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ELECTRONIC PROPERTIES OF INTERCALATED GRAPHITE AND
AMORPHOUS METALS(U) NORTHEASTERN UNIV BOSTON MA
R S MARKIEWICZ ET AL. 24 OCT 84 AFOSR-TR-84-0971

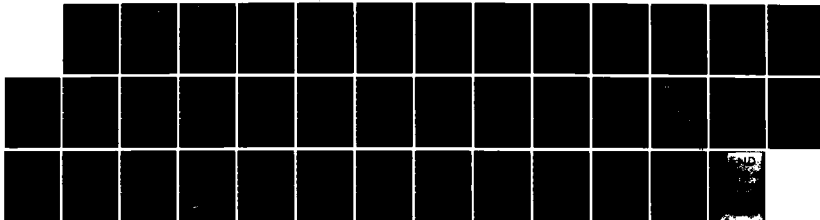
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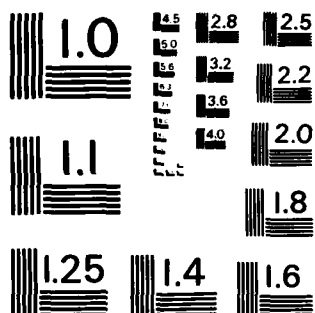
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) A general solution has been proposed to the problem of resolving the fundamental Fermi surface sections from magnetooscillations in graphite acceptor compounds, allowing quantitative measure of charge transfer and c-axis screening. Direct observation of magnetic breakdown proves that large, in-plane superlattices are responsible for some of the extra oscillation frequencies, while domain formation in Br₂-graphite reveals the strong magnetic interaction responsible for other frequencies. X-ray studies show		

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the superlattices directly, and reveal a commensurate-incommensurate transition in H_2SO_4 -graphite. In stage-1 AsF_5 -graphite, a discontinuous change of the magnetooscillations suggests a field-induced phase transition.

Negative magnetoresistance in Ca-Al metallic glasses has been attributed to localization effects. In La-Al glasses the superconductivity has been used to separate localization and interaction effects in the normal state. In Ge-Fe, the metal-insulator transition shows an unusual dependence on concentration, perhaps related to its magnetic properties, while in Au:Fe, the Kondo effect is found to persist in films $\leq 100\text{\AA}$ thick.

Infrared and optical reflectivities of Ni-P and La-Al glasses have been analysed to determine directly the carrier scattering time and plasma frequency as a function of alloying. In Ni-P these results have been explained by KKR-CPA calculations that show the density of states at the Fermi level decreasing with added phosphorous, but without filling the d-band. The remaining d-holes are believed responsible for the persistence of the anomalous Hall effect measured in the alloys.

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MATTHEW J. KENNEDY
Chief, Technical Information Division

1. Summary of Research Goal and Plans

(a) Intercalated Graphite

- i. To establish magnetooscillatory phenomena as a fundamental tool in intercalated graphite study, by sorting out the various effects which complicate the observed spectra. Progress made on acceptor compounds suggests that extension to the more complicated donor problem would be worthwhile.
- ii. To use x-ray studies of in plane order to analyze phase transitions in these compounds, to determine the nature of the low-temperature phases and to see if these phases change while the charge transfer in a given stage is varied.
- iii. To use the above characterizations of samples to study other properties of the graphites. In particular, how do the optical properties and resistivity anomalies change as electronic density is varied? Can these experiments tell us about pressure-induced phase transitions?

(b) Amorphous Metals

- i. To build a solid experimental foundation by a systematical study of transport properties of a large group of amorphous metals and to provide a critical test of the theories of transport in disordered systems.
- ii. To correlate transport measurement with infrared optical measurements of the same samples to understand the electronic structure of disordered systems.
- iii. To study the density of states structure of metallic glasses by

visible-UV spectroscopy to understand the persistence of "band" transitions in amorphous materials.

- iv. To prepare ultrathin films of spin-glasses, and see how their properties vary as the sample thickness is changed (dimensional crossover).

2. Status of the Research Effort

(a) Intercalated Graphite

(i). Magnetooscillation³

We came into this study with a feeling that the time was ripe for a detailed analysis of the Fermi surfaces of acceptor compounds: that beneath the welter of observed oscillation frequencies there was an underlying simplicity and that part of the complications could be ascribed to new Fermi surfaces produced by large in-plane superlattices. Our research has fully confirmed these beliefs. In a series of publications¹⁻³ we have shown that the principal Fermi surfaces for virtually all stages of every acceptor compound of graphite are well described by a simple model which uses only band parameters unchanged from pure graphite. In this single sandwich model the interactions among the n graphite layers between successive intercalant layers (for a stage n compound) are treated exactly, with the Slonczewski-Weiss-McClure model⁴, while the interactions with other layers are ignored and the interaction with the intercalant layer is treated on a simple screening model. The only unknown parameters are the charge transfer and a screening parameter. The derived values of charge transfer are in good agreement with earlier estimates, and we have provided the first direct experimental estimates of the screening. Fig. 1 suggests why this model works so well for acceptor compounds, whereas for donor compounds it may be necessary to include sandwich-sandwich interaction.⁵ It is now believed that there are no free charge carriers in the intercalant layer, even for donor compounds.⁶ Hence the c -axis conductivity σ_c should reflect the overlap between successive

graphite sandwiches. Fig. 1 shows that σ_c decreases exponentially with increasing sandwich spacing, with donor compounds having larger values of σ_c than graphite and acceptor compounds having smaller values and hence considerably less overlap.

A complete solution to the acceptor problem must also explain the "extra" frequencies observed in the de Haas-van Alphen studies of most acceptor compounds—that is frequencies not corresponding to the n Fermi surface sections expected in a stage n compound. There are a number of possible causes for extra frequencies, and we have found experimental evidence for at least three:

(i) Magnetic interferometer effect⁷—When two Fermi surfaces nearly intersect at more than one point, a strong magnetic breakdown can allow an electron to hop from one surface to the other at one breakdown point, and then back at a second point. This hopping electron will travel a slightly different path from one which doesn't hop, and the two electrons will interfere (just as in the two slit interference of light) producing a very low frequency corresponding to the area between the two breakdown points. We have evidence for this effect in both AsF_5 ⁸ and HNO_3 ⁹ intercalation compounds.

(ii) Magnetic interaction—The magnetic field which enters the theoretical de Haas-van Alphen expressions for the magnetization M is the magnetic induction B , which itself contains a contribution from M . Hence, any oscillation in M should be modulated by every other oscillation frequency, producing sum and difference frequencies and anomalously strong harmonics in the observed magnetooscillation spectrum.

This effect should be particularly strong in a two-dimensional system, since all carriers contribute at the same frequency. If M is large enough, the electronic system becomes unstable, and there can be a first-order transition to a state with domains of different magnetization.¹¹ We have observed prominent mixing frequencies in AsF_5 ¹ and HNO_3 ⁹ compounds, but the most spectacular results are found in Br_2 -graphite.¹² Most of our results on this compound have not yet been published, since we do not understand the behavior in detail, but we have made a number of very surprising observations:

- a) There are very strong harmonics, extending out to at best seven times the fundamental, suggesting strong interaction effects.
- b) At low fields (or high frequencies) the fundamental is at $\sim 120\text{T}$. As the field is increased, all odd harmonics (including the fundamental) vanish.
- c) As the temperature is lowered the harmonic frequencies weaken and vanish. This is the opposite of ordinary dHvA harmonics.
- d) If the sample is thermally isolated from the liquid He bath, hysteresis effects are observed: sweeping the field upwards or downwards produce qualitatively different spectra. This may suggest a coupling to the giant magnetothermal oscillations expected in a two-dimensional system.¹³ In some cases the oscillations have extremely sharp onsets, which may be resolution limited and may even be discontinuous.

Vagner, et. al.¹⁴ have suggested that in such a system an effect analogous to the quantum Hall effect may occur, with a zero resistance

state in fields where the two domains are present. We have not so far seen such an effect, and Azbel (personal communication) has suggested that it may not occur, but clearly this system bears further study.

