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MASTER

STUDIES OF THE MICROSCOPIC PHYSICAL AND CHEMICAL PROPERTIES OF GRAPHITE INTERCALATION COMPOUNDS

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Research Progress: Initial 8 months (July 1981 through February 1982)

As summarized in Appendix I the principal investigator, co-principal investigators, and graduate students have given eleven papers on DOE-related research at scientific meetings since the initial funds came on board. The papers are listed in Appendix I. Four papers were given at the 15th Biennial Conference on Carbon, U. Pennsylvania, July, 1981; one invited paper was delivered at the International Conference on the Physics of Intercalation Compounds, Trieste, Italy July 19-26, 1981; and five papers have been submitted for March 1982 American Physical Society meeting in Dallas. The University of Kentucky Research Foundation has made several contributions (totalling ~2 K$) to assist in the past travel expenses to these meetings. The publications that stem from the research reported at these meetings are beginning to appear in print, have been recently submitted, or will be submitted shortly. Manuscripts accepted or recently submitted for publication are also listed in Appendix I.

Optical Properties

The objective of the optical reflectance measurements is to determine the frequency dependent dielectric constant $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$ for several important graphite intercalation compounds (GIC's), and to correlate $\varepsilon(\omega)$ with theoretical predictions.

As GIC's are normally good metals the dielectric constant $\varepsilon(\omega)$ has strong contributions from both interband and free carrier absorption in the visible and near infrared regions. In the past, we have collected reflectance data over the range 0.2-2.5 eV and used computer modeling to determine the dielectric constants ε_1, ε_2. Although we have been successful at this modeling, a better way to arrive at this information

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is to collect reflectance spectra over a wider range of photon energy and perform a Kramers-Kronig (K-K) transform of the reflectance data. This K-K analysis yields directly values for $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$. To accomplish this we have extended our range of measurement from 0.2 → 2 eV to 0.2 → 6.0 eV. The limit (6 eV) is the practical transmission limit in air. The K-K software is functional and we are routinely processing reflectance data in this new way. Results on graphite-$SbCl_5$ (0.2 → 6.0 eV) will be presented at the Dallas APS Meeting.

We have also begun work in vacuum-ultraviolet-spectroscopy (VUV) to cover the range 6-25 eV. Important structure due to valence band → conduction band transitions and transitons involving deep core states are contained in this range. This VUV work was not mentioned in the initial (1st year) proposal. Capital Equipment funding for this research (7 K$) has so far come from the University of Kentucky Research Foundation. The VUV spectrometer was donated (Sept. 81) to the laboratory of the principal investigator by the Department of Physics. Since then we have restored the apparatus to a working condition in the 6-11 eV range. To cover the range 11-25 eV a high-speed vacuum pump is needed to differentially pump between the source (He gas ~ 3 Torr) and the granting chamber (10^{-6} Torr). Funds (~ 10 K$) for this pump would be needed in the third year. In the short term, work will be carried out in the 6-11 eV range by isolating the grating chamber from the He-source with a LiF window. (LiF has a transmission limit of ~ 11 eV). However, funds are needed immediately for a new grating (2 K$) for the VUV spectrometer. This item did not appear in a preliminary 2nd year budget because the acquisition of the VUV spectrometer was not anticipated. The spectrometer (replacement

cost ~ 40 K$) is an unexpected windfall and will produce important data needed for energy band structure modeling in the GIC's. We propose to add one graduate student to the project to work full time on the VUV spectrometer in the 3rd and 4th years.

Raman and Inelastic Neutron Scattering

Our recent Raman scattering work has primarily focused on the intercalation-induced shifts of zone-center, zone-interior and zone-edge graphitic, phonon frequencies in prototypical acceptor ($SbCl_5$-graphite) and donor (Rb-graphite) compounds. The inelastic neutron scattering work has focussed on the low energy ($\omega < 500$ cm^{-1}) c-axis modes with displacement and wavevector parallel to the c-axis. The inelastic neutron experiments were done in collaboration with H. G. Smith, Oak Ridge National Laboratory. The data analysis is being carried out in collaboration with G. Dresselhaus, M.I.T., who is making the lattice dynamics calculations. The experimental results in these areas are summarized in the Trieste paper (Appendix I). Further neutron work is planned which will also include a study of the possible development of stage 2 $SbCl_5$-graphite material (I_c = 12.72 Å) for use as a monochromator crystal for synchotron radiation. The phonon frequencies obtained from both the Raman and inelastic neutron scattering experiments are being used as calibration points for the lattice dynamics calculations which determine the appropriate lattice force constants.

