Composition (Wt. %) Non-Intercalated Metal Chloride | Composition (Wt. %) Intercalated Metal Chloride | Composition (Wt. %) Graphite | Falex Endurance Life (Minutes) |
|---|---|---|---|---|
| 19.8 wt. % $CoCl_2$, As Received | 4.6 | 15.2 | 79.6 | 390 ± 65 |
| After extraction with $H_2O$ | 0 | 16.0 | 84.0 | 119 ± 18 |
| 8.2 Wt. % $FeCl_3$ As Received | 3.5 | 4.7 | 91.8 | 187 ± 24 |
| After extraction with $H_2O$ | 0 | 4.9 | 95.1 | 110 ± 12 |
| 5.0 Wt. % $FeCl_3$ Prepared In-House | 0 | 5.0 | 95.0 | 105 ± 16 |
| 5.0 Wt. % $YCl_3$ As Received | 3.4 | 1.6 | 95.0 | 116 ± 22 |
| After extraction with $H_2O$ | 0 | 1.7 | 98.3 | 48 ± 10 |

## TABLE 5. SUMMARY OF DSC THERMOGRAM ANALYSIS ON VARIOUS INTERCALATION COMPOUNDS

| Graphite Intercalation Compound | Molecular Formula | Molecular Weight | Mole Percent Intercalant | Thermal Decomposition Onset Temp. C | Quantity of Heat Associated with Endotherm Cal/g of Sample | Reference Figure |
|---|---|---|---|---|---|---|
| Graphite | C | 12.011 | 0 | None | --- | 3 |
| 19.8 wt. % $CoCl_2$, As Received | Mixture of Intercalated compound and free $CoCl_2$ | -- | -- | 532 | 14.2 | 4 |
| 16.0 wt. % $CoCl_2$ | $C_{57}CoCl_2$ | 815 | 1.72 | 325 | 14.9 | 6 |
| 38.4 wt. % $CoCl_2$ | $C_{17}CoCl_2$ | 334 | 5.56 | 325 | 6.5 | 8 |
| 43.9 wt. % $CoCl_2$ | $C_{14}CoCl_2$ | 298 | 6.67 | 325 | 7.5 | 9 |
| 8.2 wt. % $FeCl_3$, As Receiver | Mixture of Intercalated compound and free $FeCl_3$ | --- | --- | 325 | 1.4 | 10 |
| 4.9 wt. % $FeCl_3$ | $C_{262}FeCl_3$ | 3310 | 0.38 | 310 | 1.2 | 11 |
| 15.1 wt. % $FeCl_3$ | $C_{76}FeCl_3$ | 1075 | 1.30 | 260 | 0.97 | 12 |
| 26.5 wt. % $FeCl_3$ | $C_{37}FeCl_3$ | 607 | 2.63 | 325 | 1.1 | 13 |
| 19.3 wt. % $NiCl_2$, As Received | Mixture of Intercalated compound and free $NiCl_2$ | --- | --- | 310 | 22.3 | 14<br>15 |
| 11.9 wt. % $NiCl_2$ | $C_{80}NiCl_2$ | 1091 | 1.23 | 310 | 43.4 | |
| 10 wt. % Co | $C_{44}Co$ | 587 | 2.22 | 240 | 3.2 | 16 |
| 21.2 wt. % Co | $C_{18}Co$ | 275 | 5.26 | 240 | 9.0 | 17 |
| 4.0 wt. % Fe | $C_{112}Fe$ | 1401 | 0.88 | 300 | 4.2 | 18 |
| 14.0 wt. % Ni | $C_{30}Ni$ | 419 | 3.23 | 215 | 8.1 | 19 |

TABLE 6. KINETICS OF THE DECOMPOSITION OF GRAPHITE/ 16.0 WT. % $CoCl_2$ INTERCALATION COMPOUND AT 425°C

| Time (hrs) | Wt. % of Intercalate | Wt. % of Total Compound |
|---|---|---|
| 1 | 3.63 | 0.58 |
| 4 | 14.13 | 2.26 |
| 21 | 18.75 | 3.00 |
| 64 | 33.07 | 5.28 |

