

(cf. Migdal, Ref. 8, p. 73). This is not the case in the x-ray problem as initial and final ground states have different numbers of electrons in the Fermi sea. There is still a simple relation between overlap and transition probability, however [cf. Ref. 2, Eq. (15), or Ref. 3, p. 48].

<sup>11</sup>A. A. Abrikosov, L. P. Gor'kov, and I. Ye. Dzyaloshinskii, *Quantum Field Theoretical Methods in Statistical Physics* (Pergamon, New York, 1965), p. 130.

<sup>12</sup>N. I. Muskhelishvili, in *Singular Integral Equations*, edited by J. Radok (Noordhoff, Groningen, The Netherlands, 1958), pp. 123-127. The arbitrary constant is taken to be zero since  $\varphi \rightarrow 0$ , hence  $\int d\omega' (\omega' - \omega - i\eta)^{-1} \varphi(\omega') \rightarrow 0$  as  $|\omega| \rightarrow \infty$ . The index is zero. The generalization of the Hilbert problem to distributions (like  $g$  or  $\varphi$ ) is due to H. A. Lauwerier, Arch. Ration. Mech. Anal. **13**, 157 (1967).

<sup>13</sup> $L$  is directly related to the phase shift  $\delta(\omega)$ :  $L = -\pi^{-1} \int d\omega' (\omega' - \omega - i\eta)\theta(\omega')\delta(\omega')$ , as obtained by expressing the Green's function  $g$  in terms of its advanced counterpart (Ref. 11, p. 56).

<sup>14</sup>With the asymptotic form of  $g^\mp$  suggested by ND, Eq. (9) yields asymptotically in  $t$  and  $t'$  the result of Ref. 2 for  $\varphi(t, t')$  [i.e., their Eq. (51) with  $t = \infty$ ,  $t' = 0$  and their Eq. (53) with  $t = -\infty$ ,  $t' = 0$ ], as can be verified by Lighthill's technique [M. J. Lighthill, *Fourier Analysis and Generalised Functions* (Cambridge Univ., Cambridge, England, 1958), Chap. 4]. The comparison cannot be pushed further since (i) ND's  $g^\mp$  do not satisfy Lehmann's spectral representation, and (ii) the asymptotic limit is not suitable for the evaluation of the overlap.

<sup>15</sup>Ref. 11, p. 55.

<sup>16</sup>J. Friedel, in *Theory of Magnetism in Transition Metals, Proceedings of the International School of Physics "Enrico Fermi," Course XXXVII*, edited by W. Marshall (Academic, New York, 1967), p. 296.

<sup>17</sup>To obtain the overlap coefficient  $\alpha$ , Anderson uses an expansion in powers of  $\delta_F$  [Ref. 4, Eqs. (12) and (13)] and integrates over each term of the expansion separately. A series may be integrated term by term only within its domain of convergence (i.e., for small  $\delta_F$ ). Anderson's result is therefore valid only for small  $\delta_F$ . The asymptotic solution of ND for the overlap corresponds to a small phase shift approximation since their Eq. (55) is in fact equivalent to an expansion in powers of  $\delta_F$ .

<sup>18</sup>K. D. Schotte and U. Schotte, Phys. Rev. **182**, 479 (1969). This is not entirely unexpected in view of these authors' picture of the Fermi sea as a set of harmonic oscillators [cf. their Eqs. (17) and (18)]. The potential acts to shift these oscillators. The linked-cluster expansion of the evolution operator [their Eq. (22)] gives only a second-order contribution: All higher terms vanish. The related problem of the line shape of an oscillating system subject to a Gaussian random-frequency modulation exhibits a similar disappearance of the higher order terms in the cumulant expansion of the characteristic function of the power spectrum [cf. R. Kubo, in *Fluctuations, Relaxation, and Resonance in Magnetic Systems*, edited by D. ter Haar (Oliver and Boyd, London, England, 1962), p. 23].

## Anomalous Metal-Semiconductor Tunneling Near the Mott Transition\*

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(Received 2 November 1970)

Anomalous features observed in the tunneling spectra of Schottky barrier junctions on Si:B are related to Hubbard's model of the metallic (Mott) transition.