(iii) Superlattice effects—An in-plane ordering of the intercalant molecules will create new Brillouin zone surfaces, and if these intersect the Fermi surface they can introduce energy gaps, causing new Fermi surfaces. These will show up as extra oscillation frequencies. The original Fermi surfaces may also be observed at high fields, if the magnetic field is strong enough to induce magnetic breakdown.¹⁵ Since the Fermi surface pockets are very small, the superlattice must usually be very large to produce new surface sections (very small Brillouin zone). Our x-ray studies (discussed below) demonstrated the existence of such large superlattices in almost every compound studied, and we have now found direct evidence for magnetic breakdown from analyzing the field dependence of the magnetooscillations, in both stage 3 HNO_3 graphite⁹ and stage 7 H_2SO_4 graphite¹⁶. Fig. 2 shows the case of HNO_3 -graphite: at low fields a fairly low frequency (and its second harmonic) grow in a normal fashion with increasing field. At about 9T, this frequency begins to droop and disappear, while at the same time a considerably higher frequency suddenly grows out. This higher frequency corresponds to the larger, undistorted Fermi surface expected from the graphite band structure. The lower frequency corresponds to the fragment of Fermi surface remaining in the presence of the superlattice, and Fig. 2 illustrates the effect of magnetic field in breaking down the superlattice gaps. In all cases where magnetic breakdown is observed, x-

ray studies confirm the existence of a superlattice of the appropriate size.

Fig. 3 (in stage 1 AsF_5 -graphite) looks superficially similar, but the suddenness of the transition suggests a coherent magnetic breakdown—a field-induced phase transition. Elucidation of this transition will require considerably more work, although in Ref. 17 we offer a speculative interpretation relating it to an antiferromagnetic state at low fields. The potential significance of the transition is great. First, it suggests that the phase transition at 200K which created the superlattice is electronic in origin. This in turn could be the case for many other acceptor compounds. It could explain why nearly all acceptor compounds have transition in a narrow temperature range, why such large superlattices are involved, and why the Brillouin zone so often seems to just span a Fermi surface (Fig. 4). Secondly, the transition is similar to one observed in $(\text{TMISF})_2\text{ClO}_4$.¹⁸ The TMISF family of compounds is under intensive study at present because of its lower dimensionality and the large variety of electronic phase transitions observed, including antiferromagnetic and superconducting. Study of the transition in AsF_5 -graphite may shed light on these organic compounds and more importantly, may provide evidence that the same kinds of interesting electronic phases can occur in graphite intercalation compounds.

(ii). X-ray Studies

Studies of in-plane x-ray diffractions have been undertaken in

collaboration with D. Chipman at the Watertown Arsenal (AMMRC), and a special dewar purchased to extend the studies to liquid helium temperatures. Phase transitions to large superlattice states are observed in nearly every system studied (see Fig. 4, above). Typically, the intercalant is disordered at room temperature and undergoes an order-disorder transition near 200K. An exception is SbCl_5 -graphite which has a 14×14 superlattice both at room temperature and low temperatures, but still shows evidence for some transition at 220K. In this case only one peak shows a large increase in intensity. Strangely enough, the peak again disappears gradually at lower temperatures, reminiscent of observations by Clarke, et. al.¹⁹ We have attempted structure studies on this system, to determine the molecular arrangement responsible for such a large superlattice. We find evidence that the SbCl_6 units maintain their molecular integrity and that they occupy two inequivalent sites, but so far have not been able to compose them into a completely satisfactory whole.

All of the systems studied show sluggish, hysteretic transitions of considerable complexity, which change on aging. H_2SO_4 -graphites show double transition: order-disorder near room temperature and a complicated transition to a larger superlattice near 200K. On first cooling, through the lowest transition a stage 7 sample showed a peak split into two components, which separate gradually on further cooling. On recycling, the initial and final states remained the same but the gradual transition was washed out. This is very reminiscent of commensurate-incommensurate transitions observed on other systems.²⁰ A stage one sample showed a similar transition (although without the gradual separation). However, on warming through the transition a new transition to a third ordered phase was observed.

The experiments have all been performed on HOPG (highly oriented pyrolytic graphite), so that we observe not individual peaks but powder average rings. Since the superlattices are so large, there are many rings and it is consequently quite difficult to positively identify the superlattice unit cell or say if it is commensurate or incommensurate. To solve this problem we have begun studies of graphite single crystals (from "Ticonderoga" graphite). To complement these studies, we have built a new inductive sample holder for de Haas-van Alphen studies. Our initial experiments on Br₂-graphite were successful in observing both magnetooscillations¹² and anisotropic x-ray spectra at room temperature, and we are building a rotatable sample holder for low temperature x-ray study.

(iii). High-pressure Studies

A cell has been constructed and successfully tested on pure graphite for measuring in-plane conductivity as a function of pressure. In addition, a collaboration with Prof. Perry (NU) is studying a Br₂-graphite under pressure, using the Raman effect to look for changes in the in-plane Br-Br stretch mode. These studies will be extended under our new grant. A sandblasting unit has been set up to form samples of the appropriate shape.

(iv). Collaborations

The phase transition observed in AsF₅-graphite was found in a stage 1 sample overcharged with F₂ to enhance the conductivity, prepared by J.

Milliken (NRL) and J.E. Fischer (U. Penn.). This collaboration is continuing, and we have received additional samples for both x-ray and magnetooscillation study. In addition, Fischer is preparing a series of KHg-graphites, so that we can see if Fermi surface and x-ray studies can explain the various phases observed (red, yellow, pink) in these superconducting compounds. These are donor compounds, and it will be very interesting to see if our single sandwich model can explain these materials as well. An advantage of our inductive measurements is that the samples may be sealed in glass to eliminate any possibility of deintercalation, and it is not necessary to attach probes to the sample.

Samples of HNO_3 -graphite have been prepared and sent to B. Gerstein (Iowa State) for NML studies of diffusion, but no results have yet been reported.

Our student, A. Ibrahim, is now a post-doc at BU working with G. Zimmerman, and we are beginning a collaboration to try to understand magnetic intercalation compounds. He has found one compound in which the susceptibility anomaly is considerably less sensitive to external field and we are exploring whether magnetooscillations may be observed in the low-field as well as the high field state.

Finally, our observations of magnetic breakdown, interaction, and the field-induced phase transition has stimulated considerable theoretical interest, which may hopefully suggest further experiments. We have already received a preprint from K. Sugihara (presently at MIT) and have had much interest in our work expressed by L. Falicov (Berkeley), M. Azbel, and I. Vagner (Tel Aviv). In addition, we have an ongoing correspondence with D. Schoenberg on experimental aspects of the problem.

(b) Amorphous Metals

(i). Transport Studies

At the start of this proposal, the causes of the field and temperature dependence of the resistivity of amorphous metals were not well understood, with a number of alternative theories. Now it is clear that for a great many systems, the resistance is dominated by three-dimensional localization²¹ and interaction effects.²² Our studies²³ have been instrumental in confirming this picture. In a series of alloys of Ca-Al, La-Al, and Ge-Fe, we have observed the expected $\sqrt{T}$, $\sqrt{H}$ variation of the resistivity, and have shown that both localization and interaction effects can be important in different temperature and composition ranges.

The La-Al system offered a particular advantage, in that most compositions studied went superconducting above 1.2K. From the superconducting properties we could determine all the parameters of the localization theory (inelastic scattering rate from superconducting fluctuations above the critical temperature, diffusion constant and spin-orbit scattering rate from critical field measurements). The contribution of localization effects was found to be relatively small, ($\leq 15\%$) and when subtracted off, the remaining magnetoresistance followed the predictions of interaction theory. In particular, the conductivity ($\Delta\sigma$) scales as $\Delta\sigma/\sqrt{T}$ is a function only of H/T , going as $\sqrt{H/T}$ in the high-field limit. In addition, we analyzed how the interaction parameters and superconducting transition temperature T_c vary with composition. We have found a linear relation between T_c and the density of states at the Fermi level predicted by Varma and

Dynes²⁴.

The Ge-Fe system shows a metal-insulator transition. The critical exponent of conductivity vs. concentration lies between the theoretical values of 1 and the value of 0.5 observed in Si:P²⁵ (Fig. 5).

Hall effect measurements on metallic transition metal alloys are sensitive to the magnetic interactions through the contribution of the anomalous Hall coefficient. In a series of room temperature measurements on Ni-P amorphous alloys we have determined that both the apparent Hall coefficient and the magnetoresistance change sign at about 23 at. % P.²⁷ This is exactly the concentration at which it has been observed that the temperature coefficient of resistance (TCR) changes sign.²⁸ The behavior of the TCR has been related to the Mooij correlation between TCR and resistivity.²⁹ The resistivity near the cross-over is almost exactly the 150 $\mu\Omega$ -cm value observed by Mooij³⁰ to separate alloys with positive and negative TCR.

