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SMALL-POLARON FORMATION AND MOTION IN MAGNETIC SEMICONDUCTORS†

David Emin, Sandia Laboratories,* Albuquerque, NM 87185 USA

Short Title: Small-Polaron Formation and Motion

ABSTRACT

The fundamental physical processes associated with small-polaron formation are described with various magnetic semiconductors being cited as examples. Attention is then directed toward the mechanisms of charge transfer and small-polaron hopping motion in magnetic semiconductors.

On décrit les procédés physiques fondamentaux associés avec la formation de petits polarons, citant comme exemple les semiconducteurs magnétiques. On dirige l'attention vers les mécanismes de transport de la charge et au mouvement par saut des petits polarons dans les semiconducteurs magnétiques.

Electronic charge carriers in magnetic, as well as non-magnetic, semiconductors and insulators can typically be divided into two distinct categories based on whether or not their presence is associated with significant displacements of the atoms of the material. Specifically, one class of carrier is associated with alterations of the equilibrium positions of the atoms of the host material which are much smaller than the amplitudes of zero-point atomic vibrations. In such

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instances a carrier is typically viewed as moving readily through the material, much like a free particle, with its motion only occasionally impeded by the occurrence of scattering events. The complementary situation is one in which the carrier is severely localized within the potential well associated with displacements of the surrounding atoms that are substantial compared with the amplitudes of zero-point atomic vibrations. The motion of the electronic carrier is then typically described in terms of a succession of transitions in which the carrier moves between different sites in response to changes in the displacement pattern of the host atoms. This type of motion, termed phonon-assisted hopping motion, is usually characterized by rather low carrier mobilities, $\mu \leq 1\ cm^2/V\text{-sec}$. In this work the origin and ramifications of the dichotomy as well as the concepts involved in describing small-polaron transport are addressed.

In proceeding to define a small polaron, first note that a stationary excess charge added to an otherwise perfect lattice will generally induce displacements of the equilibrium positions of the atoms of the solid. These displacements will be such as to produce a potential well about the added charge. If the mass of the added carrier is sufficiently small compared with the atoms of the material, when released the carrier will respond to the potential well produced by the atomic displacements as if it were static, i.e., a sufficiently light carrier will adjust to the instantaneous

atomic displacements. Then, if the potential well is sufficiently deep the carrier will occupy a bound state, being unable to escape from the potential well without further alteration of the atomic positions and the potential well itself. In this circumstance the carrier is said to be self-trapped. The unit comprising the self-trapped carrier and the associated atomic deformation pattern is referred to as a polaron, with the adjectives small or large denoting whether the spatial extent of the wavefunction of the self-trapped carrier is small or large compared with the dimensions of a unit cell.

To understand how the dichotomy between small-polaronic and nonpolaronic carriers arises, consider the energy of the adiabatic eigenstates of the system comprising a carrier in a deformable continuum, $E(R)$, as a function of scaling the radius of the electronic state by the factor R.[1] As the radius of the wavefunction is reduced (R being reduced) the carrier resists the contraction by increasing its kinetic energy: namely, one has that the kinetic energy varies as T_e/R^2. On the other hand, the particle's potential energy falls with decreasing R, as the well is deepened, as $-|V^s_{int}|R^3$ for a short-range interaction, while the strain energy increases as $|V^s_{int}|/2R^3$. Thus, as shown in Fig. 1, the energy which results from the competition between the kinetic and potential energy contributions is peaked about $R = \frac{3}{4}|V_{int}/T_e|$. This means that two situations are realizable.[2,2] Either the particle is unbound and spread out over the entire continuum ($R \to \infty$) or the carrier is bound

and severely localized ($R \to 0$) in a steep and deep potential well associated with a very localized deformation of the continuum.

The fact that the small-polaronic state at $R = 0$ always exists and is energetically favored results from considering a continuum rather than a discrete lattice.[1,3] The distinguishing effect of a discrete system is that the electron-lattice interaction term does not (as in a continuum) grow indefinitely in magnitude at $R \to 0$, but rather saturates when the radius of the electronic wavefunction shrinks sufficiently so as to be contained within a unit cell. In this situation further confining of the electronic wavefunction is not associated with a greater deepening of the deformation-related potential well. The ramifications of discreteness can be understood by imposing a small-R cutoff, R_c, which corresponds to the radius of the electronic wavefunction being comparable to a lattice constant. Namely, the continuum view is only appropriate for $R > R_c$. Three possibilities present themselves. As shown in Fig. 1, $R_c(R_c^1)$ may lie to the right of the peak of the $E(R)$ curve. In this case only the nonpolaronic ($R = \infty$) solution exists. Alternatively, $R_c(R_c^2)$ may lie to the left of the peak at such a value that $E(R_c^2) > 0$. In this instance the small-polaron solution is metastable with respect to the non-polaronic solution. Finally, $R_c(R_c^3)$ may correspond to a sufficiently small R so that $E(R_c^3) < 0$; the small-polaronic state is then energetically preferred. Thus within the adiabatic

theory the small-polaronic state may or may not exist and may or may not be energetically stable.

