**Superlattice Effects in Graphite Intercalation Compounds**

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**Abstract**
A new kind of two-dimensional, field-induced phase transition has been discovered in Br₂ graphite intercalation compounds. Similar to, but much more pronounced than Condon domain formation in three-dimensions, it is a Landau level instability which results in two types of domains having different numbers of Landau levels occupied. The domains display a striking nonlinear dynamics in an a.c. magnetic field, with phenomena including resonance, hysteresis, and a quasiperiodic route to chaos. A theoretical
basis for analyzing the data has been developed, and the high frequency resonance appears to be a transverse vibration of the domain array, similar to that predicted for the superconducting intermediate state.
1. **Summary of Research Goals and Plans**

i) To thoroughly examine the recently discovered Condon phase in Br₂ (and possibly other) intercalation compounds, both to understand the soliton (domain wall) dynamics and to explore the predicted connections between this phase and the quantum Hall effect.

ii) To use magnetooscillations and x-ray diffraction as probes to study superlattice formation in graphite intercalation compounds, particularly in those situations in which magnetic breakdown or field-induced phase transitions suggest that the superlattice may be generated by Fermi surface instabilities.

iii) To search for pressure-induced phase transitions in intercalation compounds, especially via resistivity probes.

2. **Status of the Research Effort**

a. **Condon domains**

The major part of our effort has been concentrated on the stage 2 Br₂ graphite intercalation compounds, where we have found convincing evidence of strong magnetic interaction with Condon domain formation. Essentially, the oscillations in magnetization M due to the de Haas-van Alphen effect mean that the differential susceptibility \( \chi = 3M/3B \) may be large, even though M is small. In the Condon domain phase, the sample acts as a perfect differential paramagnet \( 3M/3B = 1/4\pi \), and the sample is broken up into domains. For a two-dimensional system, the domains correspond to regions where different numbers of Landau levels are filled (e.g., N in one domain, N+1 in the other). This in turn means that the field through the sample is nonuniform, with excess
field flowing through regions with fewer Landau levels. This domain phase is closely analogous to the intermediate phase of a type I superconductor, where excess field flows through the sample via normal domains, or to the ferromagnetic domain state. Exploitation of these analogies has greatly aided our understanding of the Condon domain phase.

Condon domain formation has been observed previously in three-dimensional metals. However, in common with all de Haas-van Alphen phenomena, the phase of the oscillations is extremely sensitive to crystalline imperfections -- to dislocations or even to mosaic spread in a single crystal -- and the susceptibility of the sample has shown only a smooth variation with field. In sharp contrast, we find that in a two-dimensional system, the transition into or out of the Condon phase is virtually discontinuous: the steps in susceptibility are less than 5G wide, in a field of 6T. That is approximately the homogeneity of the field across the sample. And this not in a single crystal but in a polycrystalline (HOPG) specimen.

I believe this phase is worth intensive study for two reasons. First, the extreme sharpness of the transitions reveals very detailed structure within a single Landau level, affording a unique picture into the dynamics of the dense two-dimensional electron gas. The knowledge gained in studying the Condon domain phase should provide new insights into the problem of the low-density two-dimensional electron gas, in particular the quantum Hall effect. Secondly, the Condon domain phase is a new example of a nonlinear dynamical system. Such nonlinear systems are being intensely studied at present, and a number of universal features are displayed by systems as diverse as charge-density waves, electron-hole plasmas, Josephson junctions, and convective
fluids (Rayleigh-Benard effect). In the Condon domain phase, the domain wall
dynamics displays several nonlinear features -- resonance (similar to helicon
wave resonance in ordinary metals), hysteresis, and chaos. The number of
avenues for research this phase opens up is extremely large, and will keep me
busy for several years. In the following paragraphs I will briefly summarize
the present status of the research.