The anomalous Hall coefficient and the magnetoresistance are most likely related to the specific magnetic properties and electronic structure of the Ni-P alloys. Since the TCR changes sign at the same P concentration, we believe that the TCR may also be related to characteristics specific to Ni-P. In this case Ni-P may not be a good model for the (quite general) Mooij correlation. The resistivity value of the 150 $\mu\Omega$ -cm at the crossover may only be a coincidence.

(ii). Optical Studies of Metallic Glasses

In the duration of this contract we have correlated infrared conductivity, DC Hall data, and CPA calculations (in collaboration with A. Bansil and S. Khanna) to arrive at a coherent picture of the electronic structure of the important metal-metalloid glass Ni-P. Samples of electro-deposited Ni-P were produced over the range from 15 - 26 at. % P and the reflectivities studied in the spectral range $.01\text{eV} < h\omega < 2.5 \text{ eV}$.³¹ The reflectivities at frequencies below about 1 eV were found to be well fit by a free-electron Drude model, and carrier plasma frequencies and scattering times were found. Good agreement was found between the optical conductivities determined and DC conductivities from the literature, but while the conductivity decreases with increasing P concentration, the carrier scattering time was found to be increasing in the same range. This is quite contrary to the normal idea of alloy scattering in crystalline materials. When the carrier scattering is dominated by disorder, it seems that the scattering is more sensitive to the density of final states than to the presence of "impurity" atoms.

This idea was confirmed by our finding that the carrier scattering rate $1/\tau$ is linearly dependent on the square of the plasma frequency. From simple Boltzmann equation arguments ω_p^2 is dependent on the density of states at the Fermi level:

$$\omega_p^2 = \frac{8\pi e^2 N(E_F) E_F}{3m}$$

Our infrared measurements therefore indicate that the Fermi level density of states decreases as the P concentration increases. Similar conclusions can be drawn from specific heat and NMR experiments.^{32,33} At first we attributed this to d-band filling, but this was found to be inconsistent with our Hall effect measurements on the same samples.²⁷

The Hall effect in ferromagnetic materials is caused by two independent phenomena. The ordinary or classical Hall effect is caused by the Lorentz force on the electrons and is sensitive to the density of states at the Fermi level in the usual way. The extraordinary or anomalous Hall effect is related to interactions between the conduction electrons and localized magnetic moments that lead to anisotropy in the scattering.³⁴ The anomalous Hall effect disappears in non-magnetic materials and shows large changes in magnitude and sign upon magnetic ordering.

In our measurements of the room temperature Hall effect of Ni-P we determined that the Hall coefficient changes signs as a function of P concentration around 23 at. % P. We believe that it is unlikely that this represents a change of sign in the ordinary Hall coefficient. It appears more likely that the sign change is caused by a change in the anomalous Hall coefficient accompanying the ferromagnetic-paramagnetic transition at 18 at. % P. Combined with a relatively constant contribution from the ordinary Hall effect, this could explain the sign change at 23 at. % P.

The persistence of the anomalous Hall effect to above 23 at. % P, however, implies that there are still local moments (i.e., d-holes) to as large a P concentration as we have studied. This is inconsistent with a model of d-band filling to account for the decrease in the infrared plasma frequency.

To resolve this paradox we have collaborated with Prof. A. Bansil and S. Khanna of Northeastern in a KKR-CPA calculation of the electronic structure of Ni-P.³⁵ In this calculation the amorphous Ni-P is modeled as a random alloy on an fcc lattice. The real short range order of the glass is, of course, not modeled by such a theory, but the experimental density and radial distribution functions can be correctly built in. The atomic potentials are chosen assuming a certain occupancy and then justified a posteriori by the results of the calculation. The random nature of the amorphous state is taken into account in the usual CPA method by associating with each lattice site a potential which has a weighted probability of being a Ni or P potential. This calculation should accurately reproduce the features of the electronic structure that are not specifically sensitive to the particular local structure. Since many properties of amorphous metals are relatively insensitive to the method of formation, such an approach may be a reasonable approximation to the real material.

The results of the calculation are shown in Fig. 6 which illustrates the calculated density of states for a Ni₇₄P₂₆ alloy compared with the results for pure Ni. We observe that the apparent contradiction between the optical experiments and the anomalous Hall effect results is resolved in our calculation. The theoretical results shows that the density of states at the Fermi level decreases in the alloy (as indicated by the IR results) but, unlike a rigid band picture, the d-band is not filled even by 26 at. % P. This is in agreement with the persistence of the anomalous Hall effect to 26 at. % P.

Our results represent the first realistic calculation of the electronic

structure of the metal-metalloid metallic glasses. The success of this model in accounting for the qualitative behavior of the IR conductivity and Hall effect experiments verify that the overall electronic structure of Ni-P is not highly sensitive to the details of the short-range order.

A second system in which optical measurements have been made is La-Al. We have measured the reflectivity of $\text{La}_{1-x}\text{Al}_x$ sample from $x = .25$ to $x = .45$ over a spectral range from .01 eV to 2 eV.³⁶ The reflectivities were well fit over the entire range by a Drude form. This allowed a sensitive determination of ω_p and $1/\tau$ for these alloys. Fig. 7 shows the experimental reflectivities and the Drude calculation for the La-Al alloys. In Fig. 8 the dependence of the plasma frequency ω_p and the carrier scattering $1/\tau$ on aluminum concentration is illustrated. We observe a pronounced minimum in both ω_p and $1/\tau$ around 35 at. % Al. We find good agreement between the infrared conductivity ($= \omega_p^2 \tau / 4\pi$) and the measured DC conductivity for similar samples. In addition, a simple free-electron calculation gives good agreement between the plasma frequency and the Hall coefficient at $x = .30$ assuming an effective mass equal to the free electron mass. The alloy dependence of ω_p can represent either structure in the density of states or a deviation from the free electron picture ($m^* \neq 1$) away from $x = .30$. Since $1/\tau$ is nearly linear with ω_p^2 we believe that there is a significant variation in the density of states at the Fermi energy as a function of Al concentration.

The density of states of crystalline La has been calculated and displays a minimum slightly above the Fermi energy.³⁷ Calculations of liquid La show a similar but smaller dip.³⁸ If a rigid band idea can be applied, a minimum in the plasma frequency may be expected when the Fermi level is increased by

adding aluminum. Our experience with Ni-P suggests that the rigid band model may indicate the overall alloy dependence of the density of states, but is likely to be inadequate to describe the experimental results. The final word on these La-Al experiments must await a thorough experimental-theoretical collaboration.

(iii). Spin Glasses

We have prepared a series of Au:Fe films ranging in thickness from 50-4000A, and in composition from 0.1 - 2% Fe. Remarkably, the magnetoresistance is dominated by the bulk Kondo effect down to films of 100A thickness, and this effect is still strong in the thinnest films. The Fe contents were found to be too low to directly observe the spin glass freezing temperature, but the field and temperature dependence of the magnetoresistance suggests that the reduced dimensionality does not strongly affect the spin glass state, contrary to expectation.

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Figure Captions

- Fig. 1. C-axis conductivity, σ_c , of intercalation compounds, plotted against d_c' the distance between carbon layers separated by the intercalant. For comparison, the conductivity of pure graphite is also plotted, using twice the layer separation for d_c' (this is the distance that determines the second layer overlap constants γ_2 and γ_5). [Data from J.E. Fischer, in F. Levy, Ed., Physics and Chemistry of Materials with Layered Structures, Vol. 5 Intercalation Compounds (D. Reidel, Dordrecht, Holland, 1978)].
- Fig. 2. Magnetic breakdown in stage 3 HNO_3 -graphite. Upper trace = de Haas-van Alphen spectrum, lower trace = amplitude of three principal oscillation frequencies vs. field.
- Fig. 3. Field-induced phase transition in stage 1 AsF_5 -graphite [From Ref. 17].
- Fig. 4. Brillouin zones (from x-ray diffraction or magnetic breakdown studies) and Fermi surfaces (from magnetooscillation studies) for several intercalation compounds. The x-ray diffraction results give the closest match of the diffraction pattern to a commensurate superlattice. (As discussed in the text, there is some uncertainty due to the large lattice size and powder averaging). Note that in all cases there is a Fermi surface which nearly spans the Brillouin zone. For stage $n > 1$, only this Fermi surface is shown.
- Fig. 5. $T = 0$ conductivity of amorphous Ge-Fe alloys as a function of Fe concentration.

