§Present address: IBM Watson Research Center, Yorktown Heights, N. Y. 10598.
[1]J. Bardeen and C. Herring, *Atom Movements* (ASM, Cleveland, 1951), p. 87.
[2]K. Compaan and Y. Haven, Trans. Faraday Soc. 52, 786 (1956).
[3]N. Peterson, Solid State Phys. 22, 409 (1968).
[4]L. Barr and A. LeClair, Proc. Brit. Ceram. Soc. 1, 109 (1964).
[5]D. Gupta, D. Lazarus, and D. Lieberman, Phys. Rev. 153, 863 (1967).
[6]D. Gupta and D. Lieberman, in Proceedings of the Third Bolton Landing Conference, 1969 (unpublished).
[7]D. Gupta and D. Lieberman (unpublished).
[8]J. Manning, Acta Met. 15, 817 (1967).
[9]J. Manning, *Diffusion Kinetics for Atoms in Crystals* (Van Nostrand, New York, 1968), p. 121.
[10]P. Flinn and G. McManus, Phys. Rev. 124, 54 (1961).
[11]E. Elcock and C. McCombie, Phys. Rev. 109, 605 (1958).
[12]P. Wynblatt, Acta Met. 15, 1453 (1967).
[13]A. Kuper, D. Lazarus, J. Manning, and C. Tomizuka, Phys. Rev. 104, 1536 (1956).
[14]H. Domian and H. Aaronson, Trans. AIME 230, 44 (1964).
[15]A. Schoen, Phys. Rev. Letters 1, 138 (1958).
[16]J. Mullen, Phys. Rev. 121, 1649 (1961).
[17]A. LeClaire, Phil. Mag. 14, 271 (1966).
[18]G. Vineyard, J. Phys. Chem. Solids 3, 121 (1957).
[19]T. Heumann and W. Reerink, Acta Met. 14, 201 (1966).
[20]N. Peterson and S. Rothman, Phys. Rev. 154, 558 (1967).
[21]T. Hirone, N. Kunitomi, and M. Sakamoto, J. Phys. Soc. Japan 13, 840 (1958).
[22]M. Wanin and A. Kohn, Compt. Rend. 267, 1558 (1968).
[23]D. Marsh, Tracer Lab JCN, Oakland, Calif. (private communication).
[24]P. Shewmon, *Diffusion in Solids* (McGraw-Hill, New York, 1963), p. 7.
[25]T. Heumann and R. Imm, J. Phys. Chem. Solids 29, 1613 (1968).
[26]F. Buffington, K. Hirano, and M. Cohen, Acta Met. 9, 434 (1961).
[27]C. Wert and C. Zener, Phys. Rev. 76, 1169 (1949).
[28]C. Walter and N. Peterson, Phys. Rev. 178, 922 (1969).
[29]N. Peterson and L. Barr (unpublished).
[30]N. Peterson, Phys. Rev. 136, A568 (1964).
[31]*Diffusion in BCC Metals* (ASM, Metals Park, Ohio, 1965).
[32]J. Mundy and L. Barr, Phil. Mag. 14; 8, 785 (1966).
[33]N. Peterson and S. Rothman, Phys. Rev. 163, 645 (1967).
[34]D. Graham, J. Appl. Phys. 40, 2386 (1969).

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Electron Tunneling Cr-Cr_2O_3-Metal Junctions

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Conductance measurements on high-quality thin-film Cr-Cr_2O_3-metal tunnel junctions show neither structure due to the antiferromagnetic energy gap of bulk Cr nor zero-bias anomalies. The conductance is almost linear in voltage at low temperatures and biases, with fine structure at 28, 44, 62, and 82 meV. These results are in qualitative agreement with the assumption of inelastic tunneling via elementary excitations of the Cr_2O_3 barrier.

