than two orders of magnitude by the presence of 1% Ni^{2+} ions). Ni^{2+} emission may also be excited through the Mn^{2+} bands near 4300 Å, but these are superimposed on a $^3T_1$ band of Ni^{2+}. Particularly interesting is the fact that the efficiency of $Mn^{2+} \rightarrow Ni^{2+}$ energy transfer is high even for very low Ni^{2+} concentration. For example, in MnF_2 containing 15 ppm Ni^{2+} ions, the quantum efficiency for Ni^{2+} emission is about 30% at 4.2°K when exciting the $^4T_1$ band of Mn^{2+}. To illustrate this figure somewhat differently, consider a sphere about each Ni^{2+} ion such that all Mn^{2+} ions within the sphere transfer their excitation to Ni^{2+}, while those outside do not. The radius of the sphere so calculated for MnF_2 containing 15 ppm Ni^{2+} ions is about 60 Å. These findings indicate that energy transport between Mn^{2+} ions is extremely long range, just as suggested previously for nickel compounds.[2]

We are grateful to C. G. B. Garrett and G. K. Wertheim for several helpful suggestions on the manuscript.

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ZERO-BIAS ANOMALIES IN NORMAL METAL TUNNEL JUNCTIONS

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We have investigated the current flow through thin chromium-oxide layers from 1°K to 290°K. We believe that current flows by means of a tunneling mechanism, but the dependence of the dynamic resistance of the junction on voltage and temperature is completely anomalous in terms of expected tunneling behavior. Some new results on other metal-oxide junctions strongly suggest that properties of the oxide layer are responsible for the anomaly observed by Wyatt in tantalum oxide junctions.

We have investigated the current flow through thin chromium oxide layers from 1 to 290°K. We believe that current flows by means of a tunneling mechanism, but the dependence of the dynamic resistance of the junction on voltage and temperature is completely anomalous in terms of expected tunneling behavior. The dynamic resistance at zero bias increases with decreasing temperature approximately as $\log(1/T)$ and, at fixed temperature, depends on voltage as $\log(1/V)$. In contrast to previously reported anomalies at zero bias,[1-10] which were of small magnitude and which were observed only at low temperatures, the total current in chromium oxide junctions appears to participate in the anomalous tunneling mechanism, and the anomaly has been observed from 1°K to room temperature. Some new results on other metal oxide junctions strongly suggest that properties of the oxide layer are responsible for the anomaly observed by Wyatt[1] in tantalum oxide junctions. In these cases, the

results are in good agreement with the calculation of Appelbaum, who consideres the scattering by dilute magnetic impurities in the oxide layer as suggested by Anderson.[11] However, the calculation does not seem to apply to the chromium oxide junctions which are presumably strongly magnetic.

Deviations from Ohmic dependence of tunnel current (I) on voltage (V) at low voltages[12-14] appear to be so common at temperatures ~1°K that in our experience only aluminum oxide and lead oxide tunnel junctions approximate this ideal behavior. A conductance peak at zero bias in Ta-I-Al junctions has been reported by Wyatt.[1] (We describe a junction as A-I-B when the metal A is oxidized to form an insulator I and the metal B is evaporated to complete the junction.) The peak was observed below ~20°K superimposed on a background conductance $G_0(V)$ and at 1°K was such that

$$\frac{\Delta G(0)}{G_0(0)}=\frac{G(0)-G_0(0)}{G_0(0)}=0.2.$$

The peak was tentatively explained as a density-of-states effect in the bulk tantalum. A conductance peak of similar shape also occurs in heavily doped Si and Ge tunnel diodes where $\Delta G(0)/G_0(0)\sim 0.05$.[2] Resistance peaks have been observed in lightly doped Ge and Si,[2] III-V,[3,4] and lead salt[5] semiconductor diodes, and generally have $\Delta R(0)/R_0(0)<0.5$. With increasing temperature the above-mentioned peaks decrease gradually and are difficult to observe above 20°K. In some semiconductor diodes, a resistance peak which appears abruptly at a low critical temperature is caused by superconducting material in the alloy region exhibiting a gap characteristic.[6-10] This possibility should always be considered when junctions are made by alloying Sn, In, Al, or alloys thereof into semiconductors containing Pb, Ga, In, or Sn.

We prepared Cr-I-Ag tunnel junctions by evaporation of 0.25-mm-wide chromium films ~2000 Å thick, oxidation for 3 hours in a stream of air under a heat lamp which raised the temperature of film to 100°C, and cross evaporation of 2000-Å silver films. The plots of dynamic resistance $R(V)$ versus voltage were measured using modulation techniques.