Fig. 6. Calculated density of states for crystalline Ni and amorphous Ni₇₄P₂₆.

Fig. 7. Measured reflectivity of La_xAl_{1-x} samples along with fits to Drude model (solid lines).

Fig. 8. Variation of inverse scattering time (top) and plasma frequency (bottom) as a function of Al concentration derived from fits to reflectivity data.

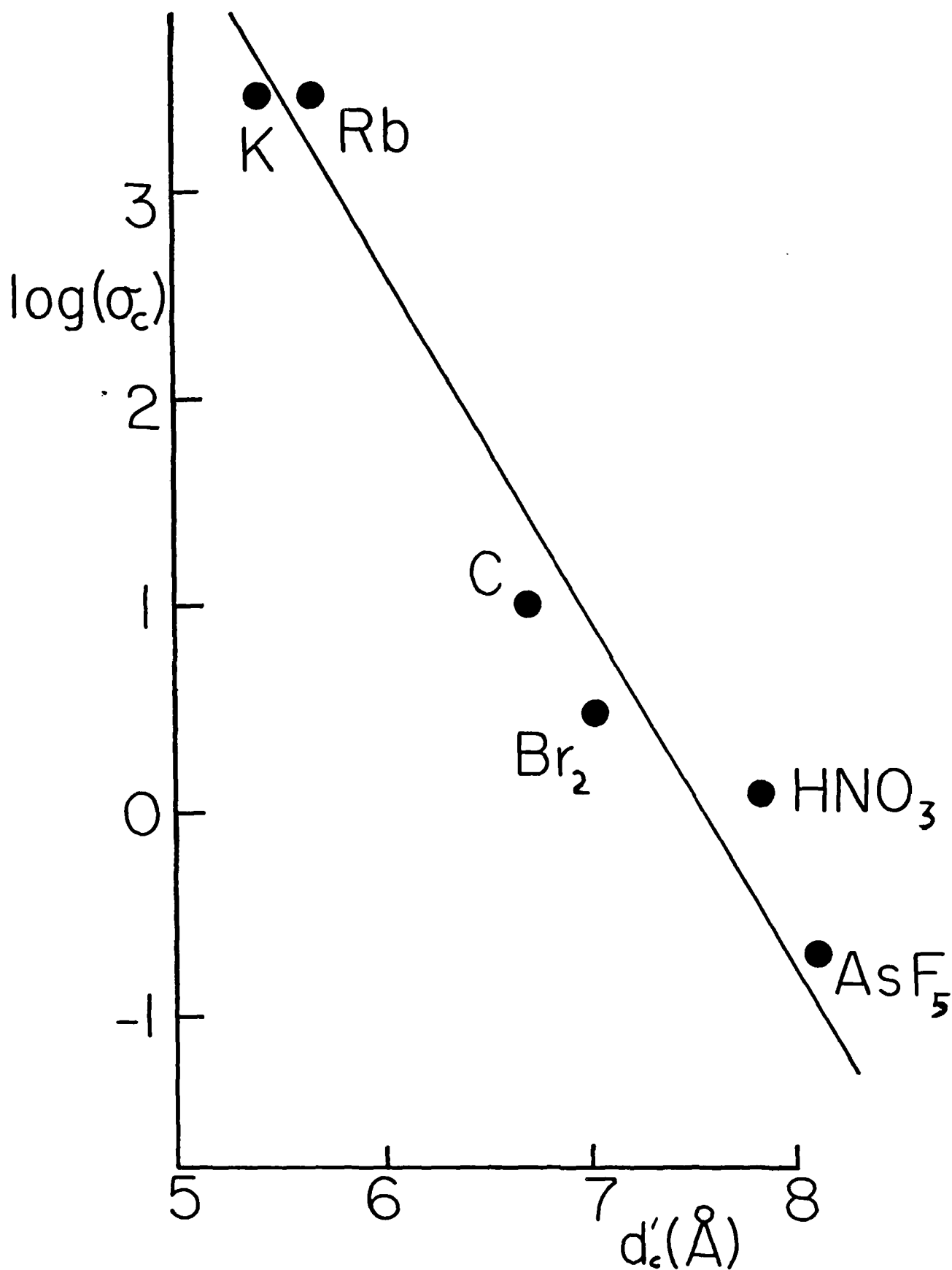


Fig. 1. C-axis conductivity, σ_c , of intercalation compounds, plotted against d'_c , the distance between carbon layers separated by the intercalant.

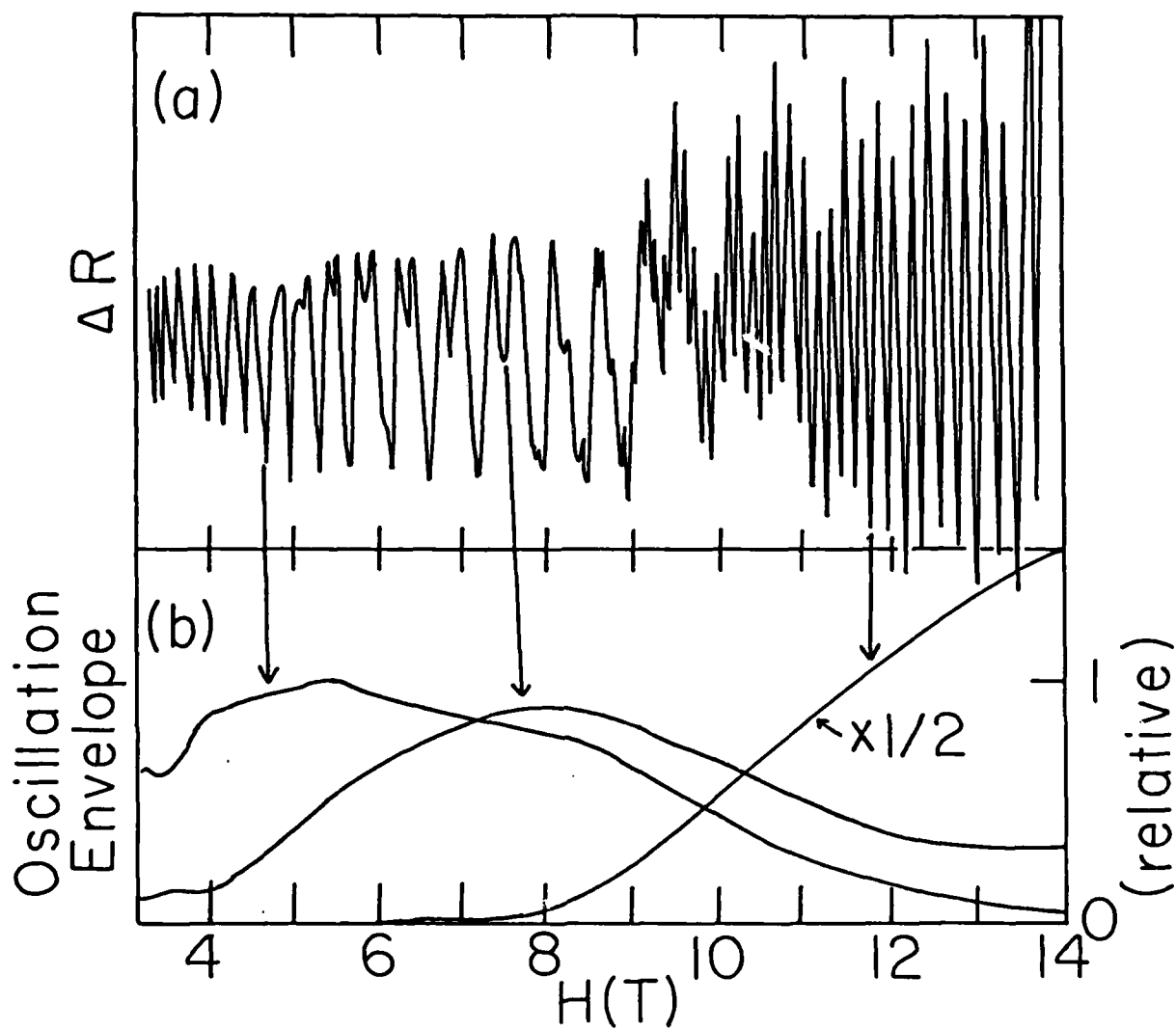


Fig. 2. Magnetic breakdown in stage 3 HNO_3 -graphite.