We have measured the temperature and magnetic field dependence of the conductance of more than 80 thin-film Cr-Cr_2O_3-M tunnel junctions, where M (metal) is Ag, Sn, or Pb. In contrast to other reports,[1,2] none of our junctions exhibit giant resistive anomalies. Although the even conductance $G_e(V) \equiv \frac{1}{2}[G(+V)+G(-V)]$ is linear in dc bias V at low temperatures, the temperature and magnetic field dependence indicate that this is not due to impurity-induced zero-bias anomalies[1-3] or small metallic inclusions.[4] In particular, (a) $G(V)$ has no observable magnetic field dependence to $<0.1\%$ for applied magnetic fields (H) between 0 and 30 kG at 1.2 °K; (b) below 4.2 °K, $G(0)$ is nearly temperature independent, having a slope of $\lesssim 0.5\%$ per °K; (c) the shape of $G_e(V)$ is independent of both magnetic field and temperature in the range $1.1 \lesssim T \lesssim 4.2$ °K, $0 \lesssim H \lesssim 30$ kG. When Sn or Pb was used as the second electrode, excellent superconducting tunnel characteristics were observed below T_c; for superconducting Pb electrodes, $G(0)$ at 1.2 °K was as low as $\approx 0.1\%$ of the normal-state conductance, and the phonon structure due to the strong coupling behavior of Pb was as large as in the best Al-I-Pb junctions.[5] We conclude that the electron transfer mechanism is

ordinary electron tunneling, that zero-bias anomalies due to scattering from magnetic impurities[1-3] or due to small metallic particles in the oxide[4] are of no importance, and that the quality of our junctions equals that of the best Al-I-M junctions.

Figure 1 illustrates the shape of the $G(V)$-versus-V plots for several different junctions at liquid He[4] temperatures in a magnetic field sufficient to quench superconductivity in the Sn or Pb films. Considering the variation of counter electrode composition and the wide range of junction resistances, the similarity in shape from sample to sample is remarkable. Our curves are also very similar to those reported by Shen[6] for tunneling into single-crystal Cr. These data are clearly characteristic of clean $Cr-Cr_2O_3$-M junctions, and earlier observations of giant anomalies[1,2] probably represent impurity effects or low-quality junctions.

In order to isolate the mechanisms responsible for the linear conductance, we fabricated a sample consisting of 1000 Å of Al with a 60-Å overlay of Cr; this sample was oxidized in the usual manner. Since the Cr overlay was roughly as thick as the oxide, and since Cr diffuses readily into Al, little or no free Cr was present near the barrier.[7] One of these Al-Cr_2O_3-M junctions is shown as A of Fig. 1. The shape of the characteristic is the same as for $Cr-Cr_2O_3$-M junctions except for a larger asymmetry which we attribute to the change in contact potential when the first electrode is Al rather than Cr. Despite the asymmetry change,

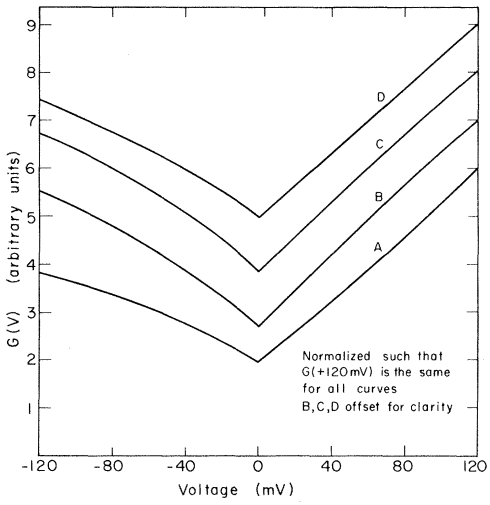

FIG. 1. Conductance versus bias voltage for several different junctions at ≤ 4.2 °K normalized at $V = +120$ mV; positive bias corresponds to Cr positive. (A) Al-Cr_2O_3-Sn, no offset, $G^{-1}(+120) = 22\ \Omega$; (B) $Cr-Cr_2O_3$-Sn, G offset +1 division, $G^{-1}(+120) = 110\ \Omega$; (C) $Cr-Cr_2O_3$-Pb, G offset +2 divisions, $G^{-1}(+120) = 1,750\ \Omega$; (D) $Cr-Cr_2O_3$-Sn, G offset +3 divisions, $G^{-1}(+120) = 25\,000\ \Omega$.

both $G_e(V)$ and $dG_e(V)/dV$ were identical for both systems. Hence, we conclude that the structure of $G_e(V)$ is due entirely to the oxide layer rather than the Cr electrode.

