1969 (unpublished); A. Laubereau and R. Zurek, Z. Naturforsch. 25, 391 (1970).

[12] R. Nava *et al.*, Phys. Rev. 188, 1456 (1969).

[13] B. Berre, K. Fossheim, and K. A. Muller, Phys. Rev. Lett. 23, 589 (1969).

[14] J. M. Courdille and J. Dumas, Solid State Commun. 7, 1623 (1969).

[15] W. Rehwald, Solid State Commun. 8, 607 (1970).

[16] The ⟨111⟩ crystal was cut from a boule supplied by the National Lead Co. approximately three years ago and was previously used in Raman-scattering experiments (Ref. 3). The ⟨110⟩ crystal was obtained from the same supplier about six months ago.

[17] We also find $\Delta\alpha_L^{\langle 110\rangle} = -6.10\times 10^{-7}$ K^{-1}. The inequality $\Delta\alpha_L^{\langle 110\rangle} \neq \Delta\alpha_L^{\langle 111\rangle}$ implies a nonrandom domain distribution.

[18] J. C. Slonczewski, private communication.

[19] G. Sorge *et al.*, Phys. Status Solidi 37, K17 (1970).

[20] L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon, London 1958), Chap. XIV.

[21] L. P. Kadanoff *et al.*, Rev. Mod. Phys. 39, 395 (1967).

[22] The discontinuity of the isothermal bulk modulus can be reliably calculated from an Ehrenfest relation. We obtain $\Delta B_T/B_T \simeq 0.47\times 10^{-2}$.

[23] We believe the contradictory results (Refs. 12-15) previously reported for the ultrasonic attenuation magnitude near T_a can be explained, in part, by differing inhomogeneous strain amplitudes and distributions in different specimens. The velocity shift of a region under a local stress ΔP is $\Delta V/V = 1/V(dV/dT)\times(dT_a/dP)\Delta P$. Just below T_a the temperature dependence of the velocity is extremely large, $1/V(dV/dT) \simeq \times 5\times 10^{-2}$K, resulting in a velocity fluctuation $\Delta V/V \sim 2\times 10^{-3}$, where we have estimated $(dT_a/dP)\Delta P \simeq 5\times 10^{-2}$ K from the transition width. It can be shown that the interference of these phase-shifted sound waves at the transducer gives rise to an apparent frequency-dependent attenuation peaking when dV/dT is a maximum, i.e., approximately 1 K below T_a.

Role of Spin Fluctuations in the Desorption of Hydrogen from Paramagnetic Metals*

H. Suhl, J. H. Smith, and Pradeep Kumar
Department of Physics, University of California, San Diego, La Jolla, California 92037

(Received 17 July 1970)

It is shown that, if the Gomer-Schrieffer induced–covalent-bond mechanism is responsible for the chemisorption of hydrogen on strongly paramagnetic metals, then the rates of chemical reactions involving the adsorped hydrogen may be dominated by energy transfers between the bond and spin fluctuations in the metal.

Recently, Gomer and Schrieffer[1,2] suggested that in chemisorption of hydrogen, at least on strongly paramagnetic metals, a type of "induced" covalency plays a certain role. Since the energy needed to form a net d-electron spin density in the vicinity of the adatom is quadratic in that density, whereas its coupling (exchange) to the adatom's electron spin is negative and linear in the density, formation of a net spin density is energetically favored.

In this note, we propose that if this idea is correct, then a possible explanation of the high efficiency of some of the d metals in catalyzing hydrogenation reactions might be found in the interaction of the adsorbate with spin fluctuations, especially when these display so-called "paramagnon" enhancement.[3] The adatom absorbs thermal spin fluctuations, gaining energy and eventually climbing over the energy barrier characterizing the reaction. We disregard all the complications accompanying the mathematical formalism needed for accurate quantitative evaluation of the Gomer-Schrieffer idea (such as energy dependence of the effective exchange "constant," etc.), and describe the coupling of the adatom of spin $\vec{S}$ to the metal spin density $\vec{s}(\vec{r})$ at $\vec{r}$ by

$$H' = \int J(\vec{R},\vec{r})\vec{S}\cdot\vec{s}(\vec{r})d\vec{r} \tag{1}$$

(or, more precisely, by the part of this interaction that protrudes outside the ground-state manifold), where $J(\vec{R},\vec{r})$ is an effective exchange energy of the (fixed) hydrogen orbital with the d orbitals and $\vec{R}$ is the position of the atom. If one disregards the transverse periodic structure, J has the form $J(\vec{R}_T-\vec{r}_T, Z, z)$ in terms of coordinates transverse and normal to the surface.

