$$B(k,\omega)=\sum_{n=0}^{\infty}R_{2n+1}\tilde{t}^{\,2n+1}=\frac{1}{L}\int dx\,dx'\,1-\tilde{t}^{\,2}\;\frac{\exp[i\omega^{1/2}|x-x'|-ik(x-x')]}{1-\tilde{t}^{\,2}\exp(2i\omega^{1/2}|x-x'|)}\quad. \tag{29}$$

The integrals in (28) for $A(\omega)$ may be performed explicitly, yielding

$$A(\omega)=(i\omega^{1/2})^{-1}(\ln\omega^{1/2}+\ln\omega^{1/2}-2i+2\ln\omega^{1/2}-i)\quad, \tag{30}$$

where we have used (8) and (13).

While a formal expansion for $B(k,\omega)$ can be obtained by expanding the denominator of the integrand in (29) and then performing the integration:

$$B(k,\omega)=2i\sum_{n=0}^{\infty}\tilde{t}^{\,(2n+1)}\frac{(2n+1)\omega^{1/2}}{(2n+1)^2\omega-k^2}\quad. \tag{31}$$

Comparing $\langle \mathcal{G}_{kk}(\omega)\rangle$ given in (26) using (30) and (31) with a similar expression of Des Cloizeaux shows that the two approaches yield identical results in this approximation.[6]

An explicit comparison is made in Des Cloizeaux's paper with the density of states calculated numerically and that calculated from (27) and he found rather good quantitative agreement between the shapes of impurity band calculated both ways.

A systematic expansion of the t matrix building in higher and higher statistical correlations is in principle possible. These terniary and higher clusters enables one to calculate the tails of the impurity band below the two-impurity electron binding energy at which the present density of state cuts off. The main feature of this expansion is that the statistical correlations are treated at the same level as the quantum-mechanical correlations. This means building in binary statistical correlations at the same time treating exactly quantum-mechanical electron-impurity pair interactions. In the work on Des Cloizeaux this procedure is accomplished by means of his articulation points, which separate statistically events before and after a particular cluster expansion by requiring that all impurities the electron meets before an articulation point is different from those it meets afterwards.

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PHYSICAL REVIEW B VOLUME 2, NUMBER 8 15 OCTOBER 1970

Sign of the Hall Effect for Hopping Transport in Molecular Crystals*

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(Received 31 December 1969)

It is shown that the Hall effect for hopping transport may be anomalous in sign, just as it may be for coherent transport in narrow bands. Anthracene is treated as a specific example.

It has been recognized for some time that charge carrier transport in semiconductors with narrow bands (with widths of order kT or less) may give rise to an anomalous (negative) Hall effect.[1,2] In such a solid, the carriers are deflected in a direction opposite to the Lorentz force. For this to happen, the band must be not only narrow but also unsymmetrical. In a narrow band, all levels are almost equally populated, so that states with negative effective mass contribute on almost equal terms with states with positive effective mass. In the Hall effect, each effective-mass contribution is weighted according to the velocity of the carrier in that state, which depends on the band structure. If the band is unsymmetrical, the various contributions receive unequal weights and the negative effective-mass contributions may dominate, leading to a negative Hall effect.

It is also well known that for sufficiently narrow bands hopping, i.e., random incoherent transfer to neighboring sites, may be a more appropriate description of transport than coherent motion in a band, except at the lowest temperatures where hopping is not possible.[3] However, there seems to be some confusion about the sign of the Hall effect in the hopping regime. Several authors in discussing the Hall effect in anthracene have tacitly assumed that for hopping the sign must be normal,[4,5] and this assumption is explicitly stated by Damask and Dienes.[6] On the other hand, Austin and Mott[7] note that the sign of the Hall effect has always been found the same in the hopping regime as in the corresponding low-temperature band regime. In this paper we present simple arguments to show how the Hall mobility for hopping transport can be anomalous in sign.

Although hopping is dominated by uncorrelated jumps to adjacent sites, these lowest-order contributions to transport do not contribute to the Hall effect. A carrier can only be deflected in a magnetic field when its jump involves at least three sites in a coherent phase-correlated manner.[8] It is the need to consider correlations of phase which makes simple concepts of hopping inappropriate for discussing the Hall effect. To treat the three-site jumps, we consider a hopping model in which quasilocalized electrons are strongly bound to intramolecular phonons. The model is essentially similar to that of Holstein,[3] but is not restricted to a linear electron-phonon coupling. In particular, the argument should also hold when the dominant electron-phonon coupling is quadratic in the vibrational coordinates, as it appears to be in anthracene.[9]

To calculate the Hall effect in this model we use the method of Friedman and Holstein,[8] based on time-dependent perturbation theory. (Similar results are obtained by linear-response theory.[10,11]) In this method the Hall effect arises from the influence of the magnetic field on the interference between the quantum-mechanical probability amplitudes for a direct hop of a carrier between adjacent sites and for an indirect hop between the same sites via a third site of equal energy. The requirement that the three sites have equal energy makes the process coherent. In the simplest case of a regular plane triangular lattice with the magnetic field perpendicular to the plane, the Hall mobility is (see, for example, Ref. 8)

$$\mu^H = (3\, q\, |\, q\, |\, d^4 / 4\hbar\, kT\mu^D)\; W_T^0\, (i \to j \to k)\,, \tag{1}$$

where q is the carrier charge (including sign), d is the lattice spacing, μ^D is the drift mobility (which is positive and proportional to $|\, q\, |$), and i, j, and k are mutually adjacent sites. The zero-field interference rate $W_T^0\, (i \to j \to k)$ is given in any lattice by a thermal average over initial phonon numbers and a sum over intermediate and final phonon numbers of rates

$$W^0\, (i \to j \to k) = (4\pi^2 V_{kj} V_{ji} V_{ij} / \hbar)\; \delta\, (E_k - E_i)\; \delta\, (E_j - E_i)\,. \tag{2}$$