We have observed an anomalous zero-bias resistance peak in metal-semiconductor (Schottky barrier) tunnel junctions which appears as the semiconductor impurity concentration approaches the Mott critical value  $N_c$ .<sup>1</sup> Evidence suggests that this peak is the result of a gap, or sharp minimum, at the Fermi energy, in the density of final states in the semiconductor. Broadening of these states, consistent with Hubbard's model,<sup>2</sup> is observed with a superconducting counterelectrode as a concentration-dependent broadening of the BCS density-of-states peaks. The resistance

peak is increased by large magnetic fields. Similarity between this behavior and anomalous positive magnetoresistance in the semiconductor substrate supports our interpretation if, at  $N_c$ , the tunneling final states occur near the reserve region<sup>3</sup> in the electrode. In addition, we show that the real-intermediate-state tunneling model of Giaever and Zeller<sup>4,5</sup> is highly instructive as an approximate interpretation of the experimental results.

In spite of continuing interest in the Mott transition,<sup>1</sup> predictions based on the Hubbard Hamil-

tonian,<sup>3</sup> the simplest model to give an electronic transition, have not been tested experimentally. This model predicts an energy gap near the center of a conduction band formed by interacting impurities as the concentration is reduced below the Mott value  $N_c$ . This originates in the Coulomb repulsion  $U$  between two electrons (of antiparallel spin) on a single site. Such charge-transfer fluctuations are produced even at  $T=0$  by interaction between impurities, with a frequency which we characterize by the corresponding lifetime energy broadening  $\Gamma$ . Localization, as in the closely related Anderson model,<sup>6</sup> and appearance of the gap occur at  $\Gamma/U \leq 1$ .

The tunneling spectrum  $dI/dV$  from a metal into an electrode containing a gap near its Fermi energy must show, at  $T=0$ , a sharp minimum when the metal Fermi level faces the gap since, in the absence of allowed final states, an increment in bias can produce no increment in current. Inherent broadening of the states in the electrode may be revealed, if the counterelectrode is superconducting, as broadening of the characteristically sharp superconducting structure in the measured conductance.

The normalized conductance  $G(V)$ , with superconducting counterelectrode, is

$$G(V)/G_0 = \int_{-\infty}^{\infty} \xi_S(E)K(E-eV)dE, \quad (1)$$

where  $\xi_S = \xi_{BCS} = |E|/(E^2 - \Delta^2)^{1/2}$  for  $|E| \geq \Delta$ , and zero for  $|E| < \Delta$ ; the kernel  $K(E-eV) = df(E-eV)/dE$ , with  $f$  the Fermi function, is a bell-shaped curve with a full width at half-maximum of  $1.8kT$ . The thermal broadening of  $G(V)/G_0$  relative to  $\xi_{BCS}(eV)$  implied by Eq. (1) has been tabulated.<sup>7</sup> If we describe broadening of the semiconductor state at energy  $E$  by a normalized function  $B(E'-E, \Gamma)$ , the generalization of Eq. (1) is of the same form with  $K(E)$  replaced by the convolution

$$K_{\Gamma}(E) = \int_{-\infty}^{\infty} K(E')B(E'-E, \Gamma)dE'. \quad (2)$$

This is a broader bell-shaped function, whose width in excess of  $1.8kT$  is a measure of  $\Gamma$ . It follows from Eq. (2) that, as a first approximation, the spectrum  $G(V)/G_0$  will be fit by Eq. (1) with an effective temperature  $T^*$  higher than the measured temperature  $T$ . Thus  $k(T^*-T)$  is a semiquantitative estimate of  $\Gamma$ . Finally,  $\Gamma$  and  $T^*$  may not be entirely energy independent.