We only discuss the simplest surface reaction: desorption of the hydrogen atom; in particular, the desorption rate. The well (or rather, the trough) in which the H atom is bound is about 1 to 3 V deep and 1 to 3 Å wide. Therefore, the atom must have between 10 and 200 excited "bound" states. In thermal equilibrium, the rate of departure of the atom from the surface is the chance that it be found in some one of the top excited "bound" states (it is presumably somewhat free to move in the plane of the surface in each one of these excited states), times the "transmission coefficient" (i.e., the probability of transition) from that level to a free state. This process is accompanied by absorption of a "paramagnon" from the metal according to the Hamiltonian (1). (Presumably, a very similar calculation of the transmission coefficient may be expected to apply to surface reactions involving transfers or rearrangements of chemisorbed hydrogen.)

The nth excited bound state of the atom on a surface area A is assumed to have the form $(1/\sqrt{A})\varphi_n(Z)\exp i\vec{k}_T\cdot\vec{R}_T$; the periodicity of the potential in the plane of the surface is to be accounted for approximately by assigning an effective (probably rather large) mass M^*. For our crude estimate, we calculate only the transition rate from the uppermost "bound state." $J(\vec{R},\vec{r})$ is taken to be Ja_0^3 times a three-dimensional δ function, a_0 being the range of J. The "golden rule" for the transition probability can be expressed in terms of the dynamic spin susceptibility χ of the d electrons at the surface. This is quite difficult to calculate; for simplicity we replace it by the susceptibility of the infinite metal. In terms of the Fourier transform $\chi(q,\omega)$ of

$$\chi(r,t)=-i\langle[s^z(r,t),s^z(0,0)]_-\rangle_{\text{therm av}},$$

we find a probability[4]

$$\frac{3J_{\text{eff}}^2a_0^7}{2\pi\hbar^2}\frac{\operatorname{Im}\int\chi(\vec{k}_T-\vec{k}_T{}',k_Z{}',\omega)dk_Z{}'}{e^{\beta\omega}-1} \tag{2}$$

[where $\omega=\hbar^2(k_T{}^2+k_Z{}^2)/2M-(\epsilon_{\max}+\hbar^2k_T{}'^2/2M^*)$] for making a transition from the highest bound state with transverse k vector $\vec{k}_T{}'$ and energy $-|\epsilon_{\max}|+\hbar^2k_T{}'^2/2M^*$ to a free final state with transverse and normal components k_T and k_Z. Also

$$J_{\text{eff}}=(a_0)^{-1/2}\int\varphi_n{}^*(z)Je^{ik_zz}dz.$$

To find the rate of desorption, the expression (2) must be convoluted with the probability ($\beta=1/kT$),

$$W=\left(\frac{A}{2\pi}\frac{2M^*}{\beta\hbar^2}\right)^{-1}[1-\exp(\beta\epsilon_0)]\exp[-\beta(V-\tfrac{1}{2}\epsilon_0)]\times\exp-\beta\left[\frac{\hbar^2k_T{}'^2}{2M^*}-|\epsilon_{\max}|\right],$$

that the adatom finds itself in the highest bound state (energy $-|\epsilon_{\max}|$) and moving along the surface with momentum $k_T{}'$. (The result is easily generalized if bound-free transitions from several upper states are important.) For simplicity, the bound level energies have been regarded as equispaced harmonic-oscillator levels of spacing ϵ_0. V is the binding energy of the atom. For values of $k_T{}'$ much in excess of k_F, the Fermi momentum χ is zero, and for $0<k_T{}'<k_F$, W is sensibly constant and equal to $2\pi\exp(-\beta V)/[A_T(2M^*/\beta\hbar^2)]$, unless kT is extremely small (~10^{-3} eV for $M^*=M$, the free atomic mass). Two cases must now be distinguished; $M^*/M\sim1$ (high mobility along the surface). Then the atoms come off with nonspherical angular distribution. However, if $M^*/M\gg1$ (essentially localized adsorbate), the

