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Concluding Remarks

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Concluding remarks

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For the complex and anisotropic compounds studied in this meeting, it is necessary to establish a hierarchy of factors and to build simplified models that take into account only the most important contributions. The flexibility of these complex compounds leads to many possible crossovers between leading factors, of potential interest for applications. Examples are given of both inter- and intra-unit interactions.

Introduction

Some general remarks can be made on the type of work reported in this meeting, as examples of a trend that has developed in the study of condensed matter. First, the compounds studied are both complex and various. To obtain reproducible and meaningful results long-term cooperation between physicists and chemists is needed. Over the years such cooperation has been successfully developed in many places. Because of this complexity and variety, it would be hopeless in most cases to start from an *ab initio* study of the atomic or electronic structure. To avoid wasted effort, one needs to define the leading factors; once such a *hierarchy* is obtained, one can hope to build a simplified effective model by using only the more important factors. This is necessary both to analyse the properties of known compounds and to suggest new ones of potential interest. Not very surprisingly, one finds in most cases that such an effective model has solutions that do not differ substantially from the classical behaviour observed and understood in more elementary solids such as pure metals, pure covalents or ionic solids.

However, because of the complexity and ensuing flexibility of the compounds described in this symposium, one often observes that the hierarchy of factors can be altered easily by changing the physical or chemical conditions. The domain of validity of an effective model is usually not very large; it is bordered by zones of *crossover*, where new leading factors take over. In such crossover conditions, a small change in composition, pressure or temperature can lead to a large change in some physical properties. Nonlinear conditions are easily attained, potentially useful for applications, despite the difficulty of producing or stabilizing many of these complex compounds.

In the one- and two-dimensional compounds studied at this meeting, the anisotropy due to low dimensionality is an obviously dominant factor. The interplay of possible interactions within the corresponding building units – chains or planes – or between such units lead, however, to a variety of crossover régimes. Furthermore, even when too weak to produce a crossover, secondary factors can have significant effects. These points will now be illustrated.

1. Interunit interactions

If electrons are localized on units, the only possible interactions are coulombic in nature. New interactions arise if electrons can be transferred from unit to unit. Only a few points need be stressed in this well known field.

(*a*) *Coulomb interactions*

As in ionic solids, one can distinguish: the long-range Madelung energy, if some charge transfer between or within units exists; the dispersion forces; the short-range electrostatic and exchange interactions.

In compounds such as TTF-TCNQ, the Madelung energy due to charge transfer between unlike chains has been balanced by dispersion forces in an attempt to explain the charge transfer and the relative stability of the observed structures: the Madelung term favours A^+B^- alternation, dispersion forces favouring AA and BB regrouping (Metzger & Bloch 1975; Friedel 1977; Barisic & Bjelis 1983; Noguera 1984). Also the stability of the various three-dimensional lattice modulations observed in TTF-TCNQ have been studied in terms of Madelung energies between the charge modulations on the chains (Saub *et al.* 1976; Barisic & Bjelis 1984; Megtert 1984).

However, the molecules involved are flat, polarizable and often not even at a centre of symmetry of the structures considered. The electrostatic interactions cannot therefore be studied as if molecules were point charges; and the local electrostatic electric field due to charge transfer polarizes the molecules. Contrary to what happens in cubic ionic solids such as NaCl, the Madelung energy involves not only a complex geometry but is cut down by a large k dependent dielectric constant; the dispersion forces are, in a similar way, cut down by a large k and ω dependent dielectric constant (Noguera 1984).

These dielectric constants are not well known. One must therefore conclude that these coulomb terms are small and hard to compute exactly. When they dominate because electrons are really localized on units, they must be compared to long-range elastic terms, which can arise from the short-range electrostatic and exchange repulsions.

(*b*) *Interunit electron transfer*

In a number of one- or two-dimensional compounds, the electrons are delocalized within each unit, as proved by a 'longitudinal' electrical conduction along the chains or planes. But then in most cases one also observes a smaller but finite 'transverse' electrical conduction in directions that involve electron transfer from unit to unit.

The exact role of the transfer integral, $t_\perp$, which allows this transfer in the transverse direction depends on its relative strength with respect to the relaxation rate $\nu_\parallel$ along the units (Shitzkovsky *et al.* 1978).

If $t_\perp > h\nu_\parallel$, the motion of electrons from unit to unit is coherent and hence described by three-dimensional Block functions. The interunit jumping rate is given by $t_\perp$, and this transverse motion warps somewhat the Fermi planes (or cylinders) that would otherwise exist for independent chains (or planes).