The metal-semiconductor (Schottky barrier) junction, described by the parabolic barrier model,<sup>8</sup> is a well-characterized tunneling system.<sup>9</sup> Such a junction on  $p$ -type material is shown as an inset in Fig. 1. Junctions were fabricated by

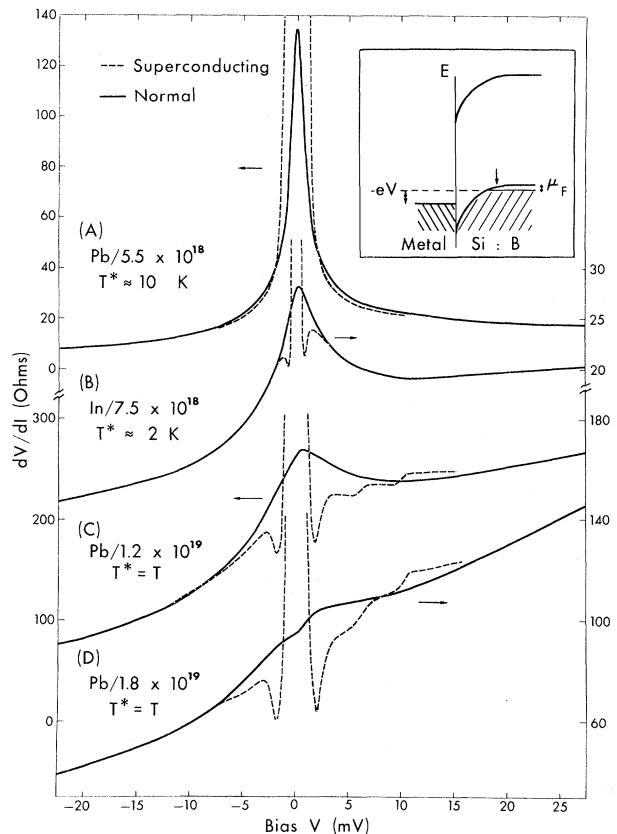


FIG. 1. Anomalous resistance peak appears as acceptor concentration  $N_A$  approaches Mott critical value  $N_c = 5.0 \times 10^{18} \text{ cm}^{-3}$ . Measurement temperature  $T$  is 1.3°K for curves A and B, 1.5°K for curves C and D. Estimated error of 10% in concentration at junction allows for local variations.

cleavage of [111] bars of Si:B in a well-trapped diffusion-pump evaporator typically at  $10^{-6}$  Torr<sup>10</sup> and rapid evaporation of either Pb after an exposure to residual gas of  $10^{-5}$  to  $10^{-3}$  Torr sec, or In after an air exposure of 1-50 Torr min. A mask provided an array of 0.02-cm metal dots; contact to a selected dot was made with a lightly tensioned gold probe. Since the evaporated junctions were not heated above 20°C, there is no reason to expect redistribution of the B impurity or the metal near the interface. We estimate the value of  $N_c$  for Si:B to be  $(5.0 \pm 0.5) \times 10^{18} \text{ B cm}^{-3}$ .<sup>1</sup>

The existence of superconducting gap structure for Pb at  $N_A > 2N_c$ , as shown in curves C and D of Fig. 1, is conclusive evidence<sup>9</sup> of tunneling. The background spectra of these junctions (not fully shown) are in qualitative agreement with the calculation for a parabolic barrier,<sup>8</sup> appropriate to a surface depletion layer. It is impor-

tant that the parameters of the barrier vary only slightly in the range  $N_c \leq N_A \leq 2N_c$ , in which the anomalous behavior appears. The conductance level of a Schottky junction<sup>8,9</sup> varies as  $\exp[-(2mV_B/\hbar^2)^{1/2}t]$ , with thickness  $t = (\epsilon V_B / 2\pi N_A e^2)^{1/2}$ . The exposures to residual gas, too brief to grow an appreciable oxide, adjust the surface Fermi level,<sup>11</sup> and hence the barrier height  $V_B$ , to maintain the tunneling exponent at an approximately constant value. Thus we have  $V_B \propto N_A^{1/2}$  and  $t \propto N_A^{-1/4}$ ; hence  $t$  is constant, to 20%, in the range  $N_c \leq N_A \leq 2N_c$ .

The data summarized in Figs. 1 and 2 include several remarkable features:

(1) The  $dV/dI$  peak, the dominant feature at  $N_A = 5.5 \times 10^{18} \text{ cm}^{-3}$  (curve A in Fig. 1), and noticeable also in curve B at  $7.5 \times 10^{18} \text{ cm}^{-3}$ , has a strong concentration dependence near  $N_c$ .