Other recent work of ours on the phonon properties of GIC's includes the first observation of Raman-active, zone-folded shear modes at low frequencies (~ 20 cm^{-1}) in (stage 2) RbC_{24} and KC_{24}. These low-frequency modes represent important low energy calibration points for lattice

dynamical modeling. Since RbC_{24} and KC_{24} have interesting in-plane structural changes associated with order-disorder transformations in the alkali metal layers, we have studied the temperature dependence of these shear modes. These modes involve rigid displacement of the carbon layers relative to the alkali metal layers. The modes present at room temperature softened by ~ 2 cm^{-1} as the temperature was lowered from 300 K through the phase transition. This temperature dependence is not in itself too interesting, but other modes are observed in the Raman spectra that grow in intensity with decreasing temperature. New phonon modes at ~35 cm^{-1} appear at temperatures below the phase transitions which we tentatively interpret as modes folded to zone center by the change in the in plane order of the alkali metal intercalate layer. We did not report this result at the Trieste Conference. The temperature dependence of these low frequency modes in C_{24} Rb are shown in the Raman spectra of Fig. (1). A manuscript concerning this work is in preparation. One puzzling aspect of the spectra seen in Fig. (1) is the mode at ~120 cm^{-1} which grows in intensity at T is lowered from 300 to 77 K. This mode may be associated with a new phase that increases its share of the sample volume as T decreases.

Hydrogen Storage in Alkali Metal-graphite Intercalation Compounds

We have been able to synthesize pure phase (single stage) $C_{24}Rb$ and $C_{24}K$ which are the starting materials for the hydrogen storage research outlined in the initial proposal. An optical cell suitable for Raman and IR spectroscopy is being developed to study the changes in the spectra attributable to H-uptake. If the hydrogen is present in molecular (H_2) form we hope to see H_2-modes in the Raman spectra.

If on the other hand, the hydrogen is bonded to either carbon (C) or alkali metal (M) atoms we hope to observe I-R active M-H or C-H strectching or bending modes. The frequency and symmetry of these modes will be used to elucidate the nature of the hydrogen intercalation. These optical experiments will be done as a function of the temperature at which the H_2 was admitted to the cell and also as a function of the subsequent sample temperature. Changes in the spectra near the in-plane structural phase transitions in $C_{24}K$ and $C_{24}Rb$ will be investigated.

Intercalation Chemistry of the MX_5-graphite Intercalation Compounds: (M = As, Sb, X = Cℓ,F)

This phase of the work has consisted primarily of complimentary x-ray and Mossbauer spectroscopy studies. The Mossbauer work is being carried out in close collaboration with Professor P. Boolchand (U. Cincinnati) under a subcontract. Recent published results in these areas are summarized in the Trieste paper (Appendix I) and details are presented in a recent article in Solid State Communications (Appendix I). The x-ray and Mossbauer results are in good agreement and indicate the presence of large concentrations of $Sb^{5+}(SbX_6^-)$ and Sb^{3+} (SbX_3) (X = Cℓ,F) in the intercalate layer. The samples of graphite-$SbCl_5$ and graphite-SbF_5 were prepared and x-ray characterized at the University of Kentucky.

Further details of the interaction of the Cincinnati and Kentucky groups can be found in the subcontractors proposal. Also contained in the new subcontract proposal is a discussion of a new, joint effort shared by these two laboratories to study the physical and chemical properties of the rare earth (RE) based intercalation compounds RE-graphite (donor) and the $RECℓ_3$-graphite (acceptor). The University of

Kentucky will synthesize and x-ray characterize these new compounds. Optical measurements will also be made by us to determine the free carrier concentration from the optical plasma frequency $\omega_p = \frac{4\pi Ne^2}{m^*}$. The Mossbauer research will determine the chemical and magnetic state of the intercalated RE ions. As explained in the enclosed 2nd year subcontract-proposal, a study of GIC systems based on Sm and Eu should suffice to map out the basic physical and chemical properties of these RE-based acceptor and donor compounds.