However, if $t_\perp < h\nu_\parallel$, the electron is scattered along the unit before it has time to transfer fully to a neighbouring unit by coherent motion. The jumping rate from unit to unit is then slowed down by the ratio of the relaxation time $\nu_\parallel^{-1}$ to the coherent jumping time $ht_\perp^{-1}$. It becomes equal to $t_\perp^2/h\nu_\parallel$ and the motion of the electron from unit to unit becomes diffusive. The Fermi surface remains flat or cylindrical, but it is blurred by a Dingle temperature $h\nu_\parallel$. In that case, which seems frequently observed in one-dimensional metallic compounds, the ratio of longitudinal and transverse conductivities is independent of temperature (both varying in proportion to $\nu_\parallel$).

The transverse transfer integral $t_\perp$ can also couple low-temperature fluctuating instabilities, which tend to develop on isolated units such as lattice or spin modulations or superconductivity. Again, two régimes are expected (Bourbonnais 1984). If $t_\perp > \Delta$, the pseudogap of these fluctuations, $t_\perp$, ensures a strong phase blocking of the fluctuations into a three-dimensional phase change at a finite temperature T_3, which is then an increasing function of $t_\perp$. The range of fluctuations above T_3 should be very small.

If $t_\perp < \Delta$, the intra-unit fluctuations reduce the effectiveness of $t_\perp$ to $t_\perp^2/\Delta$. T_3 becomes the same function of $t_\perp^2/\Delta$, while there is a large range of temperatures, up to $T_1 \approx \Delta$, where intra-unit fluctuations persist. This second régime clearly applies to most one-dimensional compounds with lattice modulations. It is reasonable to think that it also applies to superconductivity in $(\mathrm{TMTTF})_2\mathrm{X}$ compounds.

In conclusion, there are many possible crossover régimes for the interunit interactions. It would be of interest to characterize more clearly the domains where each of them is dominant. This has been partly done for one-dimensional compounds, but two-dimensional compounds have been much less studied in this way. For instance, the tunnelling between conductive layers in semiconductive superlattices have so far been assumed to be coherent; there might, however, be cases where they are diffusive. It would also be of interest to re-examine possible (but obviously small) fluctuations in two-dimensional compounds.

2. Intra-unit interactions

Here again, one has first to decide on which side of the Verwey–Mott transition the compounds are to be considered. In a number of strongly insulating chain compounds, chemists are accustomed to assuming that electrons are localized on subunits of the chains – atoms or molecules – and to describe the magnetic properties in these terms. But, as already stressed, there are a number of one- and two-dimensional compounds with sizeable conductivities, where electrons are delocalized along the units. In the latter case, the leading parameter is the valence band width. But, as usual in band theory of solids, secondary features can play an important role, especially at low temperatures. This is especially true for the compounds with low dimensionality.

The basic secondary features are the electron–phonon couplings and the electron–electron repulsions. But the possible effects of impurities or of an applied magnetic field on low-temperature uncommensurate modulations need also be mentioned.

(a) *Electron–phonon against electron–electron couplings in conductive compounds*

The *electron–phonon* couplings are obviously responsible for the low-temperature lattice modulations observed in many one- and two-dimensional compounds. They are also responsible for the dimerization gap observed at the Fermi level of polyacetylene chains, and have been reasonably invoked to predict a local change in dimerization near a charged state: extra carrier or exciton. Finally they are invoked to explain the metallic conductivity of one-dimensional (and two-dimensional) compounds, thus avoiding Anderson localization by impurity scattering.

However, *electron–electron* couplings, although not strong enough to produce Mott localization, can be a leading secondary factor.

Thus the low-temperature spin modulations observed in some *chain compounds* require positive values of the g_1 and g_2 coupling parameters describing the scattering of Fermi electrons. This in turn is only possible if the direct electron–electron repulsions dominate over the phonon-mediated attraction. The direct transition observed from antiferromagnetism to superconductivity also suggests that this is a triplet superconductivity; but analogous discussions of three-dimensional compounds show that it is not so easy to find a convincing proof of such triplet character in one-dimensional compounds.

