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FURTHER REMARKS ON METASTABILITY IN AMORPHOUS SEMICONDUCTORS.(U)
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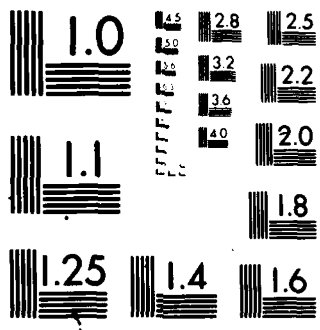

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(6) Further Remarks on Metastability in Amorphous Semiconductors*

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ABSTRACT

The bandwidths for metastable states in a simple model of amorphous semiconductors is evaluated exactly. The region of metastability in the space of the model parameters (phase diagram) is deduced and the subregion corresponding to an infinite range model is indicated. The model predicts both paramagnetic and diamagnetic metastable states and the relationship between them is discussed.

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(15)

In this paper we further examine the properties of metastable electronic states predicted for the negative U model (Anderson, 1975) of amorphous semiconductors by Licciardello, Stein and Haldane (1980) (see also, Licciardello 1980a). The presence of such states have been linked to photoinduced paramagnetism (Mott, Davis and Street, 1975; Licciardello and Stein, 1980) and conductivity changes (Licciardello, 1980b) observed in a wide variety of glassy semiconductors. Interest in the properties of metastable states stems from their defect-like behavior, although the model itself contains no defects per se. Thus the theory provides an alternative point of view to the generally accepted defect picture of glassy materials (Kastner, Adler, and Fritzsche, 1976).

We consider a spatially random distribution of localized states in which the Hamiltonian H_i corresponding to the i^{th} site is written

$$H_i = \varepsilon_i\hat{n}_i + \omega b_i^+ b_i + U\hat{n}_{i\uparrow}\hat{n}_{i\downarrow} - g(b_i + b_i^+)\hat{n}_i \tag{1}$$

where the quantity $\hat{n}_i$ is the number operator for an electron at the i^{th} site. Similarly $\hat{n}_{i\uparrow}$ ($\hat{n}_{i\downarrow}$) counts electrons at the i^{th} site with spin up $\uparrow$ (down $\downarrow$). I have also introduced the operator b_i^+ which creates a phonon at the i^{th} site with frequency ω. The parameters ε_i, U and g are, respectively, the electron energy at the i^{th} site, the Hubbard repulsion energy and the electron phonon coupling. We have ignored the zero point lattice vibrations and employ, for simplicity, an Einstein model for the phonons. We also neglect the variation of the coupling g and the Hubbard repulsion U from site to site.

The Hamiltonian has the usual form including an electronic part H_e, a pure phonon part H_{ph} and an interaction term $H_{e\cdot ph}$:

$$H_i = H_e + H_{ph} + H_{e \cdot ph} \tag{2}$$

It is useful, following Licciardello, Stein and Haldane (1980), to renormalize the pure terms by introducing displaced phonon operator d_i through the relation

$$d_i = b_i - g\,\hat{n}_i/\omega \tag{3}$$

This immediately gives the form

$$H_i = \tilde{H}_{el} + \tilde{H}_{ph} \tag{4}$$

where

$$\tilde{H}_{el} \equiv \varepsilon_i\,\hat{n}_i - \frac{1}{2}C\,\hat{n}_i\hat{n}_i + U\hat{n}_{i\uparrow}\hat{n}_{i\downarrow} \tag{5}$$

and

$$\tilde{H}_{ph} \equiv \omega\, d_i^{+}\, d_i \tag{6}$$

and where we have defined the coupling energy $C \equiv 2\,g^2/\omega$. The stationary solutions are described by quantum numbers n_i, ν_i which give the number of electrons and phonons, respectively, localized at the site i.