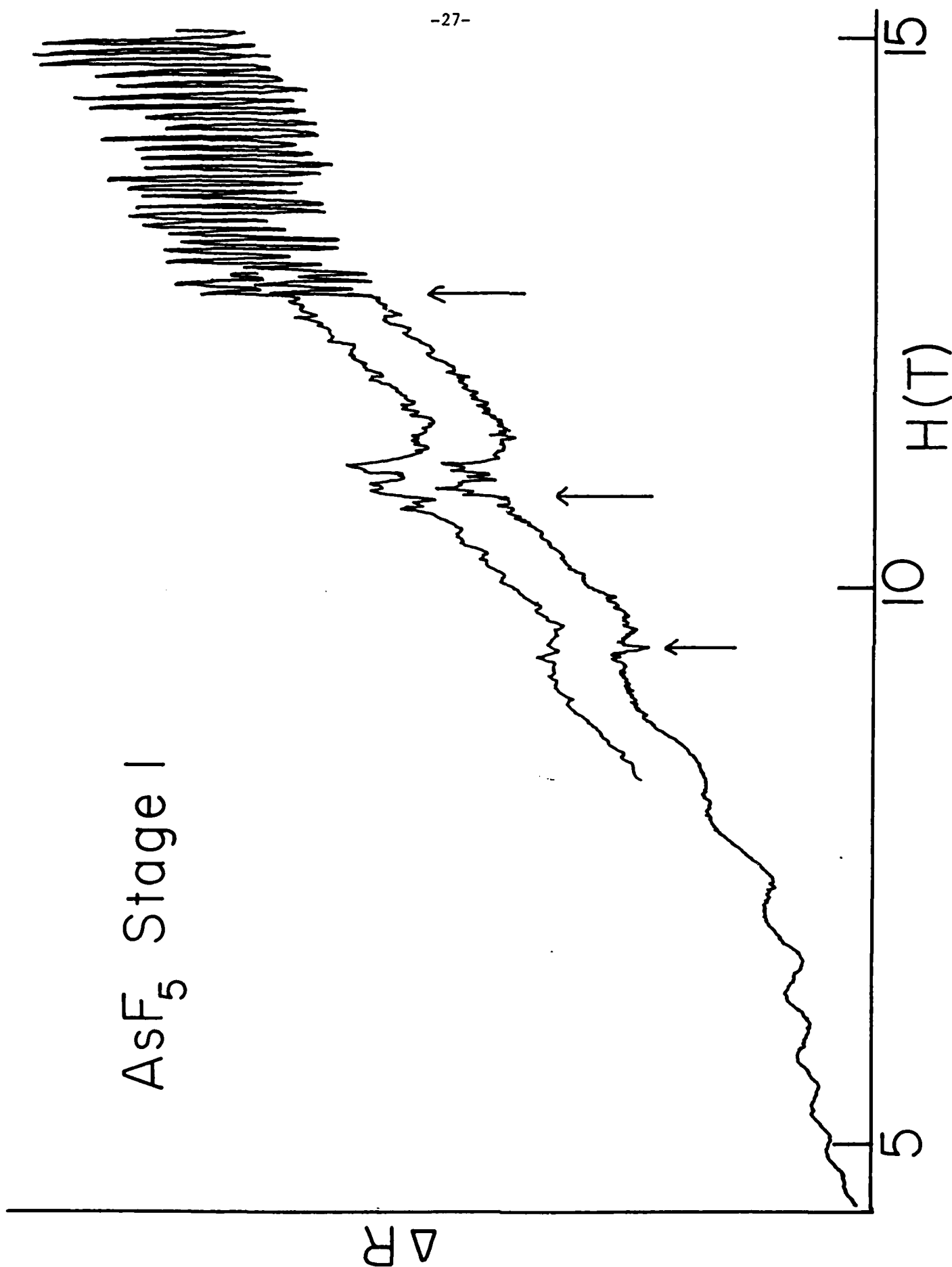
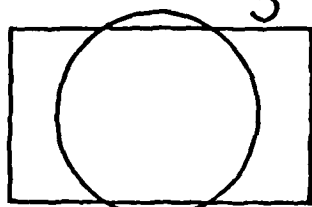
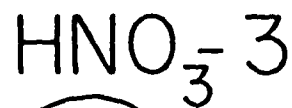
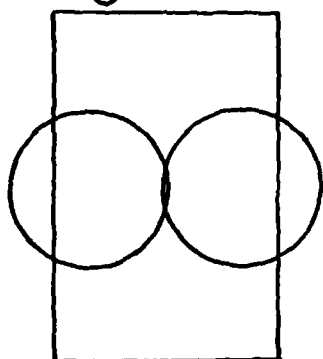
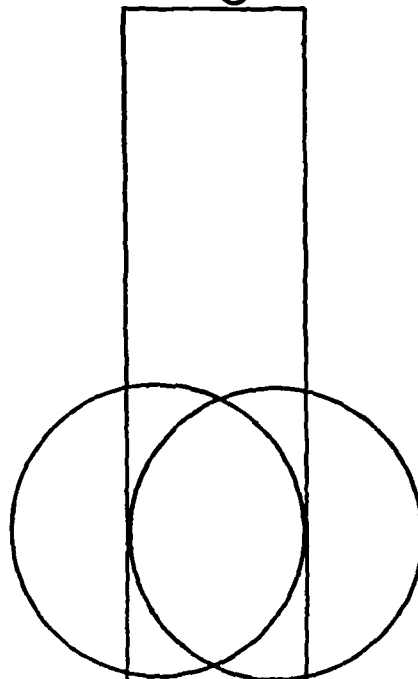
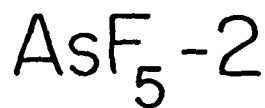
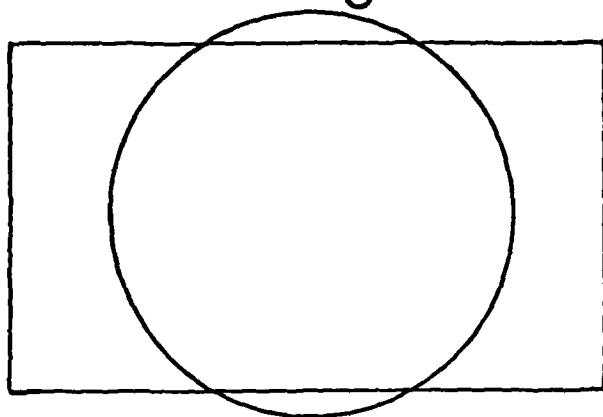


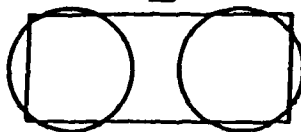
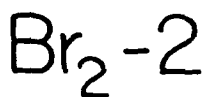
Fig. 3. Field-induced phase transition in stage 1 AsF₅-graphite .



$6\sqrt{3} \times 6$



$3\sqrt{3} \times 8$



$10\sqrt{3} \times 7$

$\sqrt{3} \times 10$

Fig. 4. Brillouin zones (from x-ray diffraction or magnetic breakdown studies) and Fermi surfaces (from magnetooscillation studies) for several intercalation compounds.