The strong 4 k_M fluctuating lattice modulations often observed in chain compounds have been attributed to strong and longer range electron–electron repulsions. This is quite possible, as repulsion between electrons sitting on two neighbouring flat molecules can clearly be as effective as when the two electrons are on the same molecule. It is coherent with the g_1, g_2 scheme, which would reduce to the diagonal $g_1 = g_2$ in a Hubbard model with only intramolecular repulsions (Hirsch & Scalapino 1983; cf. discussion in Barisic & Bjelis 1984).

Another case where electron–electron correlations are known to be large are the *polyacetylene chains*. Chemists have long been aware that these correlations are especially strong in unsaturated carbon bonds. The reason is twofold and arises from the fact that, in a Hubbard model, the stabilizing correlation energy is proportional to U^2/w, where U is the intra-atomic electron–electron repulsion and w the bandwidth or the energy difference between the occupied bonding and empty antibonding levels (Friedel 1983, 1984). First, the π-bandwidth w is smaller than the σ one. Second, U can be defined as the energy involved in the atomic reaction

$$M + M \rightarrow M^+ + M^-.$$

It is thus given by

$$U = I - A,$$

where I is the first ionization potential and A is the electron affinity. As $A \ll I$, $U \approx I \approx I + A$, is thus proportional to the electronegativity as defined by Pauling. This is much larger for C than for Si and Ge. Accordingly, large correlations explain both the larger stability of graphite than diamond and the much greater frequency of molecules with unsaturated bonds for C than for Si or Ge.

Thus electron–electron correlations should be taken into account in polyacetylene chains, and probably not as a mere perturbation, a fact stressed by chemists 20 years ago for the similar carotenoid chains. Also, the first optical excitation should be excitonic in nature.

(*b*) *Impurity effects on incommensurate modulations*

Impurities can act in two rather different ways. First, because they scatter the electrons, they introduce a Dingle temperature that broadens the Fermi level. This prevents perfect nesting, and decreases the *amplitude* of a lattice or spin modulation, destabilizing it. Second, an impurity tends to block the *phase* of the modulation to optimize its coupling with the modulation. *Three* types of effects are then expected.

Random and frozen impurities will have incompatible effects on the phase of a given modulation. This 'frustration' effect will destabilize a three-dimensional modulation by forcing it to distort spatially. Above the temperature T_3, where the three-dimensional modulation disappears, fluctuations can persist up to T_1, with no phase relation from unit to unit. The frustration effect of the impurities is then much reduced, because their distance l_1 along a unit is larger than their average distance l in three dimensions: $l_1^2 a \approx l^3$ for two dimensions and $l_1 a^2 \approx l^3$ for one dimension if a is the lateral size of a unit. Thus T_3 *should decrease* with increasing impurity concentration. Furthermore, at temperatures large enough for the coherence length of a fluctuation to become less than l_1, each impurity can pin its fluctuation independently in its most stable phase relation; this coupling stabilizes the fluctuations so that T_1 *should increase* with impurity concentration. One could also say that the normal 'wiggles' in charge, spin or lattice spacing that are set up by the impurity scattering are amplified by the spontaneous tendancy of the units to produce this modulation.

Finally, the phase blocking by an impurity should lead to a *hysteresis* characteristic of solid friction when the modulation is shifted. This shifting can be due either to a change of wavelength by a change of temperature or pressure, or to a change of phase induced (for a charge density wave) by an applied electric field. This hysteresis should be much increased if impurities are allowed to diffuse at a temperature where a three-dimensional modulation is present and then cooled so as to become immobile: in the heat treatment, the impurities will shift their positions so as to stabilize their phase relation with the undistorted three-dimensional modulation, so that it is then more difficult to move the modulation away from the configuration thus pinned down.

The effect on the amplitude is expected to be preponderant at large concentrations, while the effects on the phase should be observed mostly at small concentrations. Indeed, in irradiated one- or two-dimensional compounds, T_3 decreases but T_1 increases with the dose (Zuppiroli 1982; Mukta 1982). Solid friction is often observed in incommensurate phases (TTF-TCNQ under pressure, $NbSe_3$ under electric fields), and some of this at least is probably due to impurity pinning. The special pinning by heat treatment was first observed on a three-dimensional compound (Jamet & Lederer 1983). It would be of interest to investigate the corresponding effect in one- or two-dimensional compounds.