A significant feature of these results is the existence of a barrier to small-polaron formation.[1-4] Namely, even when the small-polaronic state is energetically stable, a particle in the metastable nonpolaronic ($R \to \infty$) state cannot adiabatically reach the small-polaronic state ($R = R_c^3$) without negotiating an energy barrier. Physically this barrier arises, in this case, because the carrier's kinetic energy increases more rapidly with a contraction of the carrier's wavefunction, and associated deformation pattern, than the potential energy of the system falls. In other words, to pass adiabatically between nonpolaronic and small-polaronic ground states requires a change of the deformation parameters which, in these circumstances, can only occur by either supplying energy to the system (going over the barrier) or by the tunneling of the host atoms between different deformation configurations. If such an impediment to a change of deformation pattern did not exist, the time required for the atoms to assume new positions would be of the order of a vibrational period, 10^{-12} sec. However with the presence of the barrier, the time characterizing the transition of a nonpolaronic carrier to a small polaron can be substantially increased. Thus the occurrence of a time delay for small-polaron formation is a manifestation of the presence of an energy barrier. Since the energy barrier and time delay arise from a competition between the carrier's kinetic and

potential energies one sees that the magnitude of the energy barrier and the time delay decrease with increase of either the carrier's mass or the electron-lattice interaction strength.

In the preceding discussion it has been assumed that the potential energy of the charge carrier depends linearly on only the local strain of the continuum. However, there are situations in which the electron-lattice interaction is not purely short-range but rather possesses a long-range component. The standard example is that of a charge interacting with the dipoles of a polar material.[1] In fact, early models of polaron formation considered this component of the electron-lattice interaction to the exclusion of the short-range portion.[5] For such a model the carrier's potential energy manifests an inverse linear dependence on R, varying as V_{int}^{L}/R,[1] rather than the inverse cube dependence characteristic of the short-range interaction. E(R) then consists of but a single stable state associated with the solitary minimum of the E(R) curve.[1,3] That is, there is a single finite-radius polaron without a barrier to its formation. Furthermore, the addition of the long-range component of the interaction to a system with a short-range component of the electron-lattice interaction generally reduces, and may even eliminate the barrier to small-polaron formation.[1] Thus the presence of the long-range interaction fosters small-polaron formation. Since magnetic semiconductors are often polar materials one may question whether substantial barriers to small-polaron formation[1] exist

at all in those magnetic semiconductors where small-polaron formation occurs.

Specifically, one might envision utilizing transient photoconductivity (drift mobility) measurements in an attempt to observe the high-mobility transport associated with nonpolaronic carriers in crystals prior to their conversion to low-mobility small polarons. Indeed, the discrepancy between the high nonpolaronic mobilities observed for holes in NiO from such experiments[6] and the low small-polaronic mobilities obtained from dc transport measurements[7] may be resolvable in these terms. Namely, the high-mobility holes observed in the transient experiment are then those holes which have been unable to relax to their small-polaronic state during their passage through the material. An interesting possibility is that the high-mobility holes may be associated with the oxygen p-band and the low-mobility small-polaronic holes may be associated with the d-orbitals of the nickel ions. To form a small polaron a hole must then move from an oxygen ion to a nickel ion about which the ligands are relaxed, with the time delay that is associated with such an event.

The discussion thus far has been based on adiabatic treatments of a continuum model of interacting electronic and atomic species. In these studies the motion of the atom is taken to be arbitrarily slow. However, some significant features of the theory of electronic carriers in semiconducting solids only emerge when the simplifications of these models are transcended.