1. **Dynamics.** Our inductive probe of magnetization offers an ideal method
of studying the dynamies of domain wall motion. We directly measure the a.c.
susceptibility, which develops an imaginary component (loss mechanism) when
the system is in the domain phase. The loss is directly attributable to
domain wall dynamics: in the two-phase region, the magnetic field inside each
domain is fixed, so the only way the sample magnetization can vary is for the
domains to grow and shrink. The resulting domain wall motion is impeded by
damping (eddy currents) and pinning mechanisms, and hence the a.c. response is
out of phase with the applied field variation, leading to a complex
susceptibility. The observed susceptibility has two forms of field
dependence, both variation within a single cycle -- corresponding to
condensation in a particular Landau level -- and a more gradual variation
between cycles (as Landau index decreases). The former contains evidence of
domain nucleation and domain-domain interactions. Each cycle corresponds to
the intermediate state of a superconductor -- there is a critical field \( H_{c1} \)
below which the uniform phase is stable, appearance of "normal" (higher field)
domains above \( H_{c1} \), which gradually grow in size and number until, at \( H_{c2} \), they
form a uniform phase. The difference with superconductors is that this new
uniform phase again corresponds to exactly filled Landau levels, only one less
level. As the field increases the whole process begins again, so \( H_{c1} \) and \( H_{c2} \) are periodic functions of inverse field. The field variation in \( \chi \) is not the same for each cycle, but varies slowly as field increases, presumably because the parameters of the domain phase (domain wall surface tension, damping, pinning, effective mass) are field dependent. Detailed analysis of the data requires an extensive theoretical development of domain energetics and dynamics. This theoretical analysis is therefore an intrinsic part of our work. I have developed a detailed description of the static properties of Condon domains,\(^3\),\(^4\) and am working on a theory of dynamic effects.\(^5\) This theory benefits greatly from the superconducting analogy, which is very close (indeed I have derived Ginsburg-Landau equations for the Condon domains). It will be discussed more fully below.

While a detailed analysis of the domain dynamics must await the full theory, the data show several significant features which can be qualitatively analyzed. Figs. 1 and 2 show the magnitude of \( \chi_i \) (the imaginary part of the susceptibility) as a function of frequency, displaying three pronounced peaks. Each peak is associated with a different physical phenomenon, and we are analyzing all three in detail.

The highest frequency peak (-12kHz) seems clearly associated with a helicon-like oscillation. Away from resonance the domain effects are quite small due to strong eddy current shielding, but at resonance the oscillations are as intense as at much lower frequencies -- as if the samples had become transparent. The theory of these oscillations -- actually transverse vibrations of the domain tubes -- has been worked out by de Gennes and Matricon\(^6\),\(^7\) for the superconducting case. I have found that essentially the
same resonance formula should hold for Condon domains. Plugging in the appropriate parameters, the predicted resonance should occur at -7kHz, in reasonable agreement with observation (12kHz). Also the second harmonic should occur at four times this frequency, and we see evidence for this near 50kHz. The "Q" of the resonance is so high that we observe it directly as a ringing in the pick-up coil at the fields at which we enter or leave the domain phase (Fig. 3).

There are two possible origins for the middle-frequency resonance (-700Hz) seen in Fig. 1. This may be a "domain-wall resonance", similar to that observed in ferromagnetic materials, where the driving frequency just happens to equal the natural frequency \( \omega_0 = \sqrt{k/m} \) of the domain wall, where \( k \) is the restoring force and \( m \) the effective mass of the wall. At present there are theoretical problems with this interpretation -- how does it differ from the above helicon resonance, and what is the appropriate expression for the effective mass. An alternative interpretation may be preferable. A similar effect is observed in superconductors, where it is interpreted as an eddy current effect. The a.c. field acts to depin the domains, with more efficient depinning at higher frequencies, until eddy currents limit the penetration of a.c. field into the sample. We have checked on a related sample (HNO\(_3\)-graphite: similar conductivity but no Condon domains at these temperatures) that eddy current effects do become important at -1kHz, and the high-frequency falloff in Fig. 2 appears to follow an \( \exp[-(\sqrt{f}/(1kHz))] \)-law, as might be expected for eddy current effects. More detailed calculations should be able to distinguish these two mechanisms.

The low-frequency peak is related with a dramatic change in the shape of
the oscillations (Fig. 4): the sharp steps are washed out as \( f \) is lowered, leaving only a nearly sinusoidal residual oscillation. Analysis of this effect is complicated, because it is not observed in all samples (indeed it is not observed on every cooldown of an individual sample). When it is clearly observed, it is found that the sharp structure can be restored by increasing the a.c. drive field at fixed frequency (Fig. 5). This suggests that the transition may be due to a "roughening transition."\textsuperscript{10,11} A classical roughening transition is associated with a moving interface in the presence of pinning centers. If there are few centers, the wall moves coherently. As the number of pin sites is increased, a sharp transition occurs above which the wall cannot move coherently, but broadens out (the wall thickness diverges). My thought is that the a.c. frequency creates a length scale for coherent motion of the domains: higher frequencies require shorter-distance motion and hence, effectively a smaller number of impurities interacting with the wall. As the frequency is lowered, the effective impurity concentration increases, and at some critical frequency, a roughening transition occurs. A prediction of the theory is that the system will escape from the roughened state if it is driven harder, and I am collaborating with Koplik and Levine at Slumberger to interpret the frequency dependence of the depinning field.