Samples were prepared by electron-beam evaporation of high-purity[8] Cr in an ion-pumped vacuum system at $< 10^{-7}$ Torr. The Cr strips, 1000–2000 Å thick and 0.5 mm wide, were usually oxidized in laboratory air in a 200 °C oven for 10–20 min. A few samples were oxidized for several months at room temperature in a small desiccator. Previous investigations[9,10] have shown that the latter method consistently yields 50-Å-thick oxide layers. Since both types of oxidation give roughly the same junction resistance and properties, the oxide thickness in all of our junctions is taken to be ≈ 50 Å. Preliminary junction capacitance measurements, using a value of 12 for $\epsilon(Cr_2O_3)$,[11] are consistent with this estimate. Following the oxidation, 0.5-mm-wide cross strips of Ag, Pb, or Sn were deposited to form the second electrode.

Cr_2O_3 is the only common oxide[12] which grows on pure Cr under oxidation conditions similar to those we used.[9,10,13] α-Cr_2O_3 is chemically and structurally similar to Al_2O_3, having the α-corundum structure and a static dielectric constant $(\epsilon/\epsilon_0) \approx 12$, but it is antiferromagnetic with a transition temperature of ~310 °K. The magnon dispersion relations and density of states have recently been determined by neutron diffraction.[14] The differences between the "ordinary" behavior of Al-Al_2O_3-M junctions and the remarkable behavior of $Cr-Cr_2O_3$-M junctions are evidently a consequence of either the antiferromagnetism of Cr_2O_3 or of exchange scattering from the localized d orbitals of the Cr^{+++} ions.[15]

According to the theory of inelastic tunneling developed by Duke, Silverstein, and Bennett[16,17] (DSB), broad-conductance dips centered at zero bias may be caused by the creation of elementary excitations in the barrier. As the bias is increased, more and more inelastic channels open up parallel to the conventional (elastic) channel, causing the conductance to increase with bias. The basic formula for the inelastic contribution to the conductance at zero temperature is

$$G_e^{\text{inelastic}}(V, 0) = \text{const} \times \int_0^{|eV|} N_b(E) |g(E)|^2 dE, \quad (1)$$

where $N_b(E)$ is the density of states for barrier excitations and $g(E)$ is the excitation-electron coupling parameter. Assuming constant elastic conductance, and neglecting bias-induced barrier changes, the voltage derivative of the conductance is given by

$$\frac{dG_e(V, 0)}{dV} \propto N_b(eV) |g(eV)|^2. \quad (2)$$

At finite temperatures, DSB calculate $G(V)$ for several types of excitation and various barrier conditions. A common feature of their curves is the disappearance of structure as a function of $k_BT/\hbar\omega_m$, where $\hbar\omega_m$ is the energy of a given peak in $N_b(E)$. In particular, the peak in $dG_e(V)/dV$ due to a peak in $N_b(E)$ is only slightly rounded at $k_BT \approx 0.1\hbar\omega_m$, reduced by ~70% when $k_BT \approx 0.3\ \hbar\omega_m$ and almost totally gone for $k_BT \gtrsim 0.5\hbar\omega_m$.

Figure 2 shows dG_e/dV as a function of V and T for a typical Cr-Cr_2O_3-M junction; at 1.2 °K there are peaks at 28, 44, 62, and 82 meV. The progressive disappearance of the lower-bias structure as T is increased is characteristic of the DSB theory; ordinary thermal smearing would reduce all peaks equally. At 77 °K, k_BT/eV for this series of peaks is equal to 0.24, 0.15, 0.11, and 0.08, respectively; at this temperature, the DSB theory predicts that the 28-meV peak will be considerably weakened, while the other structure will be affected only slightly. At 200 °K the k_BT/eV ratios are 0.62, 0.39, 0.28, and 0.22; theory indicates that the 28-meV peak will have vanished, the 44-meV peak will be significantly diminished, and the other two peaks will be somewhat weakened. These qualitative predictions accurately describe the data of Fig. 2. It is difficult to attempt a more quantitative fit because of the temperature-dependent background which is apparent on the 200 °K curve (cf. the rise in dG/dV for V > 82 mV at 200 °K). The change in background with temperature and bias precludes a direct measurement of the peak height, particularly at the higher temperatures and voltages.