Specifically, variational studies of an electron added to a discrete deformable crystal characterized by a short-range electron-lattice interaction,[3,8] indicate that while the dichotomy between nonpolaronic (conduction-band) and small-polaronic states persists beyond the adiabatic limit, small-polaronic states are only possible (dynamically stable) when the electron-lattice interaction exceeds a critical value, C_{small}. Furthermore, nonpolaronic states are only dynamically stable when the electron-lattice coupling is less than a (temperature-dependent) critical value, C_{weak}. This situation is illustrated in Fig. 2, where the energy spectrum of an excess electron added to a deformable crystal is shown as a function of the electron-lattice coupling strength measured in units of the ratio of the small-polaron binding energy, E_b, to the quantum of vibrational energy, $\hbar\omega_o$. In the extreme narrow-band limit, the complement to the adiabatic limit, where the electronic bandwidth, $12J$, is small compared with the phonon energy (corresponding to the time for intersite motion of a carrier exceeding the time required to fully displace an atom, the vibrational period), C_{weak} and C_{small} are zero and only the small-polaronic states exist.

Several features of these results deserve further comment. First, note that the stable states of a system defined by $E_b/\hbar\omega_o$, and J can change abruptly from being nonpolaronic to being small-polaronic with a relatively small alteration of the parameters. This is simply a manifestation of the clear

dichotomy which exists between the two classes of states and is not an artifact of the models. It is thus understandable that different magnetic semiconductors of a series of materials, such as the monoxides of transition metals, manifest radically different electronic properties corresponding to whether the carrier is nonpolaronic or small-polaronic. For example, it appears that the holes in MnO form small polarons[9] while those in CoO do not.[10] Second, the small-polaron band is extremely narrow; this narrowness results from the requirement that the intersite transfer of a self-trapped carrier involve the concomitant tunneling of atoms between the equilibrium locations associated with self-trapping at each of these sites. Third, the dynamic stability of the nonpolaronic state is simply associated with the condition that the carrier-induced change of atomic momenta (the product of the displacive force exerted by the carrier on the atoms multiplied by the time that a nonpolaronic carrier can reside at a site) be small compared with the characteristic vibratory momenta of these atoms.[8] In the adiabatic limit (infinitely massed atoms moving infinitesimally slowly with arbitrarily large momenta) this condition is always fulfilled and the nonpolaronic state exists.[8] The essential reason that nonpolaronic carriers are dynamically stable in wide-band crystals is that the nonpolaronic carrier simply does not reside at a site sufficiently long to produce significant atomic displacements.

When the imposition of disorder restricts intersite motion

it tends to facilitate small-polaron formation.[11] In a crystalline ferromagnetic semiconductor a carrier experiences disorder above the magnetic ordering temperature. Analogous to the collapse of a nonpolaronic carrier to a small polaron following the imposition of sufficient disorder is the shrinking of a large-radius donor state of a ferromagnetic semiconductor to a severely localized one[11] upon raising the temperature beyond the Curie temperature. In fact a version of this phenomenon has been advanced to explain the abrupt reduction of impurity conduction associated with oxygen vacancies in EuO above the Curie temperature.[12]

A mechanism to produce an abrupt semiconductor-to-semiconductor or semiconductor-to-metal transition emerges from the dependence of the energy spectrum on temperature.[8] Specifically, since the stability of the nonpolaronic states extends to an ever increasing value of the coupling strength as the temperature is raised, (C_{weak} increases with temperature), systems in which only small-polaronic carriers can exist at a given temperature, $E_b/\hbar\omega_o > C_{weak}(T)$, will be presented with the possibility of having high-mobility nonpolaronic carriers at higher temperatures. If the resulting partial conductivity of the nonpolaronic carriers exceeds that of the small polarons a significant conductivity transition will occur. Furthermore, if a significant energy gap then exists for producing the nonpolaronic carriers the transition will be of the semiconductor-to-semiconductor variety. Otherwise it will be a semiconductor-

to-metal transition. Thus one can envision a polaronic mechanism to drive such transitions, in which the low-temperature low-conductivity phase is characterized by the charge carriers forming small polarons.

Since the small-polaron band is usually extremely narrow (typically $\leq 10^{-3}$ eV), small-polaron transport is almost always described in terms of phonon-assisted hopping motion. In other words, when the mean-free-path associated with small-polaron band motion is less than an intersite distance, small-polaron motion is represented as a succession of transitions via which the charge and associated atomic deformation pattern move between adjacent sites.[13]