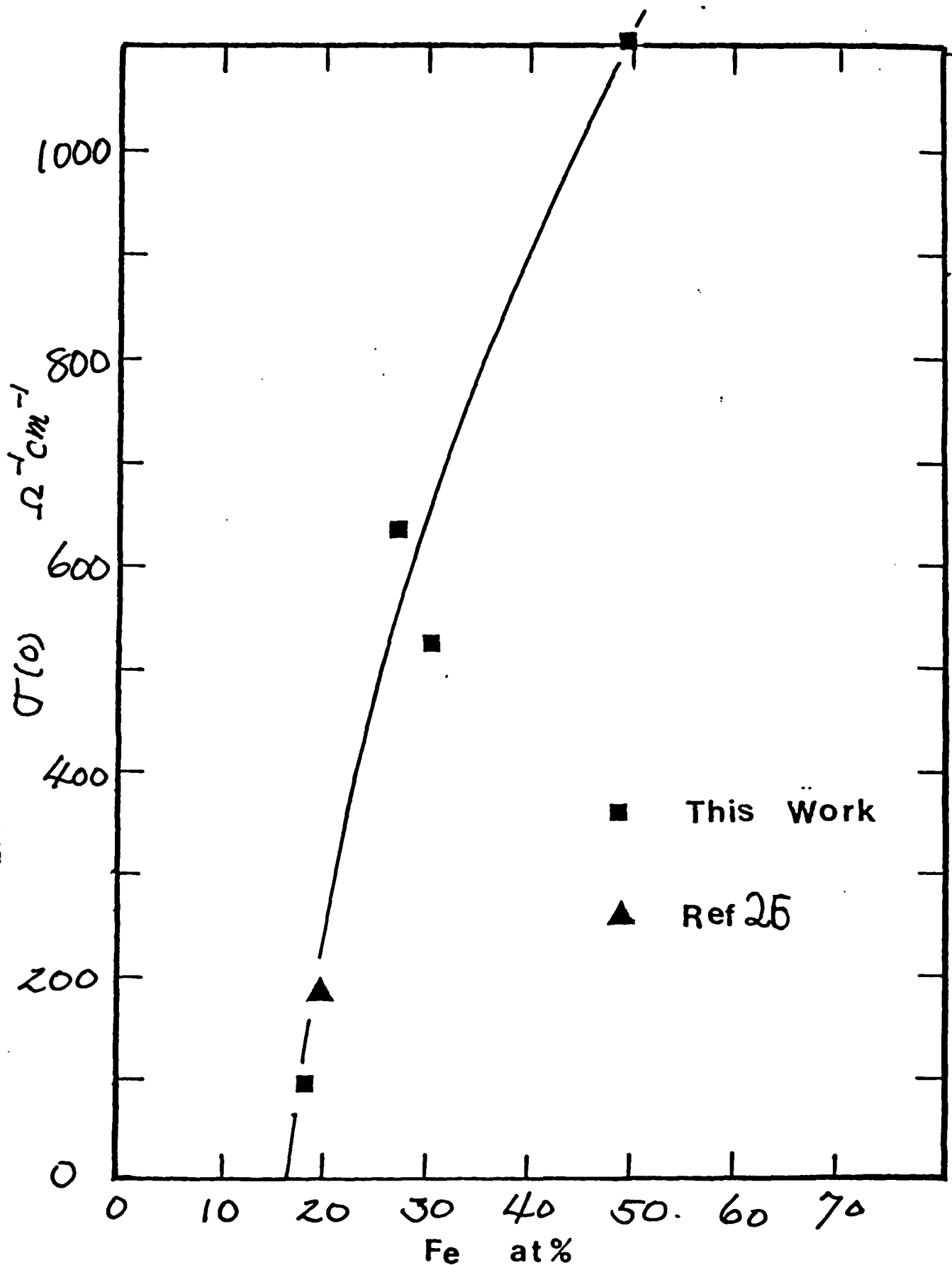


Fig. 5. $T = 0$ conductivity of amorphous Ge-Fe alloys as a function of Fe concentration.

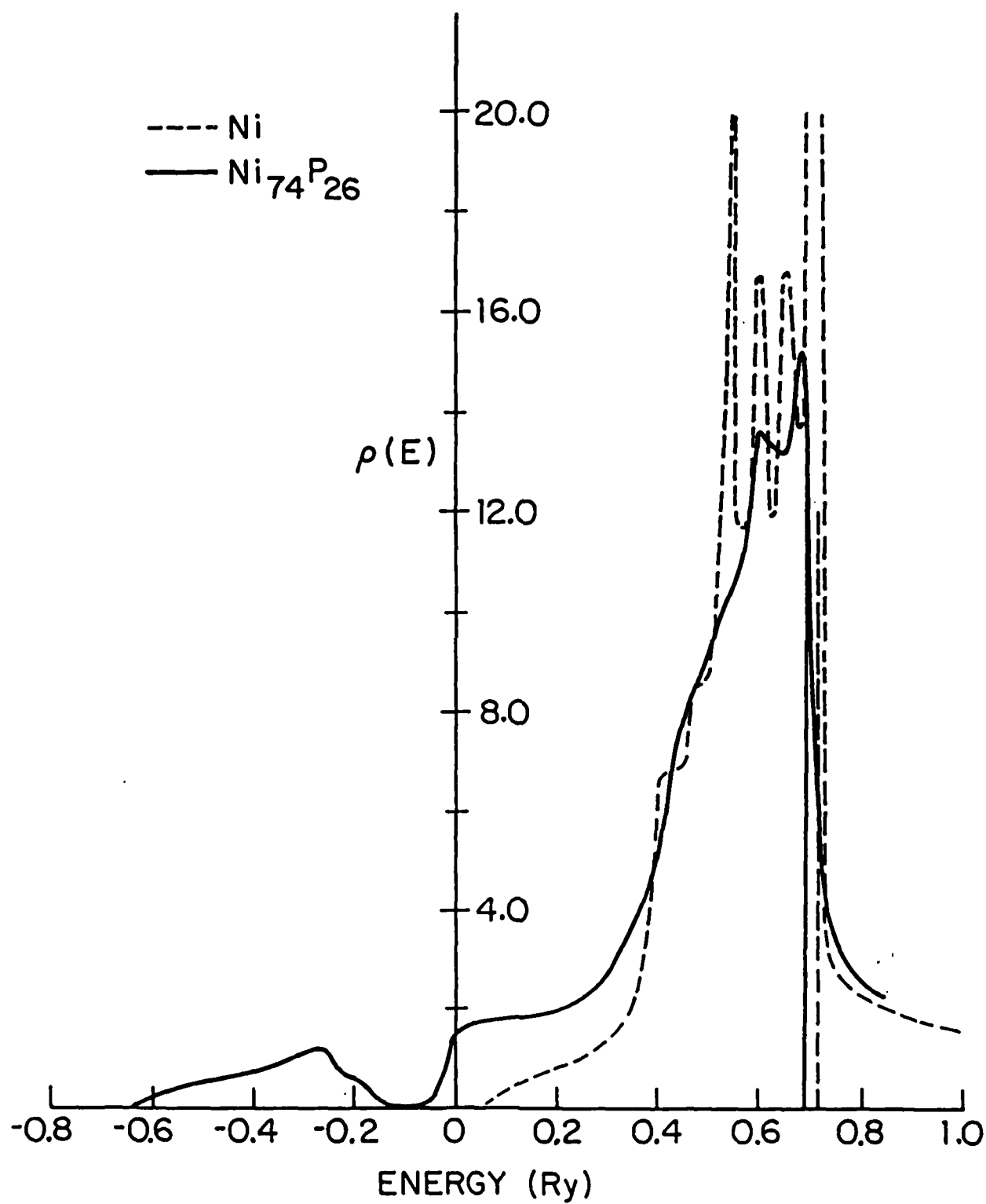


Fig. 6. Calculated density of states for crystalline Ni and amorphous $\text{Ni}_{.74}\text{P}_{.26}$.