We define a <u>local</u> equilibrium state as one which satisfies

$$\tilde{H}_{ph}|n_i,\nu_i\rangle_{eq} = 0 \tag{7}$$

or

$$d_i \equiv 0$$

It is the purpose of this note to examine conditions on the Hamiltonian parameters under which the state $|n_i,\nu_i\rangle_{eq}$ is metastable.

We consider two sites i and j whose corresponding states $|n_i,\nu_i\rangle_{eq}$ and $|n_j,\nu_j\rangle_{eq}$ each satisfy equation (7). At low temperatures, we may roughly define stability of the equilibrium states i and j with respect to spontaneous charge transfer between them by requiring the energy for the process to be endothermic, i.e.

$$
\begin{aligned}
& {}_{eq}\langle n_i \nu_i | H_i | n_i \nu_i \rangle_{eq} + {}_{eq}\langle n_j \nu_j | H_j | n_j \nu_j \rangle_{eq} \\
& < \langle n_i + \Delta n_i \nu_i | H_i | n_i + \Delta n_i \nu_i \rangle \\
& + \langle n_j - \Delta n_j \nu_j | H_j | n_j - \Delta n_j \nu_j \rangle
\end{aligned} \tag{8}
$$

where $\Delta n = \pm 1, \pm 2 \ni 0 \le n_{i,j} \pm \Delta n \le 2$. It is instructive to consider the range of electronic energies ε_i under which eq. (8) is satisfied for diamagnetic $n_i = 2$ and paramagnetic states $n_i = 1$. For the system in equilibrium defined by eq. (7) for each site, the energy eigenvalue is directly given through equation (5) for the site i :

$$
E_i = \varepsilon n_i + U\delta_{2,n_i} - \frac{1}{2} C n_i^2 \tag{9}
$$

where n_i is the number of electrons at the site i and δ is the Kronicker delta. As has been noted (Anderson, 1975), the system ground state is determined by the occupation set $\{n_i\} = \{0,2\}$ and for convenience we define the Fermi energy ε_F by the relation

$$
2\varepsilon_F + U - 2C = 0 \tag{10}
$$

Thus, in the ground state, sites for which $\varepsilon_i > \varepsilon_F$ have occupation $n_i = 0$ and sites for which $\varepsilon_i < \varepsilon_F$ are occupied by $n_i = 2$.

<u>Infinite Range Model</u>:

We define a metastable state i as an equilibrium state i (cf eq. 7) for which $\varepsilon_i > \varepsilon_f$ with $n_i \neq 0$ or $\varepsilon_i < \varepsilon_f$ with $n_i \neq 2$ and which is stable according to eq. (8) for all j . The latter condition defines an infinite range model which we consider here. This assumption has been relaxed in other works (Licciardello, Haldane, Stein, 1980; Licciardello 1980b).

Metastable Diamagnetism:

We consider a metastable state i which contains $n_i = 2$. The bandwidth for stability is given through eq. (8) and we evaluate the case $n_j = 0$ and $\Delta n_i = -1$. It has been shown that the two-electron emission process $\Delta n_i = \pm 2$ is always more severe (i.e. states are more stable energetically with respect to this process) so that it may be ignored. We obtain, using eqs. (8), (4), (5) and (6)

$$\varepsilon_i - \varepsilon_j < 2C - U \tag{11}$$

as the condition for metastable diamagnetism. The region is sketched in Figure 1 where the stable regions $\varepsilon_i < \varepsilon_F$ and $\varepsilon_j > \varepsilon_F$, and the Fermi point ε_f , defined through eq. (10), are also indicated. The metastable states occur generally in the shaded triangle. In the infinite range model which assumes non-zero electronic matrix elements between all i,j , it is easy to show that the allowed solution corresponds to the largest rectangle, with sides parallel to the axes, which may be inscribed in the metastable region. This is also indicated yielding the bandwidths

$$C - U/2 < \varepsilon_i < 2C - U \tag{12}$$

for $n_i = 2$ and

$$0 < \varepsilon_j < C - U/2 \tag{13}$$

for $n_j = 0$, in agreement with the results of Ref. 2. It is interesting to note that any relaxation of the range of the interaction increases the range of metastability. In particular, if only decays to the ground state are permitted (as may be arranged experimentally for a system with few metastable states) the bandwidths are increased by a factor of 2 (indicated by the lengths of the sides of the isosceles triangle).