Low Temperature Magnetoresistance (acceptor-GIC's) and Pressure-dependent Superconductivity (donor GIC's).

The oscillatory magnetoresistance studies of graphite-$SbCl_5$ were discussed in the initial grant proposal. However, our recent work in superconducting GIC's (e.g. donor compounds formed by reactions of RbHg and KHg amalgams with graphite) represents a new direction that appears promising. Our entrance into this new area seemed natural because the low temperature-high pressure apparatus needed for the experiments was already available at Kentucky.

The preliminary experimentation for the magnetotransport measurements on $SbCl_5$-graphite has been completed. The control and data acquisition circuitry for the 90 KOe superconducting solenoid station was tested and the control software debugged. We are now routinely able to sample ac or dc magnetoresistance for intercalated graphite ($\vec{H} \perp \vec{C}$) at 1024 preselected and stable magnetic field values in the range 0-70 KOe under routine operating conditions with the sample and solenoid both held at a temperature of ~4 K. The data acquisition software was supplemented by several data plotting and analysis programs, as well as a fast-Fourier-transform (FFT) program for the Shubnikov-de Haas oscillations.

Figure 2 shows the ac field-modulated magnetoresistance of the same HOPG sample for $H \lesssim 25$ KOe. Figure 3 shows the FFT spectrum for the ac data of Figure 3.

We are currently conducting Shubnikov-de Haas measurements on $SbCl_5$-graphite. We have preliminary results for a stage 3 sample. The fast-Fourier transform (FFT) spectrum of these data is shown in Figure 4.

We have also succeeded in performing the first measurements of the pressure dependence of the superconducting transition temperature T_c of an intercalated graphite material. Our results for T_c vs P for a sample of nominal composition C_8KHg are shown in Figure 5. These preliminary data strongly suggest that the T_c of (stage 2) C_8KHg decreases under pressure, in contrast to the behavior of other "layered" superconductors such as $NbSe_2$, whose T_c rapidly increases with pressure. We are now improving upon the metallurgical quality of our materials and shortly expect to obtain additional high pressure T_c data for other superconducting graphite intercalation compounds such as C_nRbHg and $C_nKT\ell_{1.5}$. Optical measurements on these materials are also in progress.