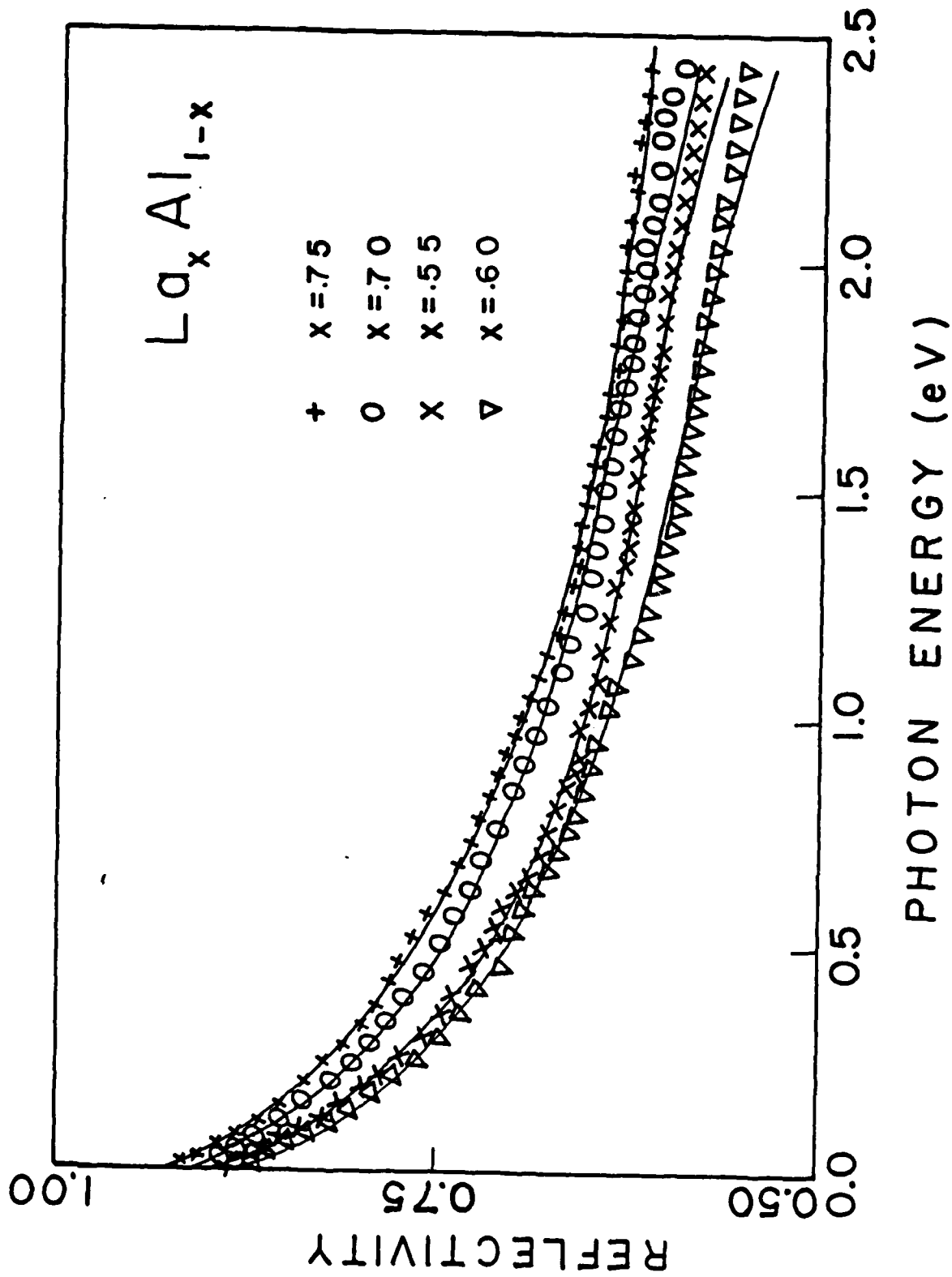


Fig. 7. Measured reflectivity of $\text{La}_x\text{Al}_{1-x}$ samples along with fits to Drude model (solid lines).

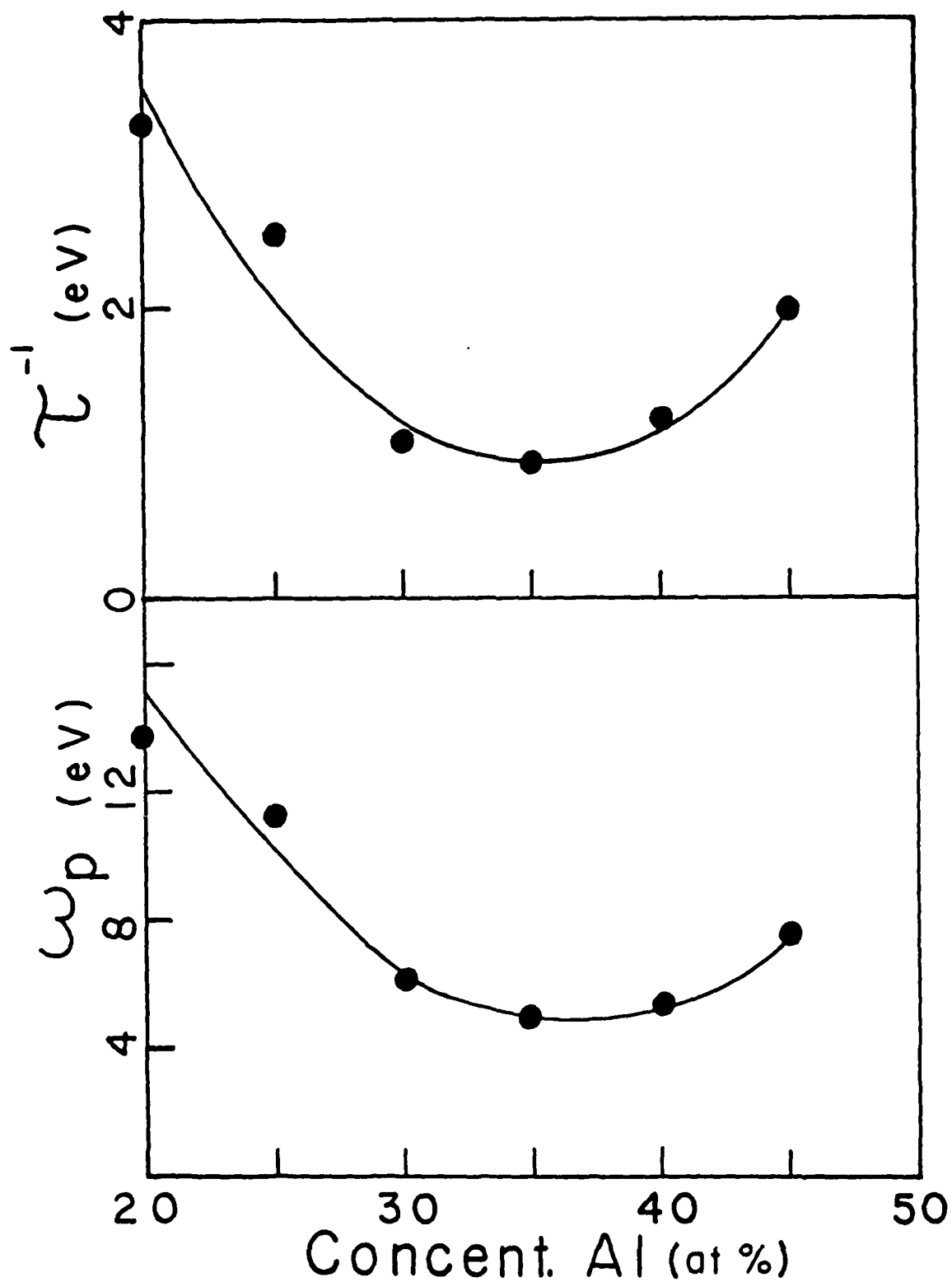


Fig. 8. Variation of inverse scattering time (top) and plasma frequency (bottom) as a function of Al concentration derived from fits to reflectivity data.

3. Research Equipment Acquired:

A Keithley model 181 digital nanovoltmeter has been bought. It is being used in connection with Hall effect measurements, and will be used later for thermoelectric power measurements.

Equipment for the construction of the vacuum UV spectrometer and UHV sample chamber has been acquired. This equipment includes:

- a. Acton Research Model 505 1/2-meter vacuum spectrometer with 120 line/mm grating blazed at 150 nm.
- b. Acton Research 7-position filter wheel for 505 spectrometer.
- c. Acton Research End-on Detector.
- d. Custom UHV chamber from Sharon Machine Company.
- e. Hamamatsu deuterium lamp and power supply.

A liquid He dewar modified for x-ray studies (2 Be windows) has been purchased from International Cryogenics, Inc.