Metastable Paramagnetism:

We also consider metastable states occupied by a single electron which, as described above, have no stable regions. Thus we consider a site i where $n_i = 1$ and consider the absorption $\Delta n = 1$ and emission $\Delta n = -1$ of a single particle through a process involving the site j. Again using the criterion (8) to define the region of metastability, the range of energy ε_i is given through the relations

$$n_j = 0 \qquad \varepsilon_i - \varepsilon_j \leq C \tag{14}$$

$$n_j = 1 \qquad \varepsilon_i - \varepsilon_j \leq U \tag{15}$$

$$n_j = 2 \qquad \varepsilon_j - \varepsilon_i \leq C \tag{16}$$

where we have employed eqs. (4), (5), and (6). The paramagnetic case is sketched in Figure 2, where the lines defining the regions satisfying the inequalities (14) and (16) are drawn. The vertical boundaries of the shaded region where paramagnetic metastable states may occur are defined through the limits of $n_j = 2$ states (eq.(12), where we use $i \to j$) within the infinite range approximation and correspondingly for $n_j = 0$ (eq. (13)). These are the vertical lines at $\varepsilon_j = 2C - U$ and at $\varepsilon_j = 0$. The same algorithm applies for determining the allowed paramagnetic states which is the largest rectangle with sides parallel to the axes. This region is indicated as (a) for the infinite range model. The band-width satisfies $\delta\varepsilon_1 < 2U$, as is seen by inspection, first predicted by Licciardello et al., and is consistent with the ineqality (15) without further restriction.

It is interesting to examine the consequences of ignoring fast particle exchange between paramagnetic states, i.e. process (15). This is entirely realizable at densities in which paramagnetism has been induced in amorphous materials up to now. If the range of metastable diamagnetic states is suppressed, (indicated in rectangle b , in Figure 2) the energy range of allowed paramagnetic states increases as shown. This is an interesting prediction and may be tested experimentally. In general, metastable diamagnetic states are produced thermally (no gap) whereas metastable paramagnetic states must be optically induced. Thus materials annealed at low temperature for long times should, according to these considerations, be susceptible to a larger density of induced paramagnetism.