(*c*) *Effect of transverse magnetic field on two-dimensional metallic compounds*

As shown in $(TMTTF)_2ClO_4$, a modulation can, in some cases, be stabilized by the application of a magnetic field. The fundamental reason, as stressed by Gorkov (1984) (cf. also Fukuyama 1981) is that a (here antiferromagnetic) modulation will be especially stable if its wavevector $\boldsymbol{Q}$ shifts the Fermi surface into a nesting condition with itself. In an effectively two-dimensional compound such as the one considered ($t_a \gg t_b \gg t_c$), the nesting produces small pockets of electrons (or holes) for which the corresponding quasicontinuum of conducting states is split into Landau levels if a magnetic field H is applied normal to the two-dimensional sheets. This splitting changes the two-dimensional nesting into an effective one-dimensional nesting, by reducing a continuous two-dimensional integration in k-space into a summation over quantized orbits, thus stabilizing the modulation. Furthermore, the system of Landau levels is especially stable if H is such that the Fermi level falls just midway between two corresponding quantized orbits of the electron (or hole) pockets. If $\mathscr{A}_Q$ is the area of the pocket for nesting $\boldsymbol{Q}$, the condition is

$$\mathscr{A}_Q = (n+\tfrac{1}{2}+\gamma)\, 2\pi eH/hc, \tag{1}$$

where n is an integer and γ a constant smaller than unity (Ziman 1972).

As pointed out by Héritier *et al.* (1984), for H near to such values, the system should continue to fulfil the same condition (1) by slightly shifting the vector $\boldsymbol{Q}$, i.e. by altering $\mathscr{A}_Q$: this is because the energy of modulation varies smoothly with $\boldsymbol{Q}$, while the Landau energy presents a cusp as a minimum when $\boldsymbol{Q}$ varies for a given H (cf. Appendix). As a result, when H varies, the system jumps by first-order transitions where one Landau level suddenly fills or empties itself completely. In this analogy to the quantized Hall effect observed in two dimensional doped semiconductors, the role of the reservoir is played by the (small) variations of $\boldsymbol{Q}$ with H. If this interpretation is correct, the two-dimensional modulation is stabilized and driven by the magnetic field, in the same way as modulating fluctuations were locally stabilized by impurities.

The same analysis should equally apply to lattice or spin modulations. The shift in $\boldsymbol{Q}$ to adapt to H and the production of a succession of first-order transitions should also be observed even when a two-dimensional modulation with a given $\boldsymbol{Q}$ was stable without H. In this context, it might be of interest to explore the properties under large H of other two-dimensional conductive compounds such as the transition metal dichalcogenides.

APPENDIX

I present here a simplified version of the treatments by Gorkov & Lebed (1984) and Héritier *et al.* (1984) and comment on it at the end.

(*a*) *Diamagnetic energy of a pocket of electrons or holes*

In a semiclassical approximation, the application of a magnetic field H normal to the two-dimensional sheet quantizes the electron orbits in the k plane (figure 1). The corresponding Landau levels are at least partly occupied if

$$n-1+\gamma < \mathscr{A}_Q/\mathscr{A}_0 < n+\gamma,$$

where $\mathscr{A}_Q$ is the area of the pocket; $\mathscr{A}_0 = 2\pi eH/\hbar c$ and γ is a phase shift less than unity (figure 2).

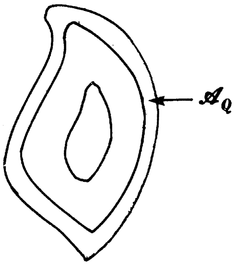

FIGURE 1. Quantized orbits in an electron or hole pocket.

Since each slice of continuum levels has an average energy equal to that of the Landau level, the energy change when H is applied is

$$\begin{aligned}\epsilon_L &= [\tfrac{1}{2}\hbar\omega-\tfrac{1}{2}(E_M-E_M)]\,(E_M-E_n)\,n(E_M)\\ &= \tfrac{1}{2}[E_M-(n-1)\,\hbar\omega]\,(-E_M+n\hbar\omega)\,n(E_M),\end{aligned} \tag{A 1}$$

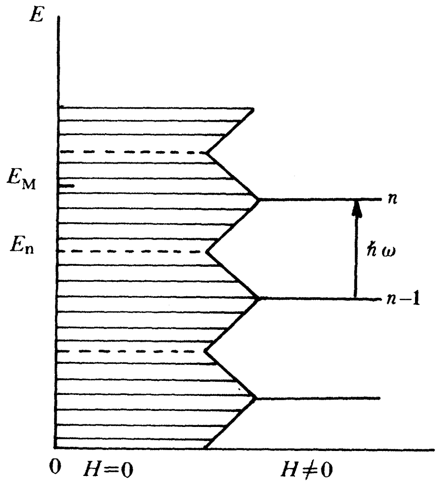

FIGURE 2. Landau levels associated with a pocket of area $\mathscr{A}_Q$.

where

$$\hbar\omega = \mathscr{A}_0\,\alpha H\,\mathrm{d}E/\mathrm{d}\mathscr{A},$$

$$E_n = n\hbar\omega$$

and $n(E)$ is the density of states of the corresponding continuum of states.