At low temperatures the I-V plots were noticeably nonlinear even over a 5-mV range and the $R(V)$-V plots taken at 0.9°K [Fig. 1(a)] reveal this nonlinearity very clearly. The symmetrical resistance peak is located exactly at zero bias and is an approximate logarithmic singularity except for being cut off within kT [1°K = 0.086 meV] of zero bias. The resistance at 100 mV is 0.03 times that at zero bias, and indicates that there is no background $R_0(V)$ in these junctions, implying that all the tunnel current is involved in this nearly singular anomalous behavior. That the current flow was indeed due to tunneling was confirmed by replacing silver by lead. The Cr-I-Pb junction obtained had a very sharp superconducting gap characteristic superimposed on an anomalous behavior similar to that in the Cr-I-Ag junctions. There was no evidence for current flow by means of a mechanism other than tunneling (at least over the voltage range 0-10 mV and at temperatures less than 4.2°K).

The effect of temperature is shown in Fig. 1(b). The peak $R(0)$ decreases with increasing temperature but even at room temperature a hint of the peak remains. At no voltage does the

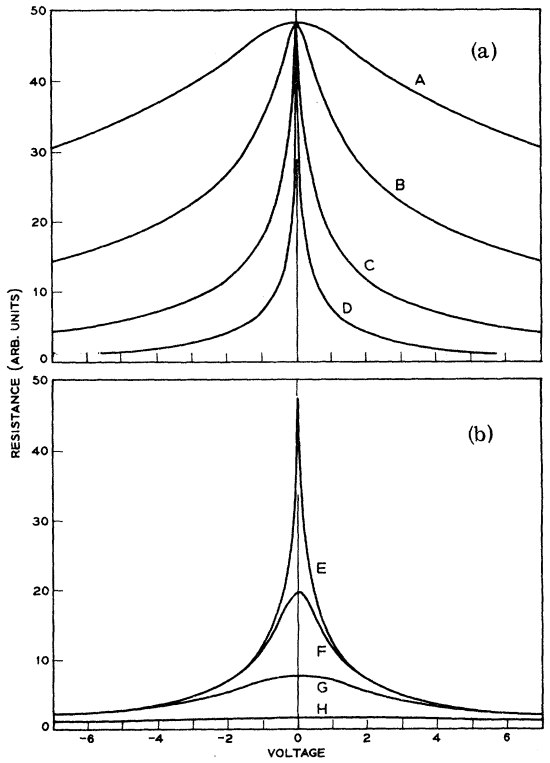

FIG. 1. (a) The dynamic resistance versus voltage for a Cr-I-Ag junction at 0.9°K. The voltage scales are A = 0.2 mV/division, B = 1.0 mV/division, C = 5 mV/division, D = 20 mV/division. (b) The dynamic resistance versus voltage for a Cr-I-Ag junction at various temperatures. E = 0.9, F = 20.4, G = 77, and H = 290°K. The voltage scale is 10 mV/division.

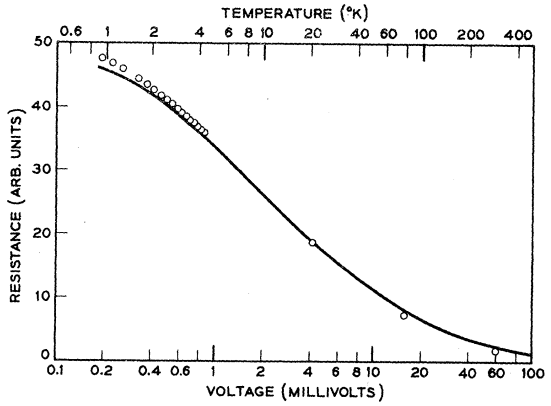

FIG. 2. The solid line is resistance versus voltage for a Cr-I-Ag junction at 0.9°K. Open circles are resistance at zero bias versus temperature. The horizontal scales are arranged so that $2.4kT$ (°K) $= V$ (eV).

resistance increase with increasing temperature. On warming up the junction to room temperature and abruptly reimmersing in liquid nitrogen and liquid helium, the values of $R(0)$ were reproduced to better than 2 in 10^3 which indicates that the effect is not due to physical defects of the oxide.