To understand the physical basis of phonon-assisted hopping motion first note, as represented by arrow a of Fig. 3, that a degeneracy exists between the groundstates of a small polaron localized at either of two geometrically equivalent sites. As a result the carrier may move between these equivalent wells provided the atomic distortion pattern is concomitantly shifted. If the alteration of atomic positions associated with such motion is large compared with the amplitudes of their zero-point atomic vibrations such motion is a rare quantum mechanical (tunneling) event with the small-polaron transfer therefore also being extremely slow. However, at finite temperatures amid the myriad of atomic configurations there is a substantial probability that the atomic system assumes configurations associated with a reduced disparity between the atomic configurations within the carrier

occupies initial and final sites. Then associated with this excited configuration of atoms there is an enhanced atomic tunneling rate, and therefore a larger small-polaron hopping rate. This situation is schematically illustrated by process b of Fig. 3. Finally, at sufficiently high temperatures, typically comparable to a significant fraction of the characteristic phonon temperature, the system has a substantial probability of assuming more distorted atomic configurations for which the electronic levels associated with initial and final sites are momentarily degenerate. Such an event is termed a coincidence event. The electronic carrier may then move between wells without tunneling of the host atoms. The small-polaron transfer rate associated with such an occurrence is therefore relatively large. Since the atomic motion associated with this type of process, process c of Fig. 3, is classical, the temperature regime in which these processes dominate the small-polaron transfer is termed the semiclassical regime. While the small-polaron jump rate increases with temperature in a nonarrhenius manner at low temperatures, once the high-temperature semiclassical regime is reached the small-polaron jump rate assumes an activated temperature dependence.[14-16] Here the activation energy, E_A, is simply the minimum energy associated with creating a coincidence event relative to the groundstate energy of the system.

Assuming that successive hops occur independently of one another,[17] and employing the Einstein relation, the hopping mobility of a small polaron in the semiclassical regime may be

written as

$$\mu = (ea^2/kT)\,(\omega_o/2\pi)e^{-E_A/kT}\,P, \qquad (1)$$

where e is the charge of the carrier, a is the hopping distance, kT is the thermal energy, and P is the probability that the charge carrier responds to a coincidence event by negotiating a hop, i.e., by moving between sites.[11] Specifically, if the time required for the electronic carrier to move between sites is less than the duration of the coincidence event, the carrier can adiabatically follow the atomic motion and P is essentially unity. Alternatively, if the carrier's response is too slow, the hop is limited by the carrier's inability to adiabatically respond to the atomic motion, $P < 1$, and the hop is termed nonadiabatic. P then depends upon the absolute square of the electronic transfer integral.

Treating small-polaron hopping between magnetic sites of a magnetic semiconductor involves several additional considerations. As an example, first envision the motion of an electron between two $s=\frac{1}{2}$ sites, or equivalently, the motion of a hole between two s=1 sites, as for a d-band hole in NiO. As illustrated in Fig. 4, due to the indistinguishability of the electrons the transfer may be associated with a two-electron "exchange transfer" in addition to the standard one-electron transfer;[18] the relative importance of these processes in a given situation depends on the relative magnitudes of the associated transfer integrals. Furthermore, it has been established that the transfer integral associated with intersite motion

depends on the initial and final spin states of the system.[18,19] However, in the example at hand this is a small effect, with the transfer integral between antiferromagnetically aligned spins being reduced by only a factor of one-half from that of ferromagnetically aligned spins.[18,19]

An important effect is associated with the fact that the magnetic environment of a carrier generally changes as a charge moves between antiferromagnetically aligned sites of an antiferromagnet.[18] As a result, each hop is a transition between nondegenerate states. In such a situation the activation energy of each small-polaron hop is typically augmented by the term $\frac{1}{2}(E_f - E_i)$, where E_i and E_f are, respectively, the electronic energies of the initial and final states involved in the hop.[11] As a result the carrier moves through an antiferromagnetic material via a succession of hops which are upward and downward in electronic energy. The small-polaron mobility is then modified from that of Eq. (1) by the factor

$$f_{mag} = \frac{\sum_{i,f} e^{-E_i/KT} \, e^{-\frac{1}{2}(E_f - E_i)/KT} \, F_{i,f}}{\sum_i e^{-E_i/KT}}$$

$$= \frac{\sum_{i,f} e^{-\frac{1}{2}(E_i - E_f)/KT} \, F_{i,f}}{\sum_i e^{-E_i/KT}} \qquad (2)$$

where $F_{i,f}$ is a relatively unimportant factor which depends on whether the hopping is adiabatic or nonadiabatic. As shown in Fig. 5, f_{mag} garners a significant temperature dependence

below the Néel temperature while retaining a much weaker temperature dependence in the paramagnetic regime. This change in temperature dependence is manifested by a drop of the mobility activation energy above the Néel temperature. Observation of such a change has been reported in the recent literature for hole transport in NiO.[7]