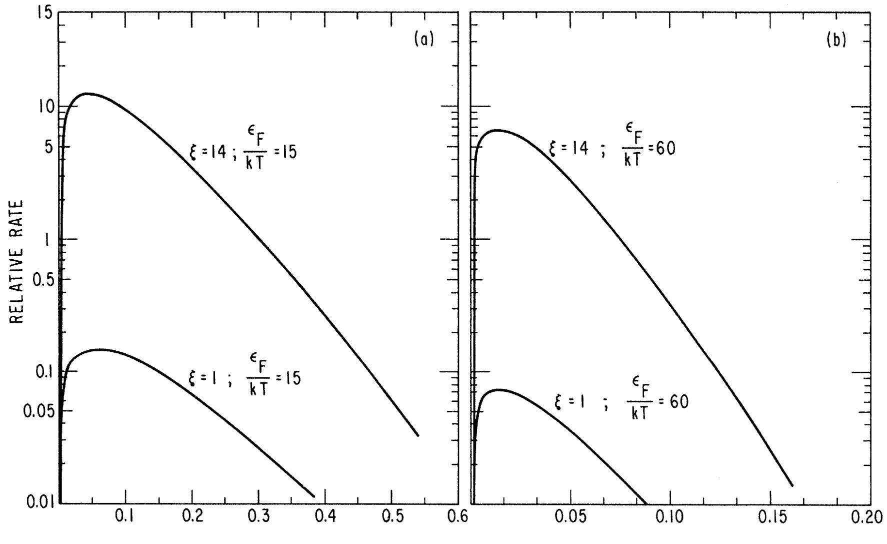

FIG. 1. The function F versus kinetic energy of the desorbed atom for various temperatures and exchange enhancements.

variation of the energy variable in χ (Eq. 2) with k_T' is negligible, χ is integrated over all transverse momenta, and the emitted pattern is spherical (or, rather, hemispherical). We have completed the calculation in the latter case only, because we are making the infinite-medium approximation for χ which will make conclusions about the former case unreliable. For $M^*/M \gg 1$, the probability of desorption per unit time per unit solid angle per unit energy is found to be, for spherical bands, with effective electron mass m^*,

$$\{e^{-\beta V}(M^*/m^*)^{1/2}(3J_{\text{eff}}{}^2a_0{}^7/64\pi^3)F(\omega,\xi,\beta)[1-\exp(-\beta\epsilon_0)]\exp\tfrac{1}{2}\beta\epsilon_0\}/\hbar, \tag{3}$$

where

$$F(\omega,\xi,\beta)=\xi^2\beta\omega^{3/2}(\epsilon^{\beta\omega}-1)^{-1}\int_{\frac{1}{4}\omega^2}^{1}\frac{x\,dx}{x[1+(\xi-1)x/12]^2+(\xi-1)\omega^2/16}, \tag{4}$$

and where, for simplicity, we have set $\epsilon_{\max}=0$. Here ξ is the ratio of the exchange-enhanced to the unenhanced uniform susceptibility. In Eqs. (3) and (4), $\epsilon_0 kT$, J_{eff}, ω, and a_0 are measured in units of the Fermi energy ϵ_F and units of $1/k_F$, respectively. The resulting rates are enormously sensitive to a_0 and V and accordingly are anywhere between 10^9 to 10^{15} sec^{-1} V^{-1}. Figure 1 shows $F(\omega,\xi,\beta)$ and Fig. 2 the integral of $F(\omega,\xi,\beta)$, over all ω. The Doniach approximation[3] to Imχ has been used in the construction of F.