From the temperature dependence of Fig. 1(b) it appears that the voltage dependence at 0.9°K is close to that to be obtained at 0°K except within a few kT of zero bias. We have plotted $R(V)$ vs log$V$ at 0.9°K in Fig. 2 as the solid line. On the same figure the temperature dependence of the resistance $R(0)$ is plotted as the open circles. The agreement has been obtained by putting $2.4\,kT$ (°K) $= V$(eV). The similarity between the voltage dependence of $R(V)$ at low temperatures and the temperature dependence of $R(0)$ implies that the expression describing $R(V, T)$ is homogeneous in V and T. It is important to note that the approximate dependence on $\log(1/V)$ and $\log(1/T)$ is only obtained when one plots dynamic resistance and not dynamic conductance. This in is contrast to the conductance peaks observed in tantalum oxide junc-

Table I. Column 1 indicates the order of preparation of the junction; column 2, the surface preparation of the first electrode; column 3, the oxidation procedure for this electrode; column 4, whether the anomaly observed is a peak in resistance or conductance; and column 5, the magnitude of this peak, $\Delta R(0)/R_0(0)$ or $\Delta G(0)/G_0(0)$. Many junctions have been fabricated by oxidizing Al, Ta, Nb, and Sn, but for the magnetic alloys and Mg generally only 5 or 10 junctions of each type have been made. The magnitude in column 5 is for a temperature of 0.9°K (except where specified) and when necessary a magnetic field has been used to destroy superconductivity.

1	2	3	4	5
Cr-I-Ag	Evaporated film	Air at 100°C for 3 h	R	>100
Ta-I-Pb	Bulk heated 1700°C in 2×10^{-8} Torr	Air at 20°C for 25 h	G	$\lesssim$0.002
Ta-I-(Pb, Al, Au, or Sn)	Etch and wash, argon ion bombardment	Oxygen at 50°C for 1 h	G	0.1 to 0.2
Ta-I-Ag	Etch and wash, argon ion bombardment	Oxygen at 50°C for 1 h	G	<0.002
Nb-I-Al	Bulk heated 2000°C in 10^{-9} Torr	Oxygen at 20°C for 24 h	G	0.14 at T_c
Nb-I-Ag	Bulk heated 2000°C in 10^{-9} Torr	Oxygen at 20°C for 24 h	G	0.04 at T_c
Nb-I-(Au or Ag)	Bulk heated 500°C in 10^{-9} Torr	Oxygen at 50°C for 4 h	G	0.05 at 1°K
Nb-I-Ag	Etch and wash, argon ion bombardment	Oxygen at 50°C for 1 h	G	0.05 at T_c
Al-I-(Pb, Sn, Sn, or In)	Evaporated film	Air at 20°C for 1 min	···	$<10^{-5}$
Al_xCr_y-I-Ag	Aluminum and chromium evaporated. Not superconducting at 0.9°K	Air at 20°C for 1 min	···	$<10^{-3}$
Al_xMn_y-I-Pb	Aluminum contained 5% Mn before evaporation. Not superconducting at 0.82°K	Air at 20°C for 1 min	···	$<10^{-3}$
Al-I-Ag_xMn_y	Evaporated film	Air at 20°C for 1 min Ag contained 0.1% Mn before evaporation	···	$<10^{-3}$
Pb-I-Pb	Evaporated film	Oxygen at 50°C for 1 h	···	$<10^{-3}$
Sn-I-Sn	Evaporated film	Air at 110°C for 2 days	G	0.03
Mg-I-Pb	Evaporated film	Air at 20°C for 1 min	G	0.20
Mg-I-Mg	Evaporated film	Air at 20°C for 1 min	G	0.25
Al-I-Mg	Evaporated film	Air at 20°C for 1 min	···	$<10^{-3}$
Silicon p-n	$n \gtrsim 5\times10^{19}$	Alloy $Al_{99}B_1$	G	~0.05
	$n \lesssim 5\times10^{19}$	Alloy $Al_{99}B_1$	R	~0.03

tions.

New results on other oxide junctions are summarized in Table I. The effect of surface preparation and oxidation procedure on the tantalum anomaly has been studied by using the same bulk starting material. A striking and consistent result is that the anomaly is reduced by a factor 100 when silver is used as the second electrode in Ta-I-Ag junctions.[15] This is shown in Fig. 3 for Ta-I-Al and Ta-I-Ag junctions. We have plotted $R(V)$ vs V to contrast the results with those for chromium and to show the bias dependence of the background $R_0(V)$, which is much larger than in aluminum oxide junctions for example.[16] The asymmetry of $R_0(V)$ about zero bias is always observed and we find a temperature dependence of $R_0(V)$ which is small compared to that of $\Delta R(0)$. We have, however, studied our results as both $\Delta G(0)$ vs T and $\Delta R(0)$ vs T and believe that the conductance plot gives slightly better agreement with the logarithmic behavior as reported by Wyatt.[1]

A study of the results of Table I reveals strong evidence that the oxide layer or oxide-metal interface is responsible for the zero-bias anomalies.