As stressed recently by Gorkov (1984), the energy ϵ_L is strongly peaked for exactly filled Landau levels and especially for a few levels where n is small. The presence of a small pocket in the Fermi geometry thus leads to a special stability, because a succession of fields H_c/n leads to $\hbar\omega = E_M$. If the pocket considered is due to the existence of an *incommensurate* (lattice or spin) modulation with a wavevector Q in nesting conditions, the energy $\delta\epsilon_Q$ of this modulation is expected to vary (usually in a continuous and smooth way) with the direction of Q (keeping in nesting conditions). This point is discussed further below.

We have then to compare $\delta\epsilon_Q$ to the change $\delta\epsilon_L$ in Landau energy when the modulation appears and pockets are formed. The change $\delta\epsilon_L$ is obtained by subtracting from ϵ_L the Landau diamagnetic energy $\frac{1}{12}(\hbar\omega)^2 n(E_M)$ of the same electrons before the modulation appeared. It is shown in figure 3 as a function of H. The cusp of $\delta\epsilon_L(H)$ for given Q leads to a cusp of $\delta\epsilon_L(Q)$ for given H. This is to be contrasted to the smooth variation of $\delta\epsilon_Q$, in nesting conditions, for varying directions of Q.

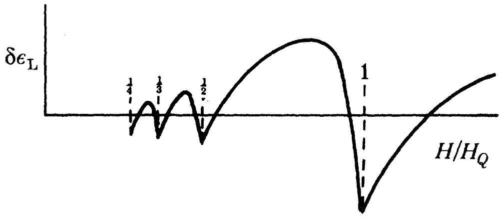

FIGURE 3. Variation with H of the Landau energy of a pocket of electrons (H_c is such that $\hbar\omega = E_M$).

If Q_0 is the wavevector for maximum stability of the modulation for $H = 0$, the same modulation will be especially stable for a succession of fields H_{Q_0}/n, where $\hbar\omega(H_{Q_0}) = E_M$. For fields H deviating somewhat from these values, the total energy $\delta\epsilon_L + \delta\epsilon_Q$ is kept a minimum by shifting Q a little from Q_0 (Héritier *et al.* 1984) so as to change $\mathscr{A}_Q$ to continue to fulfil the condition

$$\mathscr{A}_Q = (n+\gamma)\,\mathscr{A}_0.$$

Landau levels as thus kept exactly full or empty and $\delta\epsilon_L$ is kept at one of its cusps. A continuous variation of H leads to a discontinuous transition from one such solution (n) to the next, by a first-order transition with hysteresis.

(*b*) *Energy of modulation*

It would seem *a priori* that the application of the field could make a modulation Q stable if the gain in Landau energy $\delta\epsilon_L$ at one of its cusps is larger than the energy $\delta\epsilon_Q$ to spend to create the modulation. In actual fact, the discussion is somewhat different: as first stressed by Yoshioka & Fukuyama (1981) and considered also by Gorkov & Lebed (1984) and Héritier *et al.* (1984), the application of H alters the conditions of nesting in a way that stabilizes the modulation.

The energy $\delta\epsilon_Q$ of a modulation varies strongly with the length of Q near nesting conditions. In the usual *one beam approximation*, this variation is dominated by

$$I = \sum_{k_{\text{occ}}} \frac{1}{E_k - E_{k+Q}}.$$

Near nesting conditions, it is the region of k near to the point where $E_{k_0} = E_0$, where E_k and E_{k+Q} are nesting, that dominates (figure 4). Taking $\boldsymbol{k}_0$ as the origin in $\boldsymbol{k}$ space and k_1 along $\nabla_k E_k$ at $\boldsymbol{k} = \boldsymbol{k}_0$, we can develop E_k and E_{k+Q} as

$$E_k = E_0 - Ak_1 + Ck_2^2 + \dots,$$

$$E_{k+Q} = E_0 + A'k_1 + C'k_2^2 + \dots,$$

where A, A', C, C' are constants.