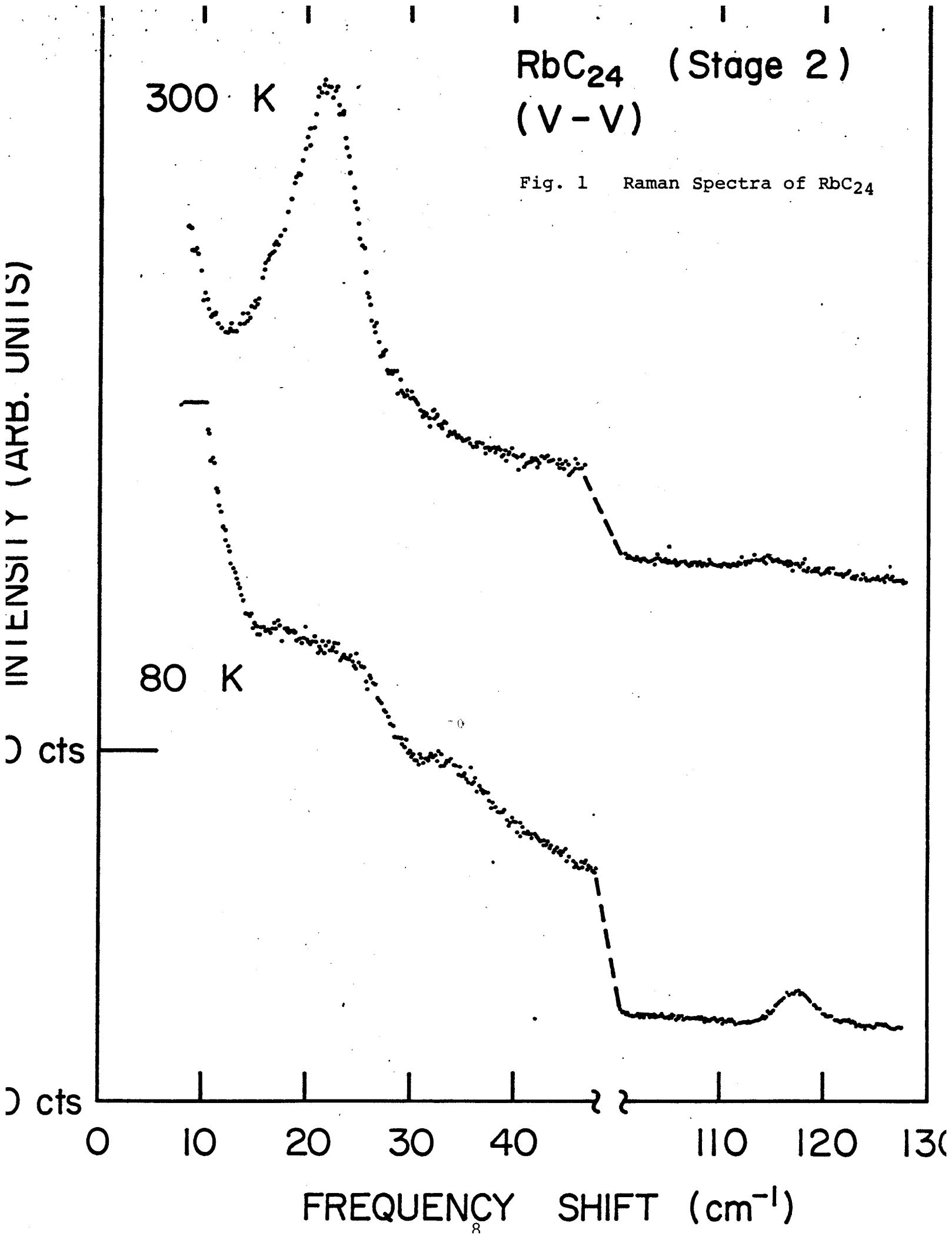

Fig. 1 Raman Spectra of RbC_{24}

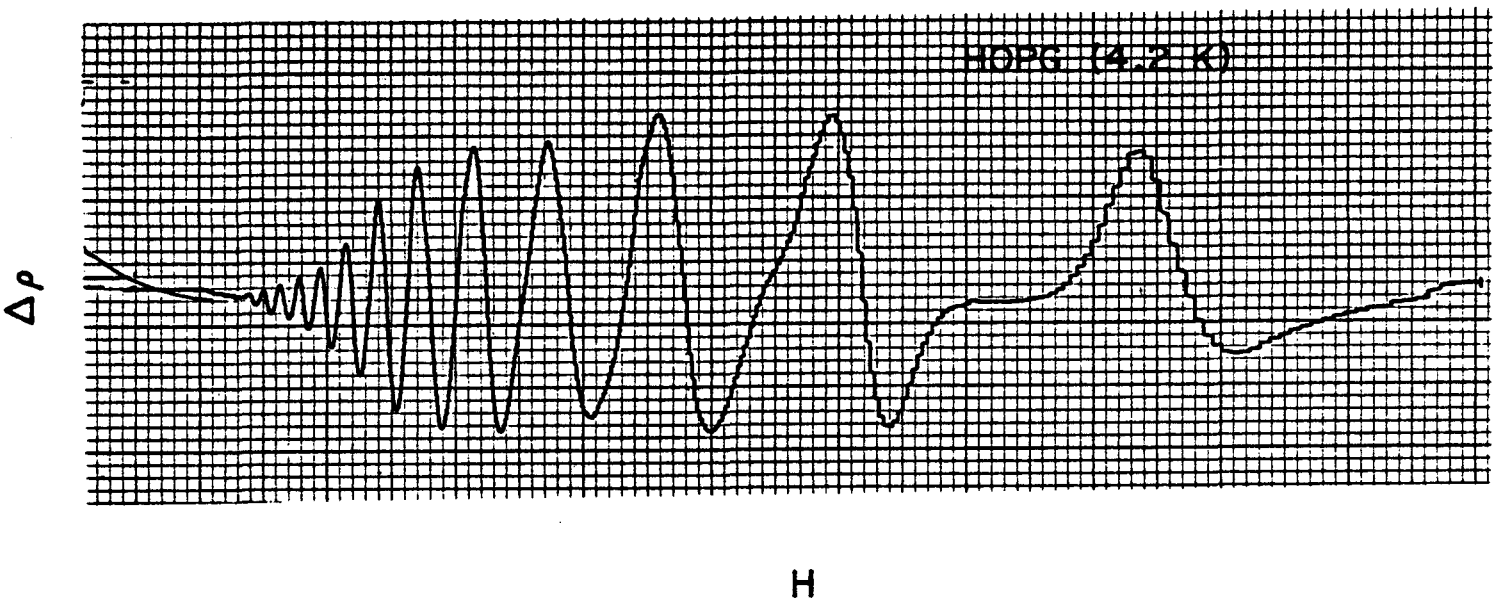

Fig. 2. Oscillatory Magnetoresistance of HOPG at T = 4.2K.