The data of Fig. 3 show another noteworthy dynamical feature. The high-frequency ringing repeats exactly the same pattern on each cycle of the a.c. drive frequency. This suggests that it is locked into the lower frequency, and that unlocking effects should be possible. We have indeed observed these unlocking effects (Fig. 6). The ringing can be observed either on each cycle, or every other, third, fourth, etc. cycle. This period doubling is very
similar to the quasiperiodicity observed in Rayleigh-Benard cells\textsuperscript{12} as a route to chaos, and indeed some of the ringing patterns in Fig. 6 appear completely chaotic. We are presently purchasing equipment for a more detailed study of this effect.

Fig. 7 shows one last dynamical effect: some samples display a strong hysteresis, in that the observed susceptibility is very different depending on whether the field is swept up or down. Again, based on the superconducting analogy, a simple interpretation comes to mind. For domains of \( N \) and \( N-1 \) Landau levels, one can have islands of \( N \)-levels in a background of \( N-1 \) sea, or islands of \( N-1 \). However the effects in Fig. 7 seem to be of a different nature, involving a competition between two different sections of Fermi surface (two de Haas-van Alphen frequencies): on the up-sweep, only the lower frequency is present, while the down sweep is dominated by the higher frequency. This competition is discussed below in greater detail.

ii. **Analogy to the quantum Hall effect (QHE).**\textsuperscript{13} Theoretically, there should be a close connection between Condon domain formation and the QHE. Both effects occur in the two-dimensional electron gas in a magnetic field. The field inside each domain is quantized at precisely the value corresponding to a particular quantum Hall step. Vagner et al.\textsuperscript{14} have used this analogy to predict that the longitudinal resistivity would vanish in the domain phase. There are a number of outstanding differences between the two effects, however: a) the Condon domains are magnetic effects, while the QHE is predominantly electric; b) the domains are observed in physically thick samples, the QHE only in very thin; and c) the domains occur at high electron density, the QHE at low. My recent theoretical investigations\textsuperscript{3,4} have shown
that the first two distinctions are not as significant as might be thought. In particular, any excitation on a quantum Hall step must display simultaneous electrical and magnetic properties. In particular, the Condon domains are electrically charged and the ratio of charge to flux is quantized. In a thick sample the magnetic effects are dominant, but as the sample gets thinner eventually electric field effects win out, since the domain contains the same net charge independent of its thickness. While domains cannot continue to exist as the film thickness vanishes, they can exist in a film 50Å thick -- i.e., of the thickness of samples in which the QHE is observed. In such thin samples there is also a domain to vortex transition, as in a type I superconductor.\textsuperscript{15} Hence the excess field will penetrate through isolated vortices which form a lattice on a Hall step. Thus not only will the longitudinal resistivity vanish, but the observed Hall effect will be quantized at the appropriate value, since isolated inclusions do not affect its value.\textsuperscript{16}

The remaining problem is the density regimes. Condon domain formation requires $4\pi\chi>1$, while $\chi$ is proportional to the carrier density. Using a noninteracting electron model for $\chi$ gives values of the correct order of magnitude for the Br$_2$-graphite (although about a factor of three too small), but orders of magnitude too small to be relevant in the QHE regime. Azbel,\textsuperscript{16} has suggested that electron-interaction effects can produce cusps in the curve of energy vs. field, and hence can enhance $\chi$ to the requisite range, but this remains to be proven.

Direct measurements of the resistivity in the Condon domain phase would be very important to test some of these ideas, and we are pursuing these
measurements. However, there are complications, since Br₂-graphite is not air stable. Essentially, whenever we have attempted to break the sample out of its sealed container or to intercalate it with leads in position, we have lost the sharp oscillations. We have now found that if the sample is broken under liquid N₂, we can maintain the sharp oscillations, and we have constructed a cell for making pressure-connect electrical contacts to the sample in liquid N₂, which will allow simultaneous d.c. and a.c. measurements of the sample. This should be important both for measuring d.c. resistivity and for studying a.c. enhanced flux-flow resistance, as seen in superconductors.⁹