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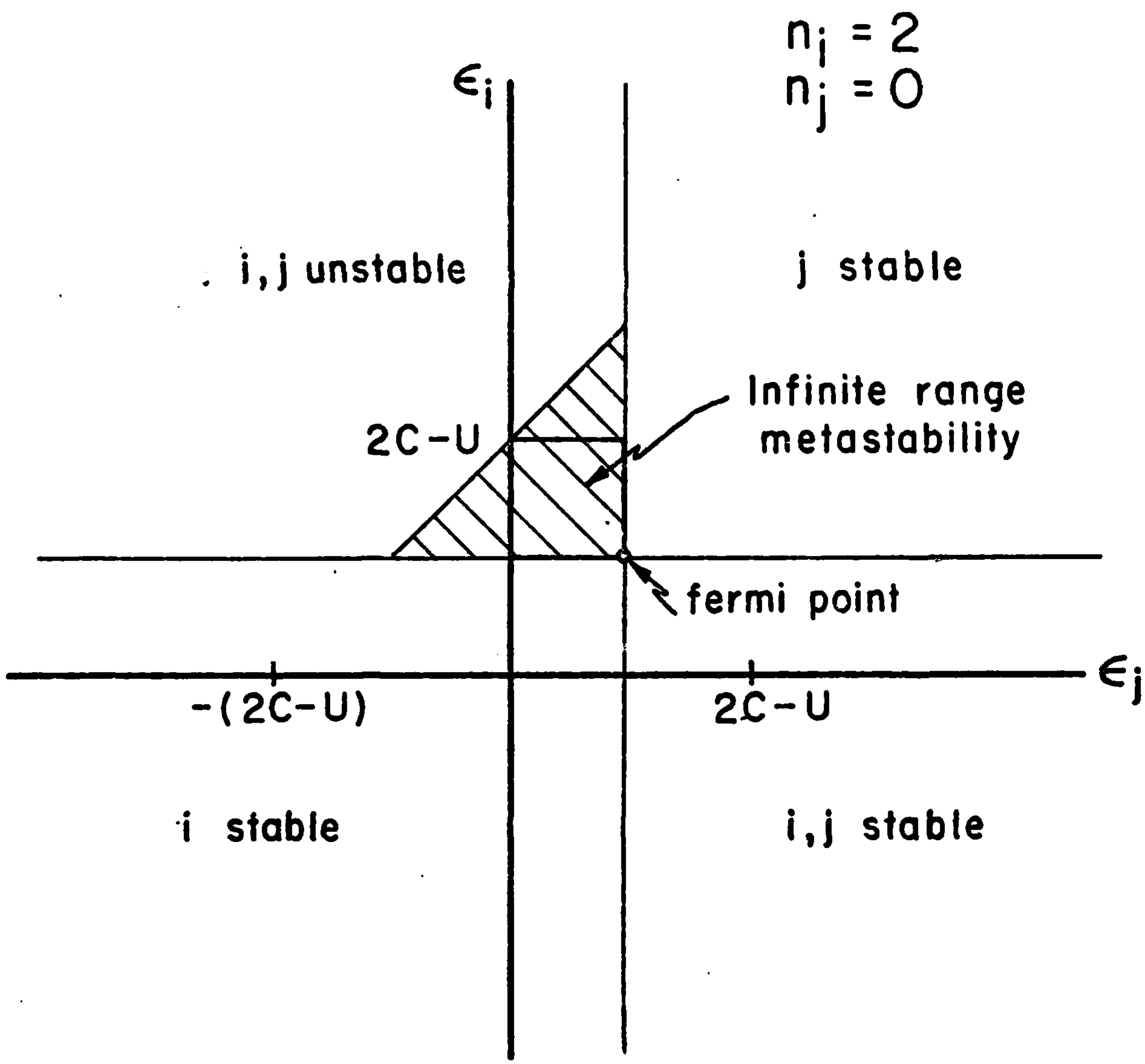
Figure Captions

Figure 1. Phase diagram for diamagnetic metastable states with energy ε_i and occupation $n_i = 2$ to fast emission of an electron to a site g with $n_j = 0$ and energy ε_j. The rectangle defines the metastable region when the process $i \rightarrow j$ is permitted for all i,j .

Figure 2. Phase diagram for paramagnetic metastable states with $n_i = 1$ and energy ε_i. The shaded region defines the region of stability for such states to fast emission of absorption of a single electron from metastable states with energy ε_j. The rectangular area (a) defines the metastable region when the process $i \rightarrow j$ is allowed for all i,j . The region (b) ignores processes involving only paramagnetic states and considers processes involving a narrower region of metastable states with $n_j = 0,2$.



$n_i = 2$
$n_j = 0$
ϵ_i
i, j unstable
j stable
Infinite range metastability
2C−U
fermi point
ϵ_j
−(2C−U)
2C−U
i stable
i, j stable