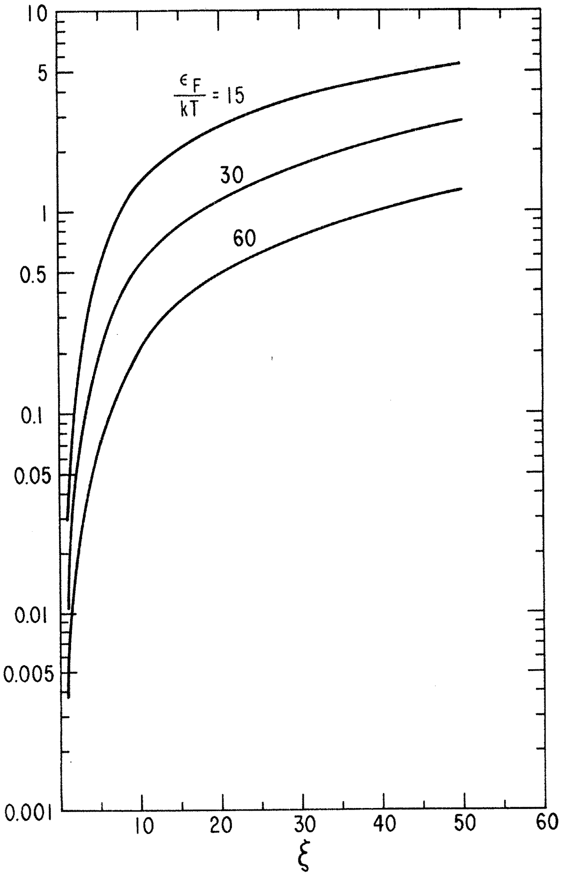

FIG. 2. The integrated rate function F versus enhancement (or versus the square of the "effective" number of Bohr magnetons of the substrate).

In next higher order, two probability amplitudes contribute [Fig. 3(b) and 3(c)]. In the one the electron and in the other the hole making up the incident fluctuation is replaced before final annihilation. Because of the spin character of the scattering, a Kondo anomaly similar to that in the resistivity of dilute magnetic alloys[5] occurs. But because of recoil of the adatom, no question of an infinity of the cross section will arise. However, the ratio of the second- to the first-order amplitude must be of order $(J/\epsilon_F)\ln(M^*/m^*)$ (for low ω), and this may be quite large. A nonperturbative calculation may thus be needed, and is currently under advisement.

Some evidence exists[6] that reaction rates on the nickel-cobalt and nickel-copper systems do indeed increase sharply with "effective number of Bohr magnetons" (that is to say, $\sqrt{\xi}$), if the change in this number is due to the enhancement varying across this series.[7] However, a direct comparison of the results for the relatively complex reactions described in Ref. 5 with the present simple process is probably not warranted.

Recently, a somewhat related suggestion that catalytic effects on ferromagnetic substances are

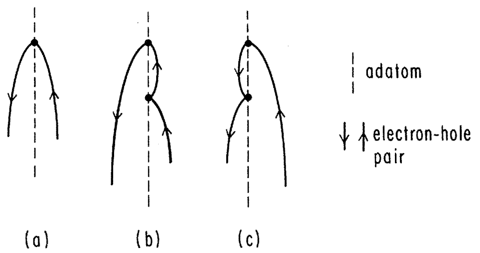

FIG. 3. (a) First-order amplitude for absorption of spin fluctuation by the adatom. (b), (c) Second-order absorption amplitudes via replacement of electron and hole, respectively.

aided by interaction with ferromagnetic spin waves has been made by Ilisca.[7]

The authors wish to acknowledge helpful discussions with Dr. Mueller-Hartmann, Dr. W. Brenig, and especially, Dr. G. Toulouse who brought Refs. 5 and 6 to our attention.

---

*Work supported by the U. S. Air Force Office of Scientific Research, Office of Aerospace Research, under Grant No. AF-AFOSR-67-0610A.

[1] R. Gomer and J. R. Schrieffer, to be published.

[2] J. R. Schrieffer, to be published.

[3] S. Doniach, in *Proceedings of the International School of Physics "Enrico Fermi," Course XXXVII*, edited by W. Marshall (Academic, New York, 1967).