(2) The relation of the superconducting density-of-states structure to the resistance peak is remarkable in curves A and B of Fig. 1. In curve B the superconducting structure for In is quite clearly revealed, in spite of the strongly varying background. This suggests that the peak here reflects a minimum in the direct, elastic conductance, rather than two-step tunneling.<sup>5</sup> The second anomalous feature is the abrupt disappearance of the superconducting density-of-states peaks in curve A at  $N_A = 5.5 \times 10^{18} \text{ cm}^{-3}$ . In the 25% reduction in  $N$ , relative to curve B, changes

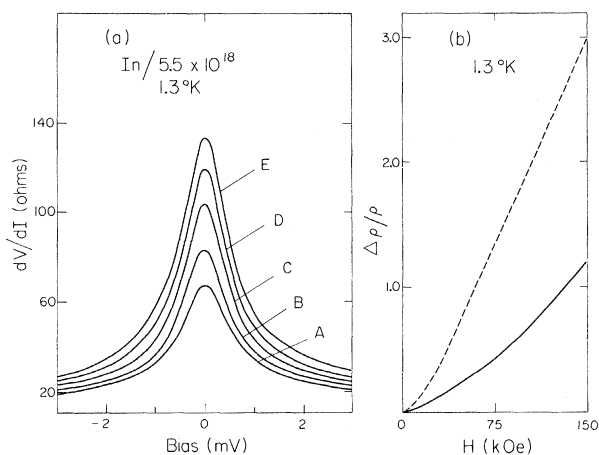


FIG. 2. (a) Effect of high magnetic fields on the resistance peak near  $N_c$ . Curves A, B, C, D, and E correspond to longitudinal magnetic fields of 0, 37.5, 75, 112.5, and 150 kOe, respectively. (b) Anomalous positive magnetoresistance of Si:B ( $5 \times 10^{18} \text{ B cm}^{-3}$ ) is shown in solid curve. Dashed curve is magnetoresistance inferred from tunneling data on a similar substrate according to model of Edwards, assuming  $dV/dI \propto 1/g$  in (a).

in the barrier parameters are small. The effective temperatures associated with the density-of-states peaks in curves A and B are near 10 and 2°K, respectively, at  $T \approx 1.3^\circ\text{K}$ . The value  $\Gamma \approx 0.85 \text{ meV}$ , corresponding to  $T^* \approx 10^\circ\text{K}$ , is comparable to a value  $\Gamma \approx 0.6 \text{ meV}$  obtained for As donor states in a magnetic scattering experiment.<sup>12</sup>

(3) The  $dV/dI$  peak increases by a factor of 2 at  $1.3^\circ\text{K}$  in a 150-kOe magnetic field, as shown in Fig. 2(a). The field accentuates the existing structure rather than contributing a new behavior not present at  $H=0$ . The width of the peak does not increase with magnetic field; this rules out spin-flip scattering as a significant contribution.<sup>9,12</sup> The sensitivity to magnetic field falls off rapidly for  $N_A > N_c$ . The magnetic field acts qualitatively as a reduction in  $N_A$ , as in Fig. 1 between curves B and A. This is consistent with decreased wave-function overlap between impurities and increased localization of carriers (i.e., "freeze-out") at high field.<sup>13,14</sup> The field dependence rules out the phonon-emission model<sup>15</sup> for a resistance peak. The solid curve in Fig. 2(b) shows the anomalous transverse magnetoresistance present in the substrate material appropriate to Fig. 2(a) and to curve A in Fig. 1.<sup>16</sup> Similar measurements have been interpreted<sup>14</sup> as a reduction, with magnetic field, in the density of states at the Fermi level. The tunneling behavior in Fig. 2(a) supports this interpretation if the conductance near zero bias is proportional to the semiconductor density of states, a reasonable assumption near  $N_c$  when the states are partially localized. The dashed curve shows the magnetoresistance inferred from the tunneling data in Fig. 2(a) using the theory of Edwards,<sup>17,14</sup> which has been applied successfully to anomalous magnetoresistance measurements.<sup>14</sup> The magnetoresistance inferred exceeds that directly measured by a factor of 3.<sup>17</sup> The magnetoresistance, however, is known to increase rapidly as  $N_A \rightarrow N_c$ , so that this difference could result from an effective impurity density in the final-state region only 15% lower than the bulk density.<sup>14</sup> A similar condition occurs near the inner edge of the reserve region, indicated by the arrow in Fig. 1 (inset), where the local hole density falls below  $N_A$ . A consistent interpretation thus requires that tunnel transitions occur to a distribution of final states peaked near the reserve region. This seems reasonable, as a short mean free path is expected near the transition where transport occurs by quantum mechanical hopping.