Here E_i is the energy with the carrier localized at site i, and the V_{ij} are the matrix elements for carrier exchange between sites i and j in zero external field. We confine ourselves to the slow-electron limit, in which carrier bandwidths are much narrower than phonon bandwidths. The matrix elements can then be factorized into a carrier exchange integral J_{ij} and a vibrational overlap factor, while the δ functions can be expressed as densities of phonon states. Since the vibrational overlap factors and densities of states are intrinsically positive, it follows from Eqs. (1) and (2) that μ^H has the sign of $qJ_{kj}J_{ji}J_{ik}$.

The exchange integrals J_{ij} are normally negative for electrons and positive for holes. A chemical mnemonic for this is to note that electron exchange between atoms increases electron density between them, enhancing the bonding, and thus lowering the energy. Hole exchange decreases the electron density and hence the bonding, and so raises the energy. In Holstein and Friedman's triangular lattice, all J_{ij} are equal and are put equal to $-J$ so that J is normally positive for electrons but negative for holes. Then μ^H has the sign of J for electrons and of $-J$ for holes.

In anisotropic lattices Eq. (1) assumes a more complicated form, since not all contributing triangles are equivalent. However, we have verified for anthracene that the partial sums over all equivalent triangles have the sign of $qJ_{kj}J_{ji}J_{ik}$, so that these quantities still determine the sign of μ^H. Since the J_{ij} are now different and can occur with either sign for either carrier,[12] the sign of the total sum is not immediately clear.

More generally, one can consider a circuit of N sites instead of just three, and then the sign of each contribution to μ^H is determined by the sign of the product of the carrier charge and N factors J_{ij}. Hence this contribution is negative for electrons if an even number of the N factors J_{ij} are negative, and negative for holes if an odd number of the N factors J_{ij} are negative. From this conclusion follows the observation of Austin and Mott[7] that the sign of the three-site Hall effect is normally the same for holes and electrons, while the sign of the four-site effect differs for holes and electrons. However, for small J_{ij} three-site contributions are expected to dominate.

On the basis of the signs calculated for the J_{ij} for electrons and holes in anthracene, the occurrence of both normal and anomalous Hall mobility components can easily be rationalized, not only with the conventional narrow-band model, but also with slow-electron hopping. Hence the sign of a Hall mobility cannot be used as a criterion for deciding between these two transport models. However, given the signs of the J_{ij}, the signs of Hall mobilities can give information about the magnitude of the J_{ij}, i.e., about the width of the bands. Thus if all mobility components are found to be positive when the narrow band and hopping models predict some to be negative, the bands must be very wide compared with kT. The existence of any anomalous Hall mobility components, on the other hand, implies that at least in some directions the bands are not wide compared to kT. For anthracene some of the bands appear to be appreciably wider than kT,[12] so that theoretical prediction of the sign is only possible on the basis of quantitative calculations. A detailed discussion of the Hall effect in anthracene is given elsewhere.[13]

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*Issued as N.R.C.C. Report No. 11507.

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PHYSICAL REVIEW B VOLUME 2, NUMBER 8 15 OCTOBER 1970

Theoretical Investigation of the Possibility of Chemical Binding of Neutrons in F Centers*

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(Received 31 December 1969)

A recent paper [Phys. Rev. Letters 23, 741 (1969)] reported experimental evidence that neutrons can be chemically bound to trapped electrons. The spin-independent electron-neutron interaction due to the electromagnetic structure of the neutron is found to be inadequate to produce such a bound state.

In a recent paper[1] Grant and Cobble report experimental evidence that neutrons are retained in LiF at 4 °K for periods greater than 30 sec and that this retention is related to the existence of trapped electrons in the LiF. Although the experiment does not identify the nature of the trapped electrons, both the method of producing the trapped electrons and the method of removing them point to F centers as the most likely candidate. If this interpretation of the experimental data is accepted then it is necessary to find a physical mechanism that will give a weak bond between a neutron and the electrons trapped in LiF. It is the purpose of this paper to investigate one such mechanism.

The model we investigate uses the following basic assumptions: (a) The neutron is bound to the F-center electron. (b) The F center consists of a negative ion vacancy with an electron trapped in it. (c) The interaction between the electron and the neutron is the attractive spin-independent electrostatic interaction determined by the neutron electromagnetic form factor.[2] (d) The interaction between the neutron and electron is sufficiently weak that we can neglect modifications to the F-center electron wave function due to the presence of the neutron.

The simplest "back of an envelope" calculation using the measured strength of the electron-neutron force is not encouraging. However, there are enough examples of the failure of crude estimates because of unexpected details of the physics that it seems worthwhile to investigate this problem in a little more detail. The calculations reported here take into account two distinctive features of the relevant neutron-electron system, the fact that the electron is already bound in the lattice of LiF and