Fig. 1

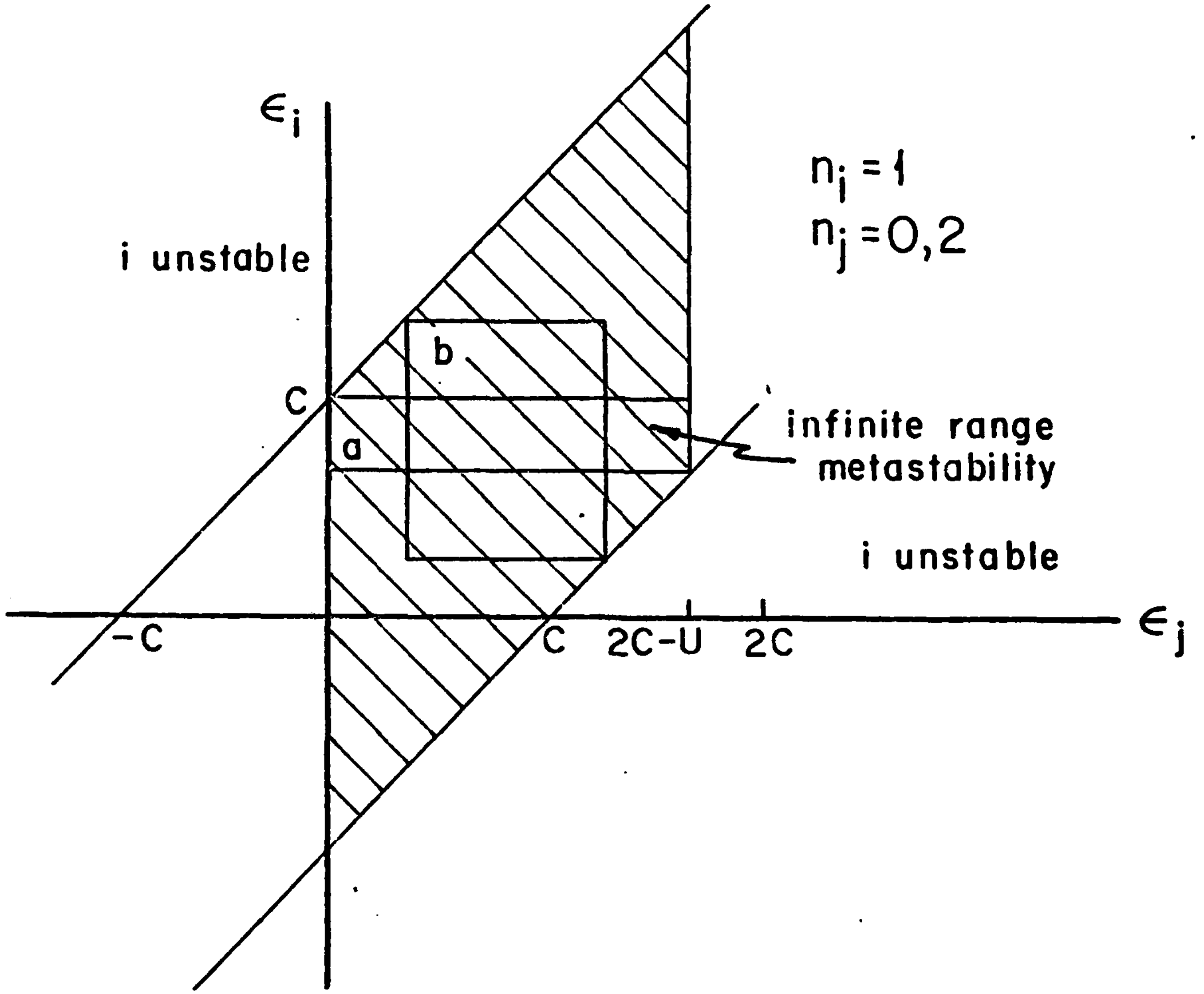

ϵ_i
i unstable
$n_i = 1$
$n_j = 0,2$
b
C
a
infinite range
metastability
i unstable
$-C$
C
$2C-U$
$2C$
ϵ_j

Fig. 2

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The bandwidths for metastable states in a simple model of amorphous semiconductors is evaluated exactly. The region of metastability in the space of the model parameters (phase diagram) is deduced and the subregion corresponding to an infinite range model is indicated. The model predicts both paramagnetic and diamagnetic metastable states and the relationship between them is dicussed.

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