In this review several of the recent areas of progress and interest involving the application of small-polaron theory to magnetic semiconductors have been succinctly discussed. Presently a growing number of transient experiments have been designed to observe the time delays associated with the self-trapping of both charge carriers and excitons. Furthermore, analyses of dc transport data on various magnetic semiconductors, such as MnO and NiO, indicate that the equilibrated charge carriers in these materials form small polarons. Due to space limitations a number of very important additional topics which are currently applicable to magnetic semiconductors have not been broached. These are the questions of correlated small-polaron hopping and the Hall effect. For an introductory discussion of these phenomena the reader is referred to other reviews.[11,20,21]

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FIGURE CAPTIONS

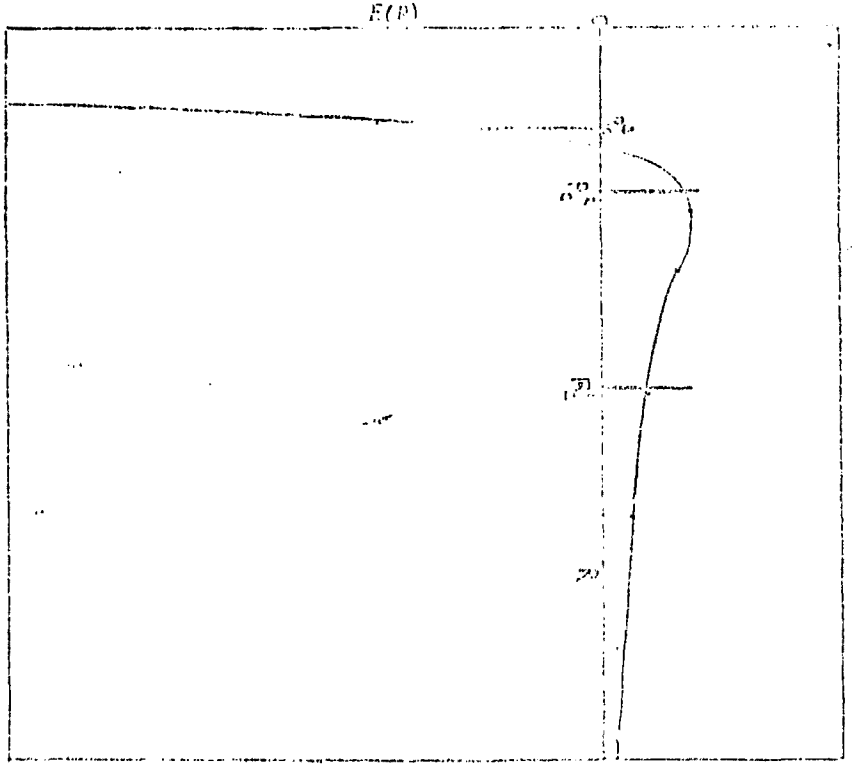
Fig. 1 E(R) is plotted against R for a short-range electron-lattice interaction. The three possible cut-off values of R are labelled as R_c^1, R_c^2, and R_c^3.

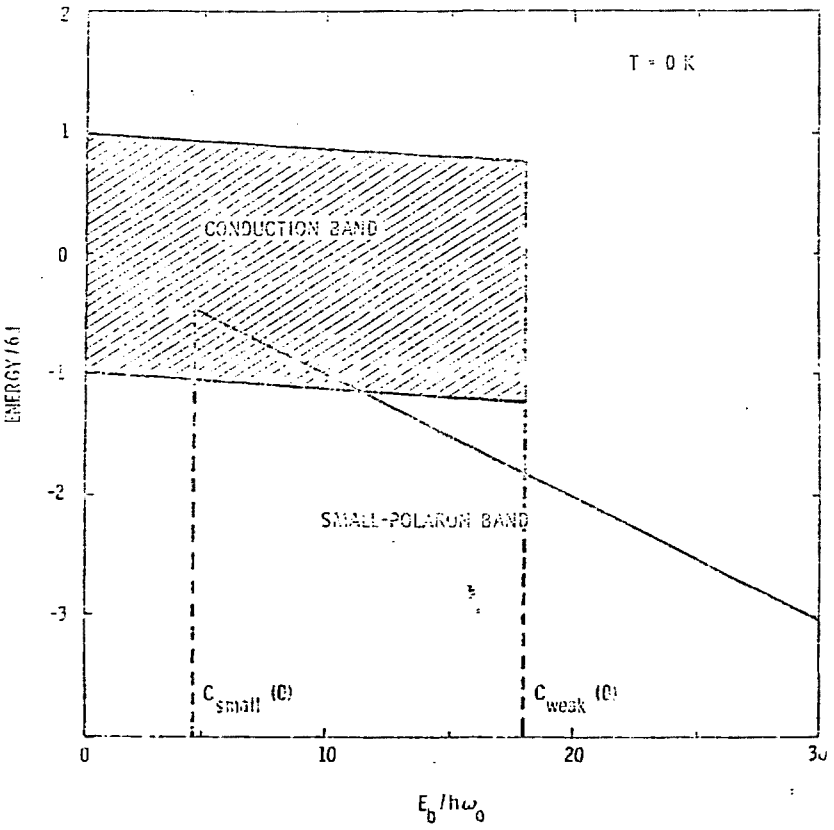
Fig. 2 The zero-temperature energy spectrum is shown as a function of the electron-lattice coupling parameter $E_b/\hbar\omega_o$. J is the rigid-lattice electronic transfer integral. This plot is for the adiabaticity parameter of $6J/\hbar\omega_o = 10$.