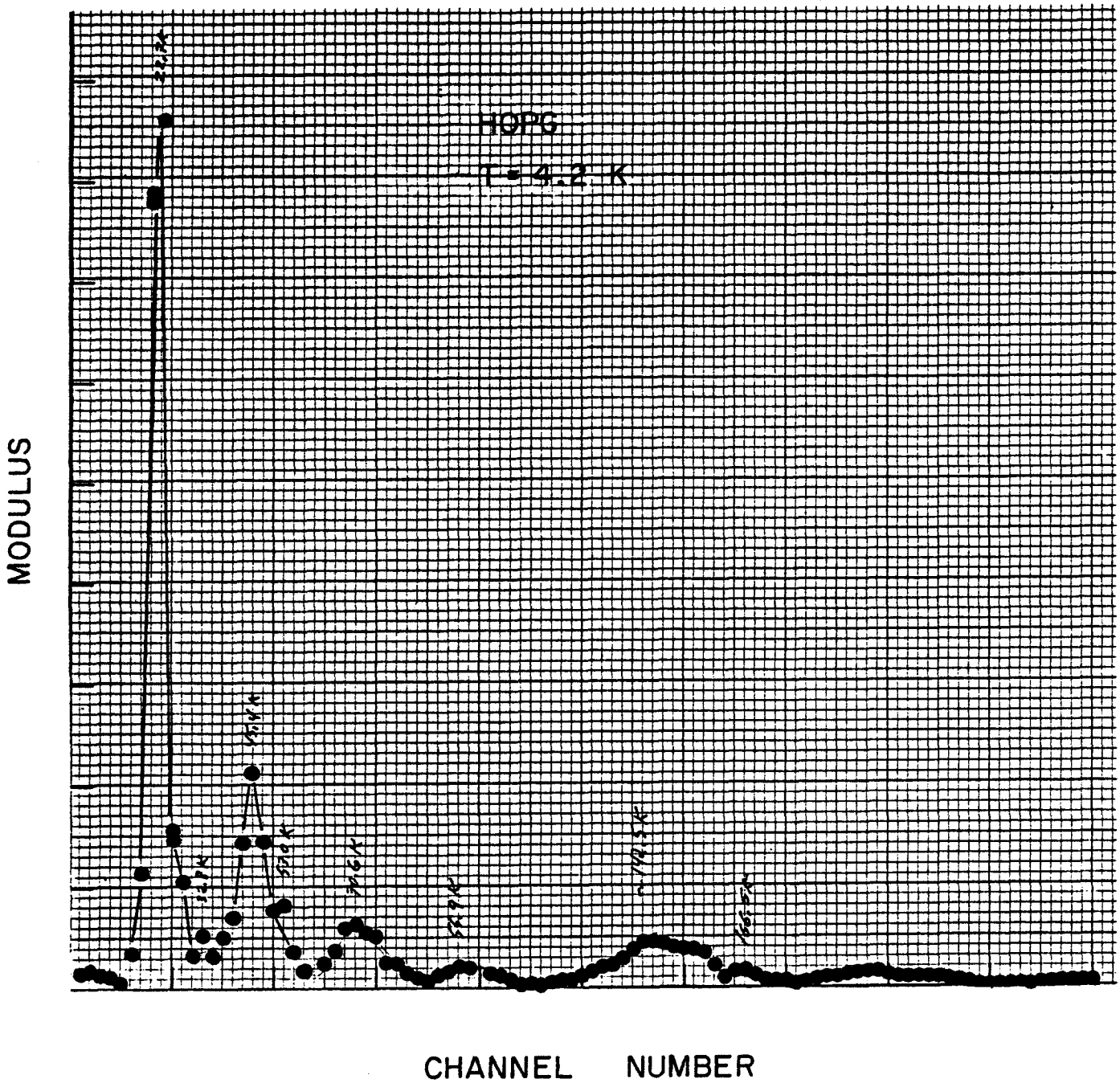

Fig. 3. FFT Spectrum of SdH effect in HOPG (T = 4.2K)