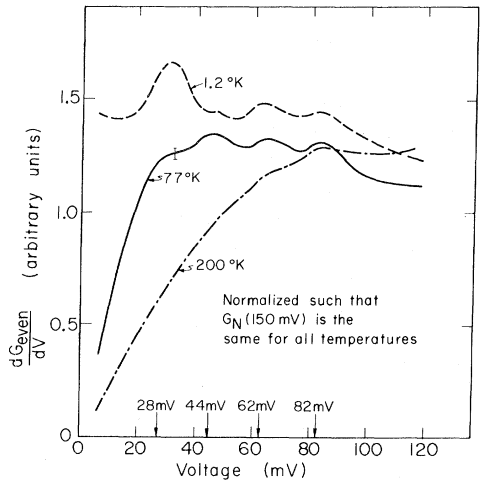

FIG. 2. Voltage derivative $dG_e(V)/dV$ of the even conductance as a function of bias for a Cr-Cr_2O_3-Sn junction at several temperatures. $G_e(V)$ for all temperatures was normalized to be the same at 150 mV for data-reduction purposes; to obtain an absolute comparison, dG_e/dV (77 °K) should be multiplied by a factor of 1.1 and dG_e/dV (200 °K) by a factor of 1.2. The error bar indicates typical scatter in the value of the derivative. Sample-to-sample variation of the estimated position of the various peaks is $\lesssim \pm 3$ mV, which approximates the accuracy to which the data may be read.

Although qualitative agreement seems to be good, we cannot obtain a quantitative line-shape fit for our data. The linear dependence of $G_e(V)$ on V at low biases, although due to nonanomalous tunneling mechanisms, is not derivable from existing models. We note that the excitations contributing to $G_e(V)$ near $V=0$ are necessarily either acoustic phonons or antiferromagnons. However, present calculations[16–18] predict that $G_e(V, 0) \propto V^n$, where $n = 2$ for incoherent acoustic-phonon processes, $n = 3$ for magnons, and $n = 4$ for coherent acoustic phonons. Although none of these models fits our data (for which $n = 1$), it should be pointed out that each model makes specific assumptions about $|g(E)|^2$, which depend upon the nature of the postulated coupling of the tunneling electron to the barrier. It is also assumed that the excitation-dispersion relations are essentially the same in the thin oxide layer as in the bulk. The accuracy of these assumptions is more questionable in the case of our thin oxide layers than in the Schottky-barrier diodes analyzed by DSB.

Despite the difficulties in fitting the conductance line shapes, the qualitative agreement of the temperature dependences of both $G_e(V, T)$ and the peaks in dG_e/dV with the DSB theory leads us to believe that it is applicable to our experiments. We tentatively conclude that we are observing inelastic tunneling via elementary excitations of the oxide layer, although a different model for the coupling appears to be necessary to obtain quantitative agreements at low biases.

We have attempted to identify the peaks in dG_e/dV with known excitations in Cr_2O_3.[15] Infrared reflectivity experiments[11] have shown that there are strong optical modes in bulk single-crystal Cr_2O_3 at 66 and 74 meV, with other weaker modes distributed between 35 and 90 meV; this determines the $\vec{k} = 0$ optical-phonon frequencies for six transverse and six longitudinal branches, but gives no indication of the corresponding energies near the Brillouin-zone edges. The magnon density of states[14] in Cr_2O_3 rises quadratically to a sharp peak at 53 meV, falling rapidly to zero at 56 meV; although DSB predict[18] that $dG_e(V)/dV \propto N_b(eV)$ for such magnons, we observe no structure in the vicinity of the measured Cr_2O_3 magnon peak. The acoustic-phonon spectrum is presently unknown. The 28-meV peak may be due to acoustic phonons while the 28- and 44-meV peaks

might also be due to magnons or hybrid phonon-magnon modes at branch crossings. Assuming large momentum transfers, all of our peaks might also be ascribed to optical phonons near the edges of the zone. Conspicuously absent from our data is structure corresponding to the antiferromagnetic gap in bulk Cr.[19]

We have also made Fowler-Nordheim plots of our higher-resistance junctions to determine the barrier height. We derive a value for $s\bar{\phi}^{3/2}$ of $8.4\ \text{Å}\,\text{eV}^{3/2}$, where s is the oxide thickness and $\bar{\phi}$ the mean barrier height. Using the previous estimate of 50 Å for s, $\bar{\phi} \gtrsim 0.3$ eV. This indicates that all of our data are "true" tunneling at energies below the mean barrier height. We also estimate from the above that $s\bar{\phi}^{1/2} \approx 20\ \text{Å}\,\text{eV}^{1/2}$ for Cr_2O_3, which is quite close to the commonly accepted value for Al_2O_3; for these high values of $s\bar{\phi}^{1/2}$, the WKB approximation used in the theory is sufficiently valid for computing the tunneling matrix elements.