Fig. 3 The predominent hopping processes for low (a), intermediate (b), and high (c) temperatures. Process c depicts the establishment of a coincidence event.

Fig. 4 Direct and exchange transfer processes are schematically illustrated; electrons with like spins are indistinguishable.

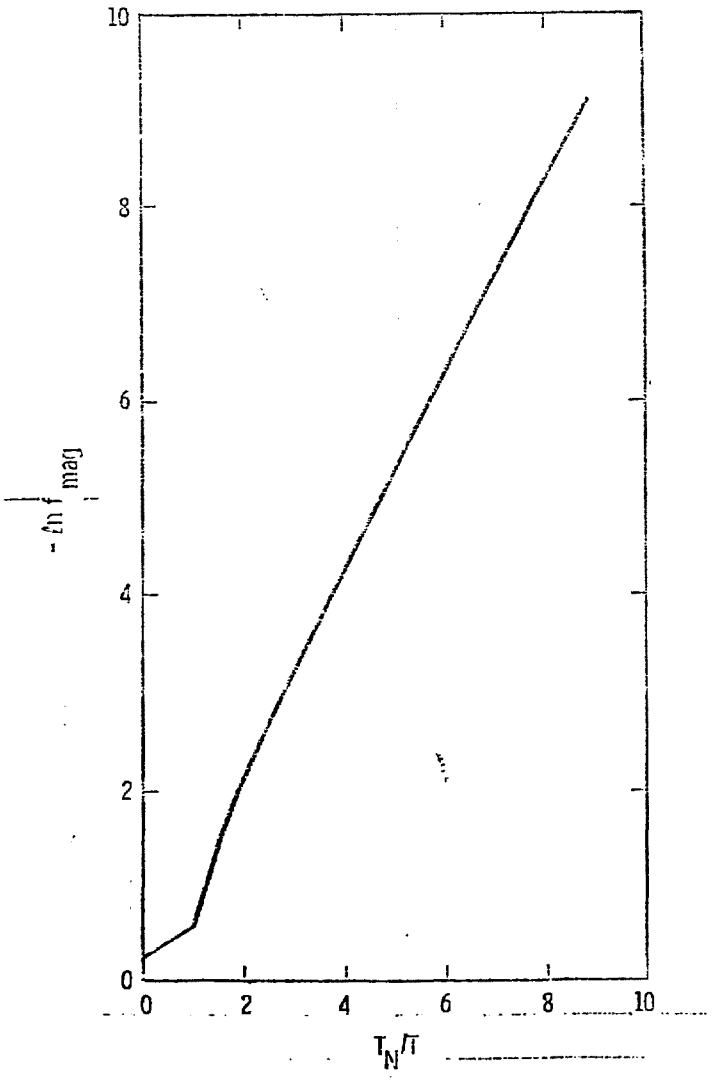
Fig. 5 For an antiferromagnet $-\ln f_{mag}$ is plotted against T_N/T, where T_N is the Néel temperature.


E(P)


T = 0 K
CONDUCTION BAND
SMALL-POLARON BAND
C_{small} (0)
C_{weak} (0)
ENERGY/61
$E_b/\hbar\omega_0$
2
1
0
-1
-2
-3
0
10
20
30

C
C
C

direct
transfer
exchange
transfer


10
8
6
4
2
0
0
2
4
6
8
10
$-\ln f_{mag}$
T_N/T