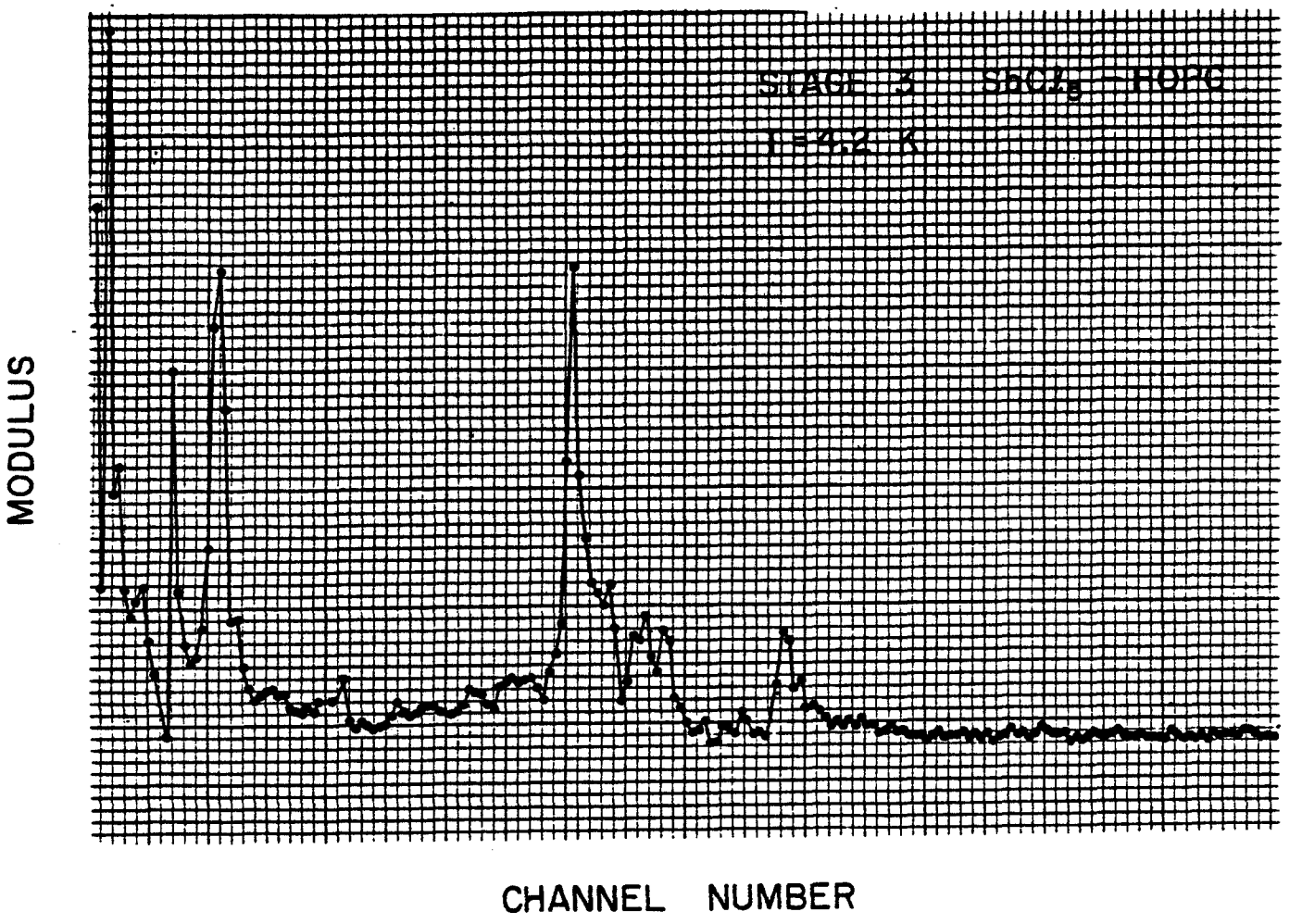

Fig. 4. FFT Spectrum of the SdH effect in Stage 3 $SbC\ell_5$-graphite (T = 4.2K).