4. List of Publications

1. R.S. Markiewicz, C. Lopatin, C. Zahopoulos, "Fermi Surfaces of Acceptor Intercalated Compounds: Evidence from AsF_5 -Graphite," Mat. Res. Soc. Proceedings. Vol. 20, Intercalated Graphite, M.S. Dresselhaus, G. Dresselhaus, J.E. Fischer, and M.J. Moran, Eds. (North Holland, New York, 1983), p. 135.
2. C.L. Tsai, "Temperature Dependence of Electrical Resistivity on $\text{Ca}_{60}\text{Al}_{40}$ Metallic Glasses," Phys. Rev. (to be submitted).
3. F.C. Lu and C.L. Tsai, "On the Electron-Electron Interaction of La-Al Metallic Glasses," submitted to Phys. Rev. Letters.
4. F.C. Lu and C.L. Tsai, "Electrical Resistivity and Magnetoresistivity of La-Al Metallic Glasses," Phys. Rev. (in preparation).
5. F.C. Lu and C.L. Tsai, "Superconductivity of La-Al Metallic Glasses," Phys. Rev. (in preparation).
6. F.C. Lu and C.L. Tsai, "Paraconductivity of Superconducting La-Al Metallic Glasses," Phys. Rev. (in preparation).
7. F.C. Lu and C.L. Tsai, "Hall Coefficients of La-Al Metallic Glasses," Solid State Comm. or Phys. Lett. (in preparation).
8. R.S. Markiewicz and C. Zahopoulos, "Magnetic Interferometer in a Graphite Intercalation Compound," Phys. Rev. B27, 7820 (1983).
9. S.W. McKnight and A. Ibrahim, "Infrared Properties of Amorphous Ni-P Alloys," Phys. Rev. B29, 6570 (1984).
10. F.C. Lu and C.L. Tsai, "Superconducting Properties of La-Al Metallic Glasses," Bull. APS 28, 485 (1983).
11. A. Ibrahim and S.W. McKnight, "Optical Properties of Amorphous Nickel-Phosphorus Alloys," Bull. APS 28, 484 (1983).
12. R.S. Markiewicz and C. Zahopoulos, "Fermiology of Graphite Acceptor Compounds," Bull. APS 28, 306 (1983).
13. S.W. McKnight and A.K. Ibrahim, "Determination of Transport Parameters of Ni-P from Infrared Reflectivity and Hall Measurements," J. Non-cryst. Solids 61/62, 1301 (1984).
14. A.K. Ibrahim and S.W. McKnight, "Hall and Magneto-resistance Measurements of Amorphous Ni-P," in preparation.

15. R.S. Markiewicz, "c-axis Charge Distribution in Stage-3 and -4 Graphite Acceptor Compounds," Phys. Rev. B28, 6141 (1983).
16. C.L. Tsai and F.C. Lu, "Electronic Transport Properties of La-Al and Ca-Al Metallic Glasses," J. Non-cryst. Solids, in press.
17. C.L. Tsai and F.C. Lu, "Electronic Transport Properties of La-Al Metallic Glasses," J. Mag. & Mag. Mats., in press.
18. C.L. Tsai, "S-d Hybridization and Thermal Stability of Metallic Glasses," submitted to Sol. St. Commun.
19. F.C. Lu, C.L. Tsai, and B.C. Giessen, "Mechanical and Thermal Stability of La-Al Metallic Glass," 1983 MRS meeting.
20. R.S. Markiewicz and C. Zahopoulos, "Magnetic Breakdown in Graphite Intercalation Compounds," Bull. Am. Phys. Soc. 29, 294 (1984).
21. C.L. Tsai, F.C. Lu, and R.D. Lorentz, "Magnetoresistance of Amorphous Ge-Fe Alloys," Bull. Am. Phys. Soc. 29, 301 (1984).
22. S.W. McKnight, A.K. Ibrahim, and C.L. Tsai, "Infrared Properties of La-Al Metallic Glasses, Bull. Am. Phys. Soc. 29, 361 (1984).
23. A.K. Ibrahim and S.W. McKnight, "Galvanomagnetic Properties of Ni-P Amorphous Alloys," Bull. Am. Phys. Soc. 29, 337 (1984).
24. "Magnetic Breakdown of Superlattices in Graphite Intercalation Compounds," R.S. Markiewicz and C. Zahopoulos, submitted to Phys. Rev. Lett.
25. "Magnetic Breakdown in Graphite Intercalation Compounds," R.S. Markiewicz and C. Zahopoulos, to be published, Proceedings of the XV Int. Conf. on the Physics of Semiconductors, 1984.
26. "Field-induced Phase Transition in AsF₅-graphite," R.S. Markiewicz, C. Zahopoulos, D. Chipman, J. Milliken, and J.E. Fischer, to be published, Mat. Res. Soc. Proceedings, 1984.
27. "Magnetic Interference and Breakdown in Intercalated Graphite," C. Zahopoulos and R.S. Markiewicz. ibid.
28. "Magnetoooscillations in Intercalated Graphite Single Crystals," M. Meskoob, C. Zahopoulos, and R.S. Markiewicz, ibid.

5. Professional Personnel:

R.S. Markiewicz, Co-Principal Investigator

S.W. McKnight, Co-Principal Investigator

C.L. Tsai, Co-Principal Investigator

C. Zahopoulos, Graduate Student

A. Ibrahim,[†] Graduate Student

F.C. Lu,[‡] Graduate Student

J. Dugas, Programming Consultant

A. Dudkin, Special Program Graduate Student

H. Hamdeh, Graduate Student

C. Rollins,^{*} Graduate Student

S. Oliver, Graduate Student

[†]Received Ph.D., 8/84. Thesis "Transport and Electronic Properties of Metallic Glasses."

[‡]Presently writing Ph.D. thesis on La-Al films.

^{*}Received Ph.D., 5/84. Thesis "Localization and Interaction Effects in Thin Films: Pd, Pt, Au" included work on Au:Fe films under the present grant.

6. Interactions

a. Papers presented at scientific meetings:

- (i) C.L. Tsai, D.L. Waldorf and F.C. Lu, "Electrical Transport Properties of Superconducting La-Al Alloys," Materials Research Soc. Meeting, Boston, 1982.
- (ii) R.S. Markiewicz, C. Lopatin, and C. Zahopoulos, Ref. 1 above, Materials Research Soc. Meeting, Boston, 1982.
- (iii) Refs. 10 - 12 above, at APS March Meeting, 1983.
- (iv) Refs. 13 and 16 above, at International Conference on Liquid and Amorphous Metals, V, Los Angeles, 1983.
- (v) Ref. 17 at 1983 MMM Conference, Pittsburgh, Pa.
- (vi) Ref. 19 at 1983 MRS Meeting, Boston.
- (vii) Ref. 20 -23, at APS March Meeting, 1984.
- (viii) Ref. 25, at International Conference on the Physics of Semiconductors, San Francisco, 1984.
- (ix) Ref. 26 - 28, to be presented at Materials Research Society Meeting, Boston, Nov., 1984.

b. Seminars given or arranged:

- (i) W.A. Hines, University of Connecticut, "Magnetic Studies of Metallic Glasses," Northeastern University, February, 1983.
- (ii) S.W. McKnight, "Optical Properties of Metallic Glasses," University of Connecticut, Storrs, Connecticut, April, 1983.
- (iii) D.M. Pease, University of Connecticut, "Soft X-ray Absorption Measurements of Metallic Alloys and Amorphous Metals," Northeastern University, May, 1983.

- (iv) C.L. Tsai, "Electronic Properties of Metallic Glasses," Physics Department, Boston University, April, 1983.
- (v) F.C. Lu, "Electronic Transport Properties of Metallic Glass," Northeastern University Physics Department Journal Club, December 5, 1983.
- (vi) R.S. Markiewicz, "Fermiology of Intercalated Graphite," Materials Science Division Group Meeting, Northeastern, April 23, 1984.

c. Collaboration:

- (i) Prof. W.A. Hines, University of Connecticut, Storrs, Connecticut 06268: NMR and Magnetic Susceptibility Study of the La-Al Metallic Glass System, Magnetization and optical properties of amorphous Ni-P.
- (ii) Dr. David Chipman, A.A.M.R.C., Watertown Arsenal, Transmission X-ray Studies.
- (iii) Prof. J. Fischer, University of Pennsylvania, Philadelphia, Pennsylvania 19174: separating conductivity changes into density changes and scattering rate changes in stage 1 AsF_5^- samples subjected to varying degrees of overcharging.
- (iv) Prof. B. Gerstein, Iowa State University, Ames, Iowa, 50010: High-resolution NMR studies of AsF_5 -graphites.
- (v) Dr. L.G. McKnight, Bell Labs, Murray Hill, introducing CONCEPTS, Bell Labs process control software to Solid State Labs, Northeastern University.

- (vi) A. Bansil, and S. Khanna, Northeastern University, CPA
Calculations of Electronic Structure of Ni-P.
- (vii) Robert Lorentz, Stanford Synchrotron Lab, metal insulator
transition in sputtered Ge:Fe films.
- (viii) Prof. J.S. Brooks, Physics Department, Boston University:
Ultra low temperature study of La-Al superconductivity and
localization.
- (ix) Prof. M. Pessa (Tampere Univ. of Technology, Finland)
photoemission studies of amorphous NiP.
- (x) N. Dixon and L. Fritz (NU) Mossbauer/Optical studies of Ge-Fe
and Tm-Cu.
- (xi) D.G. Naugle (Texas A & M) heat capacity of LaAl.
- (xii) J. Allen (Xerox, Palo Alto) photoemission of CaAl.

7. Patents — None

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