# APPENDIX A - PROPERTIES OF METALS AND METAL CHLORIDES USED AS INTERCALANTS

| Metal Halide | Molecular Weight | Crystal Structure | Density g/cc | Lattice Constants |  |  |  | Melting Point, C | Atoms Per Unit Cell | Volume of Unit Cell Å$^3$ |
|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  | a | b | c | angle° |  |  |  |
| CoCl$_2$ | 129.84 | Hexagonal | 3.36 | 3.544 | - | 17.430 | - | 740 | 3 | 189.58 |
| NiCl$_2$ | 129.62 | Hexagonal | 3.55 | 3.543 | - | 17.335 | - | 1001 | 3 | 188.44 |
| FeCl$_3$ | 162.21 | Hexagonal | 2.90 | 6.06 | - | 17.38 | - | 306 | 6 | 552.73 |
| AlCl$_3$ | 133.34 | Pseudo Hexagonal | 2.44 | 5.91 | - | 17.52 | - | 193 | 6 | 529.94 |
| CaCl$_3$ | 158.35 | Hexagonal | 2.76 | 6.00 | - | 17.30 | - | 1150 | 6 | 539.35 |
| RuCl$_3$ | 207.43 | Hexagonal | 3.11 | 5.97 | - | 17.20 | - | d 500 | 6 | 530.88 |
| SbCl$_5$ | 299.02 | Hexagonal | 2.34 (liq.) | 7.49 | - | 8.01 | - | 2.8 | - | 389.15 |
| WCl$_6$ | 396.57 | Hexagonal | 3.52 | 6.09 | - | 16.68 | - | 248 | 3 | 535.4 |
| CuCl$_2$ | 134.44 | Monoclinic | 3.39 | 6.70 | 3.30 | 6.85 | B = 121 | 620 | 2 | 129.82 |
| AlCl$_3$ | 133.34 | Monoclinic | 2.44 | 5.92 | 10.22 | 6.16 | B = 108 | 193 | 4 | 354.45 |
| YCl$_3$ | 195.26 | Monoclinic | 2.67 | 6.92 | 11.94 | 6.44 | B = 111 | 721 | 4 | 496.76 |
| InCl$_3$ | 221.18 | Monoclinic | 3.46 | 6.41 | 11.10 | 6.31 | B = 110 | 586 | 4 | 442.4 |
| TaCl$_5$ | 358.21 | Monoclinic | 3.68 | 18.30 | 17.96 | 5.89 | B = 91 | 216 | 12 | 1935.1 |
| MoCl$_5$ | 273.03 | Monoclinic | 2.93 | 17.31 | 17.81 | 6.08 | B = 96 | 194 | 12 | 1864.8 |
| NbCl$_5$ | 270.17 | Monoclinic | 2.75 | 18.30 | 17.96 | 5.89 | B = 91 | 205 | 12 | 1935.1 |
| PtCl$_4$ | 336.90 | Cubic | 4.30 | 10.45 | - | 5.89 | - | d370 | 8 | 1147.2 |
| ZrCl$_4$ | 233.03 | Cubic | 2.80 | 10.32 | - | - | - | - | 8 | 1099.1 |
| PdCl$_2$ | 177.31 | Orthorhombic | 4.00 | 3.81 | 11.0 | 3.34 | - | d500 | 2 | 139.98 |
|  | Atomic Wt. |  |  |  |  |  |  |  |  |  |
| Ni | 58.71 | Face-centered cubic | 8.90 | 3.52 | - | - | - | 1453 | 4 | 43.99 |
| Cu | 63.55 | Face-centered cubic | 8.92 | 3.61 | - | - | - | 1083 | 4 | 47.05 |
| Rh | 102.91 | Face-centered cubic | 12.4 | 3.80 | - | - | - | 1966 | 4 | 54.87 |
| Pd | 106.40 | Face-centered cubic | 11.4 | 3.88 | - | - | - | 1552 | 4 | 58.41 |
| Pt | 195.09 | Face-centered cubic | 21.45 | 3.92 | - | - | - | 1772 | 4 | 60.24 |
| Co | 58.93 | Close Packed Hexagonal | 8.9 | 2.51 | - | 4.07 | - | 1495 | 2 | 22.21 |
| Ru | 101.07 | Close Packed Hexagonal | 12.30 | 2.70 | - | 4.27 | - | 2310 | 2 | 26.96 |
| Fe | 55.85 | Body centered cubic | 2.86 | 7.86 | - | - | - | 1535 | 2 | 23.39 |