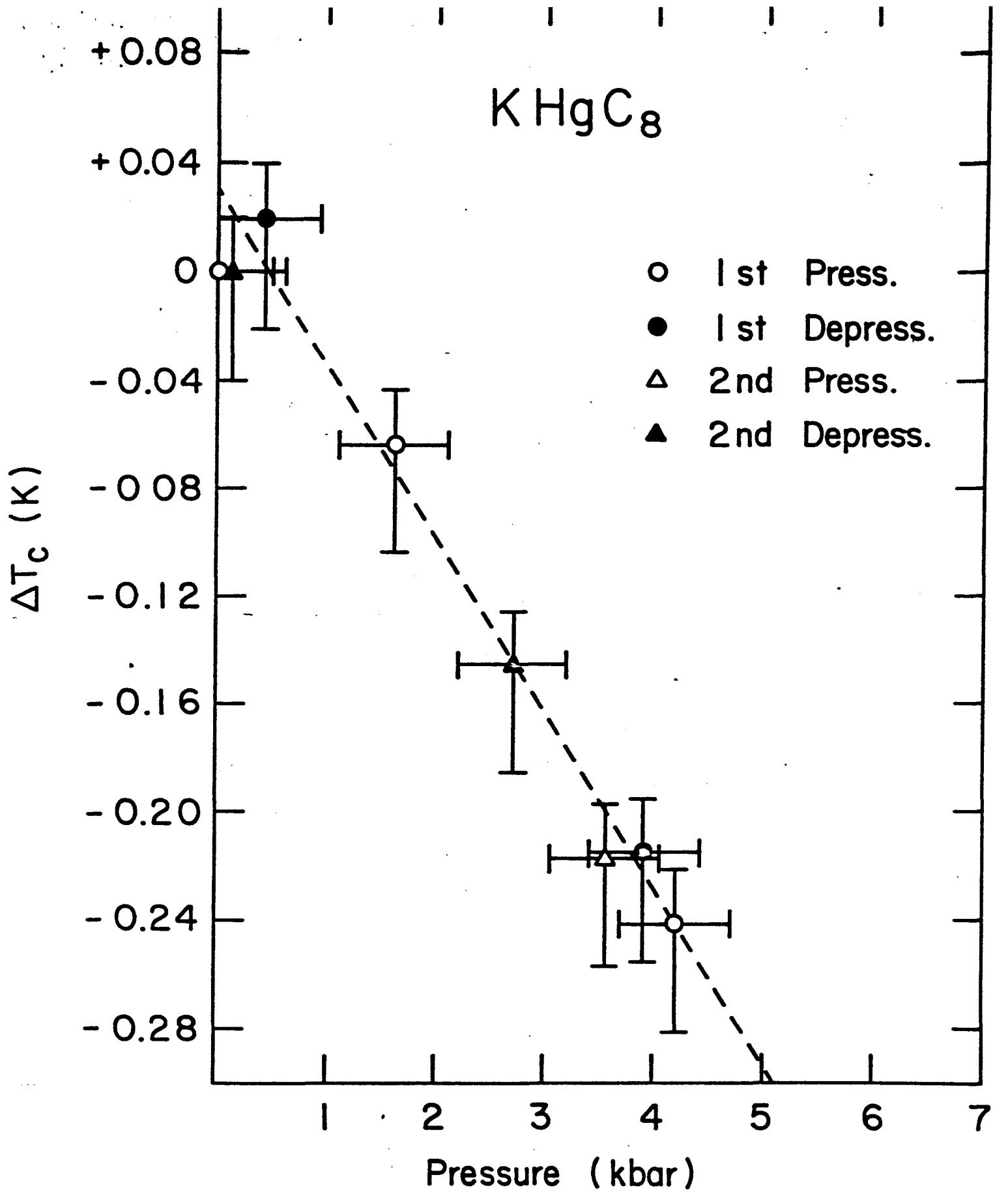

Fig. 5. Pressure dependence of the Superconducting Transition Temperature (T_c) of $KHgC_8$.