In summary, the rapid concentration and field

dependence, which correlate satisfactorily with the Mott transition and the related anomalous magnetoresistance in the semiconductor bulk, are strong evidence that the resistance peak is associated with the Mott transition, and represents, in fact, the Hubbard gap.

One can come to the same conclusion, and gain additional insight, by considering the data in terms of the real-intermediate-state tunneling model.<sup>4,5</sup> In this model, the resistance peak arises by freezing out, at low bias voltage and low temperature, two-step tunneling paths which require activation energy to reach real intermediate states in the barrier region. The depletion-layer barrier in our experiment, as we have pointed out, is almost unchanged in the small concentration range in which the resistance peak appears, and in addition is not affected by a magnetic field.<sup>18</sup>

Intermediate states on weakly interacting localized neutral acceptors at the inner edge of the depletion layer<sup>12</sup> would not lead to the strong concentration and field dependences.

The resistance peak correlates closely with the appearance, at the Mott transition, of localized states in the bulk. We therefore assume that any real intermediate states of importance occur on strongly interacting neutral acceptors in the electrode near the inner edge of the reserve region. Transposing, for clarity, to the analogous *n*-type situation, we imagine a two-step process in which an electron first tunnels from the metal to localize on a neutral donor, thereby forming a negative donor ion. This is possible for small  $\Gamma$  and requires as activation the Coulomb energy  $U$ . In the second step the electron tunnels to a second donor in the semiconductor electrode. The observed linear temperature dependence of the conductance at zero bias appropriate to curve *A* in Fig. 1 (not shown) and the distortion of the superconducting structure observed as  $N_A$  approaches  $N_c$  are qualitatively consistent with the model.<sup>5</sup> The Giaever-Zeller model cannot explain the concentration dependence, however, as it does not include the interaction between impurities which must give the critical dependence.

The important point is that the second step in the above process, i.e., the hopping of the electron via the interimpurity interaction to a second impurity, is characteristic of a final state in Hubbard's model. Thus we regard tunneling as occurring directly into the set of interacting impurity states, whose nature properly includes the

continuing motion. The necessary additional physics, of course, which is included in Hubbard's model is the interimpurity interaction  $\Gamma$ , which overcomes the repulsion  $U$  at the Mott transition  $\Gamma \approx U$  to cause delocalization and to remove the energy gap and hence the resistance peak. One would expect a complete solution of Hubbard's model to predict directly the observed dependence on magnetic field, as well as the critical concentration dependence.

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\*Work performed in part at Francis Bitter National Magnet Laboratory. Illinois portion supported in part by Joint Services Electronics Program Contract No. DAAB 07-67-C-019, and in part by Jet Propulsion Laboratory Contract No. 952383.

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<sup>5</sup>H. R. Zeller and I. Giaever, *Phys. Rev.* **181**, 789 (1969).

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<sup>9</sup>C. B. Duke, *Tunneling in Solids* (Academic, New York, 1969).

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<sup>16</sup>We are indebted to R. P. Khosla for making this measurement.

<sup>17</sup>S. F. Edwards, *Phi. Mag.* **3**, 1020 (1958) derives the relations  $\sigma = (ne^2\tau/m^*)g^2$  and  $R = 1/neg$  for the conductivity and Hall constant, where  $g < 1$  is the density of states at the Fermi level in the presence of partial carrier localization relative to a standard conduction

band. It is assumed in Ref. 14 that  $g$  is further reduced by a high magnetic field. The dashed curve in Fig. 2(b) was obtained using the above and taking the magnetic-field variation of  $g$  from the tunneling data in Fig. 2(a), assuming  $dV/dI$  at  $V=0$  proportional to

$1/g$ . The available theories are limited in their validity to  $T=0$ .