At present, however, I do not think that we will see a zero-resistance state of Condon domains. The reason is that there are two Fermi surfaces in Br₂-graphite, and there is evidence for a competition between the two types of carriers. A Condon domain is associated with the Nth Landau level of one or the other carriers. For instance, if it is associated with the light-mass carrier, the heavy-mass carrier will not be on a Hall step. Hence its highest Landau level will be partly filled, allowing a finite resistance. Fig. 8 shows this competition directly in the de Haas-van Alphen oscillations. The trace shows three cycles of the lower field oscillation. Over the lower half of each cycle, the system is in the Condon domain phase associated with the lower frequency; over the half, in the phase associated with the higher frequency. The hysteresis observed is associated with a transition between these two types of domain -- indeed Fig. 7 is just an extreme case of the same phenomenon, where the up- and down-sweeps are essentially associated with the two types of domain. Note that when the system is in the low-frequency Condon domain state the high-frequency oscillations are completely wiped out (there
is no sign of the Landau levels numbered 101, 102, 105, 106, 109-11 in Fig. 8). Note also the direct evidence of competition near 11T: both Landau levels cross the Fermi level at the same field, and the oscillations have a much more complicated structure.

iii. Other aspects. A requirement for seeing strong two-dimensional Condon domain formation is that the electronic bandwidth parallel to the magnetic field be smaller than the Landau level separation. To estimate this width, I developed a theory of the c-axis conductivity for warped cylindrical Fermi surfaces. This not only showed that the bandwidth in Br$_2$-graphite was of the correct magnitude, but it should also be important in its own right, since it gives a simple, coherent picture of c-axis conductivity, applicable in principle to all graphite intercalation compounds, both donor and acceptor.

We are looking for Condon domain formation in other graphite intercalation compounds, to understand more about what drives the formation and, hopefully, to find the effect in a stage I compound. This would eliminate the competition between Fermi surfaces and could allow observation of the zero-resistance state. So far, we have found the effect in a stage 2 HNO$_3$ compound, but only at high fields (≥13T) and low temperature (≤2K). In contrast, the domain phase in Br$_2$-graphite persists up to at least 40K, although the threshold field is correspondingly higher at higher T.

A direct observation of the domains would be extremely important in confirming the overall picture, and could provide a great deal of information about domain size, shape, mobility, and nucleation. The only previous direct observation was by Condon and Walstedt, who used NMR to detect the presence of domains in a three-dimensional electron gas in Ag. We tried a similar
experiment, using R. Meservey's low temperature NMR equipment at MIT, but did not have enough sensitivity, due to the small skin depth in the sample. We are trying a more direct observation technique. In a collaboration with IBM, we are using a fine Bi wire (1-1.5 μm diameter) as a probe of inhomogeneous magnetic fields. Initially, we will hold the probe stationary and try to cause the domain to move, but if necessary, we will try to move the probe along the sample surface.

b. x-ray studies. Working with D. Chipman (AMMRC), I have now amassed a considerable amount of data showing that graphite intercalation compounds suffer from a "virgin cooldown syndrome". By this, I mean that in the initial cooldown we observe effects which are lost on subsequent cooldowns. Fig. 9 is a very clear example of this. In FeCl₃ graphite (provided by G. Zimmerman (BU)), we have discovered a low temperature phase transition -- I think the first observed by x-rays in an acceptor graphite intercalation compound below 100K. It's characterized by the appearance of a single sharp new peak in the in-plane spectrum of the incommensurate phase. By doing a scan along the ℓ-axis, we find that this phase is associated with a high degree of c-axis order -- the unit cell size is nearly 100Å. The new peak appears on cooling at about 60K, and then disappears at 20K. A similar disappearing peak also occurs in SbCl₅-graphite. In neither case is the reason for this unusual behavior understood. On warming there was considerable hysteresis before the peak reappeared. As we watched, over several cycles of warming and cooling, the peak gradually disappeared. Fig. 9 shows the intensity variations as a function of time. On a subsequent cooldown no such peak was observed.

Similar behavior has been observed in several other compounds. In AsF₅-
graphite we found evidence for three phase transitions -- the lowest of which seemed to be incommensurate along the c-axis. On subsequent cooldowns this phase did not reproduce. In H$_2$SO$_4$-graphite, we observed what appeared to be a commensurate-incommensurate transition, in which a peak split into two peaks, which continuously shifted as the temperature decreased -- on the first cooldown. On subsequent cooldowns the transition was more abrupt, with the single peak being replaced by two well-split peaks. The reason for this behavior is apparently that lattice mismatch strains introduced on cooling gradually degrade the superlattice. However, it makes any detailed study of the new phases quite difficult. We have gotten a series of fresh FeCl$_3$-graphite samples (and H$_2$SO$_4$-graphite), in order to reproduce the effects and see how they vary with stage.

c. Pressure studies. We are now using pyrrhophylite gaskets in the tungsten carbide pressure cell, and have been able to get reproducible measurements of the in-plane resistivity of pure graphite. Present measurements are limited to about 20 kbars, at which point the lead wires break off. This is still an interesting pressure range and we will soon be repeating Christos Zahopoulos' (ungasketed) measurements on SbCl$_5$ and FeCl$_3$-graphite.
References


2. R.S. Markiewicz, M. Meskoob, and C. Zahopoulos, Phys. Rev. Lett. 54, 1436 (1985) (Section 4, Ref. 4); R.S. Markiewicz and M. Meskoob, to be published (Ref. 4.7).