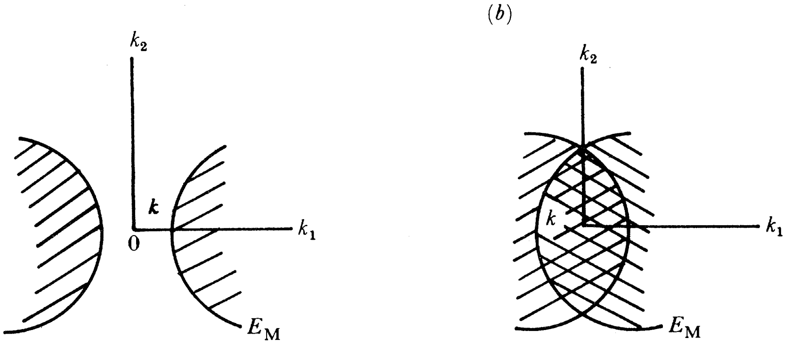

FIGURE 4. Nesting: (*a*) $k_M > 0$; (*b*) $k_M < 0$. (Special case where $A = A'$, $C = C'$.)

Then, in the absence of magnetic field,

$$I \approx -\sum_{\substack{k_1 k_2\\ \text{occ}}} \frac{1}{(A+A')\,k_1} \approx -\frac{1}{\left(\dfrac{C}{A}-\dfrac{C'}{A'}\right)^{\frac{1}{2}}}(\alpha - \beta k_M) \quad \text{for} \quad E_M > E_0,$$

$$I \approx -\frac{\alpha}{\left(\dfrac{C}{A}-\dfrac{C'}{A'}\right)^{\frac{1}{2}}} \quad \text{for} \quad E_M < E_0,$$

where α and β are positive and slowly varying functions of E_M. When the length of Q varies for a given direction of Q near nesting conditions, E_0 is fixed and k_M varies. The sudden increase of I for $k_M > 0$ can favour the nesting condition $k_M = 0$. In such nesting conditions, I, and thus $\delta\epsilon_Q$, vary in a smooth way when the direction of Q varies, thus E_0, A, A', C, C' vary. One would, however, expect a special stability of nesting for points of the Fermi surface with equal curvatures. This is topologically possible for $(TMTTF)_2ClO_4$ in the disordered case (or for $(TMTTF)_2PF_6$) for inflexion points at the Fermi surface. Then, in this approximation, I and $\delta\epsilon_Q$ should have a negative divergence (figure 5).

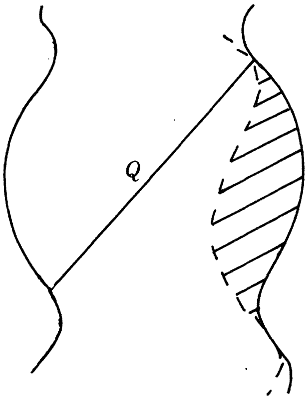

FIGURE 5. Nesting on inflection points of $E_k = E_M$.

Now in the presence of a magnetic field normal to k_1, k_2, the integration over k_1, k_2 is replaced by an integration over occupied quantized orbits in the k plane. I then obviously diverges logarithmically if the orbits are in *any* nesting conditions. The situation is mathematically the same as for a one-dimensional modulation with no magnetic field.

All these logarithmic divergences are removed if one uses a more correct *two beams approximation* (Pick & Blandin 1964). As in real one-dimensional problems, the cut off in the logarithm is then related to the energy gap, due itself to the modulation potential. It varies, as does $\delta\epsilon_Q$, in a smooth way with the direction of Q, even across nesting on inflection points: this insures that these are not pinning points against the variation of Q with H. The negative value of $\delta\epsilon_Q$ associated with the logarithm insures the stability of the modulation under magnetic field.

Discussion

The discussion developed here is limited to magnetic fields weak enough for a semiclassical discussion using quantized orbits to hold. In large fields, tunnel effects between neighbouring pockets should be considered. They would complicate the effects.

The discussion is also not valid for very weak fields, where the transfer integral t_c in the direction parallel to H is no longer negligible, however small t_c. Furthermore the order of ClO_4 introduces new Brillouin zone boundaries that complicate the geometry of the pockets involved, while the disorder of ClO_4 introduces a Dingle temperature that gives another limitation for nesting and for the minimum field H, for which nesting is essentially one-dimensional.

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