We would like to make some speculations based on the results described above. The tunneling current between two metals depends on a tunneling matrix element $|M|^2$ and the density of electron states in the two metals. The density of states also enters $|M|^2$ through an electron velocity,[17] and one would not expect to see density-of-states effects in normal metal tunneling except at band edges[18] or unless the density of states has a very rapid variation with energy. However, when one considers the results for tantalum, namely, that the conductance peak varies in magnitude with tantalum surface preparation, oxidation procedure, and the second metal electrode, a bulk density-of-states effect can no longer be considered seriously. As tunneling is a measurement of the density of states at the metal surface, however, it is conceivable that in the presence of the oxide layer the local density of states could be different from that in the bulk. Alternatively, if we assume the density of states to be a smoothly varying function of energy, we must assign the anomalies to the tunneling matrix element $|M|^2$. It appears that any simple potential-barrier representation of the oxide will give an Ohmic behavior near zero bias. But, if the oxide layer contains allowed states through which the tunneling electron can scatter to states in the second metal, then anomalies near zero bias will be obtained. Magnetic scattering has been considered by Kim[19] and by Appelbaum,[11] who points out that the effects calculated by Kim are much smaller than those found experimentally. Appelbaum considers the scattering by localized states in the oxide or at the oxide interfaces and obtains expressions which agree with the results for the tantalum junctions. One would also expect such an effect to vary with surface and oxide preparation and possibly with the second electrode, as we observe. Our results on Sn-I-Sn and Mg-I-Pb junctions, therefore, suggest that the oxides produced in these cases also contain localized states. Our measurements of the films containing magnetic impurities (Cr in Al and Mn in Ag) confirm that the magnetic impurities must be in the oxide layer rather than in the metals.

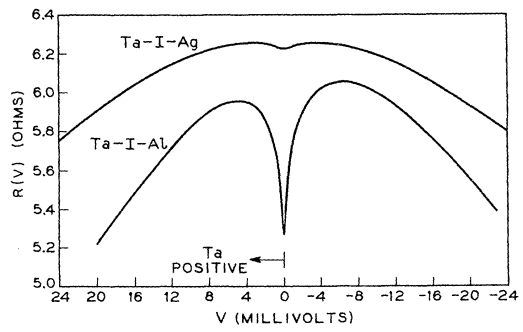

FIG. 3. Dynamic resistance versus voltage for Ta-I-Al and Ta-I-Ag junctions at 0.9°K. A field of 3 kG was used to drive the tantalum normal.

The effects described above for chromium oxide junctions should not be compared with Appelbaum's calculation. In this case, we do not have a small conductance peak or dip $\Delta G(V)$ superimposed on a background $G_0(V)$ but have a completely anomalous behavior of the total tunneling current. The anomaly also seems to occur in $R(V)$ rather than $G(V)$. It is possible that a very low potential barrier (~10 mV) would produce a similar variation of $R(V)$ at voltages greater than 10 mV, but it is difficult to explain the temperature dependence of $R(0)$ using such a model, especially at temperatures less than 4.2°K where we know a tunneling current is flowing (rather than a Schottky emission current). A magnetic effect still appears as the most likely explanation for the anomaly

as we expect the oxide to be either CrO_2 which is ferromagnetic or Cr_2O_3 which is antiferromagnetic.

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NONEXISTENCE OF HYPERBOLIC EXCITONS

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The optical-absorption strength function near a hyperbolic (M_1) energy surface is calculated in the effective-mass approximation using three model electron-hole interactions. The models are compared with a treatment of the Coulomb interaction in the adiabatic approximation. The results imply that the concept of a "hyperbolic exciton" as defined within the framework of a simple effective-mass approximation does not provide a satisfactory explanation for peaks in experimental optical-absorption data.

In this Letter we present a quantum-theory calculation of the optical-absorption strength function associated with a nondegenerate M_1 hyperbolic energy surface ($m_1, m_2 > 0$; $m_3 < 0$) in which the consequences of attractive final-state interactions between the electron and hole are derived. Peaks in the optical absorption of insulators have been observed near both M_0 and M_1 interband absorption edges.[1] Although these peaks can be described by a resonance-theory parametrization of the dielectric function,[1] the dynamics of the electron-hole binding have been calculated in the effective-mass approximation only for the M_0 (parabolic) edge.[2] There is some experimental[3] and theoretical[1,4] evidence that the peaks assigned to the M_1 edges should be attributed to localized ("molecular") electron-hole excitations. However, Phillips's hypothesis[1,6] that they are best described in terms of quasistationary ("resonance") states associated with effective-mass "hyperbolic excitons" seems widely accepted.[1] We present evidence that in contrast to the case for an M_0 surface, a monotonically increasing attractive final-state interaction does not lead to a "resonant" peak for an M_1 surface. We consider models of the electron-hole interaction for which the Schrödinger equation can be separated and the analysis performed without further approximations. For these models (a) the hypothesized quasistationary states do not exist for M_1 surfaces, (b) the nonexistence of these states is a necessary[5] but not sufficient condition for the effective-mass-theory calculation to lead