APPENDIX I

Invited Talks, Papers, and Publications

A. Invited Papers

"Phonons in Graphite Intercalation Compounds" (P. C. Eklund) presented at the International Conference on the Physics of Intercalation Compounds, Trieste, Italy (July, 1981).

B. Talks

"X-Ray Diffraction Studies of the Intercalate Layers in Antimony Chloride-Graphite", M. L. Saylors, M. H. Boca, D. S. Smith, and P. C. Eklund, presented at the 15th Biennial Conference on Carbon, Philadelphia, PA (1981).

"Intercalant Species in $SbC\ell_5$:Graphite from Mossbauer Spectroscopy", P. Boolchand, W. J. Bresser, D. McDaniel, K. Sisson, P. C. Eklund, and V. Yeh, presented at the 15th Biennial Conference on Carbon, Philadelphia, PA (1981).

"Electronic Excitations in $SbC\ell_5$ Intercalated Graphite", J. J. Ritsko, E. J. Mele, and P. C. Eklund, presented at the 15th Biennial Conference on Carbon, Philadelphia, PA (1981).

"Two-Phonon Raman Scattering from Graphite Intercalation Compounds", J. Giergiel, P. C. Eklund, and C. Underhill, presented at the 15th Biennial Conference on Carbon, Philadelphia, PA (1981).

"Identification of the Intercalant Species in $SbC\ell_5$-Graphite and SbF_5-Graphite Using Mossbauer Spectroscopy", K. Sisson, P. Boolchand, W. J. Bresser, D. McDaniel, V. Yeh and P. C. Eklund (Dallas APS Meeting, March 1982).

"Optical Reflection Studies of Graphite-Antimony Chloride Intercalation Compounds", R. E. Heinz, D. S. Smith, P. C. Eklund, and R. Clarke (Dallas APS Meeting, March 1982).

"Low Temperature Specific Heat of Some $SbC\ell_5$ and $A\ell C\ell_3$ Graphite Intercalation Compounds", D. G. Onn, L. Q. Wang, Y. Obi, G. Hooley, and P. C. Eklund (Dallas APS Meeting, March 1982).

"Raman Scattering from Low Frequency Phonons in KC_{24}", J. Giergiel, P. C. Eklund, R. Al Jishi, and G. Dresselhaus. Postdeadline paper. (Dallas APS Meeting, March 1982).

C. Publications

"Identification of the Intercalant Species in $SbC\ell_5$-Graphite Using Mossbauer Spectroscopy", P. Boolchand, W. J. Bresser, D. McDaniel, K. Sisson, V. Yeh, and P. C. Eklund, Solid State Comm., in press.

"Experimental Studies of Phonon Dispersion and C-axis Structure in Graphite Intercalation Compounds", P. C. Eklund, J. Giergiel, and P. Boolchand in Proceedings of the Conference on the Physics of Intercalation Compounds, Trieste, Italy, E. Tossatti and L. Pietronerro, eds., Springer Series in Solid State Sciences (1981).

"Direct Evidence for Sb^{3+} in Graphite-SbX_5 (X=Cℓ, F) using Mossbauer Spectroscopy", P. Boolchand, W. J. Bresser, M. H. Boca, and P. C. Eklund, submitted for publication.

"X-Ray Studies of the Intercalate Layers in Stage 1, 2, 3 Graphite-Antimony Chloride Intercalation Compounds", M. H. Boca, M. L. Saylors, and P. C. Eklund, submitted for publication.

"Raman Scattering Study of the Phase Transition in the Stage 2 Graphite-Rubidium Intercalation Compound", J. Giergiel, P. C. Eklund, R. Al Jishi, and G. Dresselhaus, submitted for publication.

"X-Ray Diffraction Studies of the Intercalate Layers in Antimony Chloride-Graphite", M. L. Saylors, M. H. Boca, D. S. Smith, and P. C. Eklund, Proceedings of the 15th Biennial Conference on Carbon, Philadelphia, PA (1981).

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