[4] The focusing or defocusing of paramagnons near the adatom might change this probability numerically, but it is hard to see how it could change its energy dependence.

[5] J. Kondo, Progr. Theor. Phys. 32, 37 (1967).

[6] E. I. Evzerikhin and G. D. Lyubarskii, in *Scientific Selection of Catalysts*, edited by A. A. Balandin *et al.* (Israel Program for Scientific Research, Jerusalem, Israel, 1968), Vol. XI.

[7] Where nickel-cobalt is ferromagnetic, the spin fluctuations are (a) noncollective with a gap in their spectrum equal to the exchange energy, (b) spin-wave excitations filling this gap. Only the former of these are considered here, and Eqs. (3) and (4) must be modified to allow for the gap. However, spin-wave excitations will likewise contribute to the desorption.

[8] E. Ilisca, Phys. Rev. Lett. 24, 797 (1970).

Localization in Disordered Materials: Existence of Mobility Edges*

E. N. Economou† and Morrel H. Cohen
The James Franck Institute and Department of Physics, The University of Chicago, Chicago, Illinois 60637

(Received 19 October 1970)

Anderson's theory of localization in disordered systems is extended. It is shown that mobility edges exist, in agreement with the Mott–Cohen–Fritzsche–Ovshinsky model. As the randomness increases, the mobility edges move inwards into the band, and their coincidence is termed Anderson's transition. A criterion is developed restricting the energy regions where mobility edges can be found; explicit results are obtained for a Lorentzian distribution of single-site energies.

Recent models of the electronic structure of disordered materials suppose that there are continuous bands of extended states with tails of localized states.[1,2] Current interpretations of experimental data rest heavily on this notion,[1,2] but no rigorous proof has been given. There seems little doubt of the existence of localized states in the tails,[3] but whether the character of the eigenstates changes abruptly from localized to extended at certain critical energies (termed mobility edges[2]) remains in question. Anderson[4] had demonstrated that for an electron moving in a rigid lattice subject to a Hamiltonian with random matrix elements satisfying certain conditions, the states in the middle of the band are localized, and transport ceases when the randomness in the matrix elements of the Hamiltonian exceeds a certain critical value related to the bandwidth. Mott[1] synthesized Anderson's result with the work on localization in the band tails by arguing for sharp transitions from localized to extended states and back to localized states within the band, for randomness smaller than Anderson's critical value. This model, proposed independently by Cohen, Fritzsche, and Ovshinsky,[2] we refer to as the Mott-CFO model.

We consider the motion of a particle in a three-dimensional periodic lattice[4,5] such that at each site $\vec{n}$ of the lattice the particle can occupy a Wannier state $|\vec{n}\rangle$ of energy $\epsilon_{\vec{n}}$. The Hamiltonian is

$$\langle\vec{l}\,|H|\,\vec{m}\rangle=\epsilon_{\vec{m}}\delta_{\vec{l}\vec{m}}+V_{\vec{l}\vec{m}}, \tag{1}$$

where $V_{\vec{l}\vec{m}}=V_{0,\vec{m}-\vec{l}}$ and $V_{\vec{l}\vec{l}}=0$. The disorder is introduced into the system by allowing the single-site energies $\epsilon_{\vec{m}}$ to be random variables; any two quantities $\epsilon_{\vec{n}}$, $\epsilon_{\vec{l}}$ are taken as statistically independent whenever the distance $r_{\vec{n}\vec{l}}$ is longer than a finite correlation length. This eliminates long-range order from our system. For simplicity we assume that $V_{\vec{l}\vec{m}}$ is a constant, V, for nearest neighbors, and zero otherwise.

Following Anderson we use as a criterion for the existence of localized states overlapping with a given site $\vec{l}=0$ the absence of complete diffusion from this site, i.e., $p_{00}\neq 0$, where p_{00} is the probability of finding the particle in the state $|0\rangle$ at $t=\infty$ if initially $(t=0)$ it was in $|0\rangle$. It can be shown that

$$p_{00}=\lim_{s\to 0^+}\frac{s}{\pi}\int_{-\infty}^{\infty}dE\,G_0(E+is)G_0(E-is), \tag{2}$$