<sup>18</sup>This is verified by our observation that the background tunnel conductance, away from  $V=0$ , is negligibly affected by the high field.

## Phonon-Induced Nuclear Spin-Wave Instabilities in $\text{RbMnF}_3$ <sup>†</sup>

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(Received 4 December 1970)

We report the first observations of nonlinear phonon-induced nuclear spin-wave instabilities in an antiferromagnet possessing a nuclear magnetic moment. The observed instabilities are associated with the transverse nuclear mode of cubic  $\text{RbMnF}_3$ . The nuclear relaxation rates are obtained as a function of the magnon frequency and wave number. This observation verifies a recently published prediction by Platzker and Morgenthaler that a sufficiently intense elastic wave of the proper frequency and polarization can indeed drive antiferromagnetic spin waves unstable.

Based upon measurements on  $\text{RbMnF}_3$ , we wish to report the first successful observations of nonlinear phonon-nuclear magnon interactions in an antiferromagnet. In a paper published last year, Platzker and Morgenthaler<sup>1</sup> showed the feasibility of phonon-pumping electronic and nuclear spin-wave pairs in a low-anisotropy, nuclear-magnetic-moment-bearing antiferromagnet such as  $\text{RbMnF}_3$ . Their analysis is applicable to the "flopped" ground state. When a sufficiently intense elastic wave of the proper frequency, polarization, and direction of propagation propagates through a single crystal of such an antiferromagnet, nuclear as well as electronic spin-wave pairs can be driven unstable parametrically. Because of the equilibrium configuration of the sublattice magnetizations and the nature of their precessional motions, only this method of excitation—rather than the more customarily used photon pump—is capable of exciting the spin-wave pairs directly, i.e., without the participation of the linear susceptibility. As a result, this method is the most efficient one, requiring the lowest threshold power. Although the threshold powers for the excitation of both electronic and nuclear spin-wave pairs were predicted to be low, the frequency regimes at which the experiments have to be conducted preclude, at least for the time being, an attempt to excite electronic spin-wave pairs. The reason is that the lowest possible pump frequency must be comparable to twice the electronic resonance frequency, which for  $\text{RbMnF}_3$  lies in the high  $X$ -band region. Unfortunately, the fabrication of sufficiently effi-

cient transducers in this frequency range is not yet within the current state of the art.

The nonlinear phonon-nuclear magnon instabilities were investigated in a  $\langle 110 \rangle$   $\text{RbMnF}_3$  rod, 1 cm long with a square  $4 \times 4$ -mm cross section. The sample was placed in a transverse dc magnetic field oriented along a  $\langle 001 \rangle$  axis. Longitudinal-wave echo trains were excited and detected single-endedly by a sputtered ZnO transducer which had sufficiently low insertion losses at  $T=4.2^\circ\text{K}$  over the frequency range 600-1150 MHz. The transducer had a round-trip insertion loss of  $\sim 40$  dB and the echo trains a propagation loss of  $\sim 5$  dB. From this an upper limit of 2.5 dB/cm was obtained for the intrinsic acoustic attenuation of  $\text{RbMnF}_3$  over the above-mentioned frequency range at  $4.2^\circ\text{K}$ .

Under the proper acoustic frequency and dc magnetic field conditions, spin-wave instabilities were excited in the sample rod when the acoustic power levels were higher than a certain threshold. The observed effect of the instabilities was a breakdown in the trailing edges of the echoes. At constant frequency and dc magnetic field values, the depth of the breakdown increased with increasing acoustic power. A definitive identification of these effects as a manifestation of magnon-pairs creation was supplied by the fact that no similar breakdowns were observed at acoustic power levels either below threshold or above threshold outside a limited range of the dc magnetic field values. At any fixed acoustic frequency, this range was centered about the dc magnetic field value which corresponded to the field-