Clearly, the only significant difference between Cr_2O_3 and Al_2O_3 is the magnetic behavior of the former, which must be responsible for the enormous enhancement of the inelastic tunneling in Cr_2O_3 barriers. As previously mentioned, the present theory of magnon-assisted inelastic tunneling predicts a cubic dependence of conductance on bias voltage for both coherent and incoherent mechanisms. The incoherent scattering model involves impurities in the oxide layer. It seems unlikely to us that all our junctions would be so similar, and in such good agreement with other experiments,[6] if impurity mechanisms dominated. The coherent scattering mechanism couples the electrons to magnons via the highly localized d orbitals on the Cr^{+++} ion sites by s-d exchange. Such a model explains why Al_2O_3 shows so little structure, and predicts the amplitude of the effect to be very large in Cr_2O_3. However, we do not observe the change in $G(0)$ with magnetic field, which is predicted by the magnon models. A reasonable alternative hypothesis is that of strong coupling to barrier-phonon modes via coherent or incoherent scattering of the tunneling electrons by the Cr^{+++} ions. It remains to be seen whether a quantitative model based on a physically reasonable coupling will predict the observed linear dependence of conductance on bias.

Further neutron studies on Cr_2O_3 to determine the phonon spectrum would be of great value. In particular, the energies corresponding to the cutoff of the acoustic-phonon spectrum and the optical-phonon frequencies at the edges of the zone are required if we are to make detailed comparisons with the structure observed in dG_e/dV.

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[1]L. Y. L. Shen and J. M. Rowell, Phys. Rev. 165, 566 (1968).

[2]J. M. Rowell, in *Tunneling Phenomena in Solids*, edited by E. Burstein and S. Lundquist (Plenum, New York, 1969), p. 385.

[3]J. A. Appelbaum, Phys. Rev. Letters 17, 91 (1966); Phys. Rev. 154, 633 (1967).

[4]H. R. Zeller and I. Giaever, Phys. Rev. 181, 789 (1969).

[5]W. L. McMillan and J. M. Rowell, Phys. Rev. Letters 14, 108 (1965).

[6]L. Y. L. Shen, J. Appl. Phys. 40, 5171 (1969).

[7]R. P. Agarwala, S. P. Murarka, and M. S. Anand, Acta Met. 12, 871 (1964). Furthermore, if a thin layer of Cr remained at the interface, we would expect large zero-bias anomalies [cf. F. Mezei, Phys. Letters 25A, 534 (1967)].

[8]"Iochrome" single crystals, 99.996% nominal purity; they were obtained from Materials Research Corp., Orangeburg, N. Y. 10962.

[9]R. M. Hill and C. Weaver, Trans. Faraday Soc. 54, 1140 (1958).

[10]J. Cohen, J. Appl. Phys. 36, 1504 (1965).

[11]D. R. Renneke and D. W. Lynch, Phys. Rev. 138, A530 (1965).

[12]The other common oxide, CrO_2, is metallic.

[13]O. Kubaschewski and B. E. Hopkins, *Oxidation of Metals and Alloys* (Academic, New York, 1968).

[14]E. J. Samuelsen, M. T. Hutchings, and G. Shirane, Solid State Commun. 7, 1043 (1969); Brookhaven National Laboratory Report No. BNL-14040 (unpublished).

[15]There is, of course, some question as to whether a discussion of our 50-Å films in terms of bulk Cr_2O_3 properties is meaningful. In particular, the bulk phonon and magnon properties may have no relevance to our observations whatsoever. We have included these in our discussion because they constitute the only "benchmark" presently available for purposes of comparison. Also, the possibility of nonstoichiometric oxide composition cannot be positively excluded. However, the argument attributing the differences between Al- and Cr-oxide junctions to the localized d orbitals on Cr-ion sites is not invalidated by any of the above considerations.

[16]C. B. Duke, S. D. Silverstein, and A. J. Bennett, Phys. Rev. Letters 19, 312 (1967).

[17]A. J. Bennett, C. B. Duke, and S. D. Silverstein, Phys. Rev. 176, 969 (1968).

[18]C. B. Duke (private communication).

[19]A. S. Barker, Jr., B. I. Halperin, and T. M. Rice, Phys. Rev. Letters 20, 384 (1968).