3. Ref. 4.8.

4. Ref. 4.9.

5. Ref. 4.10.


18. Ref. 4.7.
Figure Captions

Fig. 1. Domain wall resonance in Br$_2$-graphite: imaginary part of susceptibility ($\chi_i$) vs. frequency showing peaks at 400 and 700 Hz.

Fig. 2. Helicon wave resonance in Condon domains: $\chi_i$ vs. frequency in a higher frequency range (1-25kHz).

Fig. 3. "Ringing" in the domain phase. Figure shows photos of four oscilloscope traces. The low frequency oscillations correspond to the applied a.c. frequency. The high frequency modulation is due to excitation of the helicon resonances when the system suddenly enters the domain phase.

Fig. 4. Real part of susceptibility ($\chi_r$) vs. field for a series of frequencies near the low frequency resonances of Fig. 1. Dashed lines are indicative of "ringing."

Fig. 5. Susceptibility vs. field at 112Hz for two values of a.c. excitation voltage.

Fig. 6. Pick-up signal, voltage vs. time, showing high-frequency ringing superposed on the fundamental a.c. frequency. All are taken at the same a.c. voltage but slightly different d.c. magnetic fields. In trace (a), ringing repeats at the fundamental frequency; trace (b) shows period 2; (c), (f) are period 3; (d) period 4(?); and (e) is chaotic.

Fig. 7. Susceptibility vs. field for a different sample of Br$_2$-graphite. Sweeps with increasing vs. decreasing field show prominent hysteresis.
Fig. 8. Detail of trace of susceptibility vs. field, showing the competition between the two Fermi surfaces, with periods 262T and 1162T. Numbers below (above) curve show the occupied Landau level of the smaller (larger) Fermi surfaces.

Fig. 9. Phase transition in FeCl$_3$-graphite. Curve shows x-ray intensity vs. T for extra peak in spectrum. Traces are presented as a function of time, showing gradual loss of intensity of the extra peak.
Fig. 

Variables and labels are as follows: 

- $\omega$ (angular frequency) 
- $X_r$ (complex resistance) 
- $B(T)$ (magnetic field in Tesla) 
- Frequencies indicated include 912 Hz (x0.2), 715 Hz (x0.2), 615 Hz (x0.4), 415 Hz, 315 Hz, and 165 Hz (x2.5).
\[ L_r \propto f^{-112} \]
3. **Research Equipment Acquired:**

None yet.

4. **List of Publications**


5. **Professional Personnel:**

R.S. Markiewicz, Principal Investigator

C. Zahopoulos, Graduate Student†

M. Meskoob, Graduate Student

K. Chen, Graduate Student

B. Maheswaran, Graduate Student

L. Fotiadis, Graduate Student

X. Wu, Graduate Student (Reading Course)

M. El Rayess, Post Doc

†Received Ph.D. 3/85. Thesis "Fermiology of Acceptor Graphite Intercalation Compounds Using de Haas-van Alphen and Shubnikov-de Haas Measurements."
6. **Interactions**

a. Papers presented at scientific meetings:
   

   (ii) Ref. 5 presented at APS March Meeting, Baltimore, MD, March 1985.

b. Seminars given or arranged:


c. Collaborations

   (i) Dr. David Chipman, A.M.M.R.C., Watertown Arsenal: Transmission x-ray studies.


   (iii) Dr. J. Milliken, NRL: magnetooscillations and x-ray studies of AsF$_5$-graphite with excess F.

(v) M.J. Brady, R. Webb and Dr. E. Pakulis, IBM, Yorktown Heights: formation of Bi microprobes to observe domains in Br₂-graphite.

(vi) Prof. J. Brooks, B.U., Boston, NMR of Br₂ in Br₂-graphite.

(vii) Prof. L. Falicov, U.C., Berkeley: calculation of magnetic breakdown in 2-d.

(viii) Prof. G. Zimmerman and A. Ibrahim, B.U.: magnetic intercalation compounds (FeCl₃)

7. Patents

N.U. lawyers are doing patent search regarding possible patent on d.c. transformer based on Condon domains.
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1988