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Electron Tunneling in Cr-Cr<sub>2</sub>O<sub>3</sub>-Metal Junctions

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ABSTRACT

Conductance measurements on high-quality, thin film Cr-Cr<sub>2</sub>O<sub>3</sub>-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<sub>2</sub>O<sub>3</sub> barrier.

We have measured the temperature and magnetic field dependence of the conductance of more than 80 thin-film Cr-Cr<sub>2</sub>O<sub>3</sub>-M tunnel junctions, where M (Metal) is Ag, Sn, or Pb. Contrary to other reports,<sup>1,2</sup> 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<sup>1-3</sup> or small metallic inclusions.<sup>4</sup> In particular: (1)  $G(V)$  has no observable magnetic field dependence to  $< 0.1\%$  for applied magnetic fields ( $H$ ) between 0 and 30 kG at 1.2K. (2) Below 4.2K,  $G(0)$  is nearly temperature-independent, having a slope of  $\leq 0.5\%$  per K; (3) the shape of  $G_e(V)$  is independent of both magnetic field and temperature in the range  $1.1K \leq T \leq 4.2K$ ,  $0 \leq H \leq 30$  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 1.2K 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.<sup>5</sup> We conclude that the electron transfer mechanism is ordinary electron tunneling, that zero-bias anomalies due to scattering from magnetic impurities<sup>1-3</sup> or due to small metallic particles in the oxide<sup>4</sup> are of no importance, and that the quality of our junctions equals that of the best Al-I-M junctions.

Fig. 1 illustrates the shape of the  $G(V)$  vs  $V$  plots for several different junctions at liquid He<sup>4</sup> 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<sup>6</sup> for tunneling into single crystal Cr. These data are clearly characteristic of clean Cr-Cr<sub>2</sub>O<sub>3</sub>-M junctions, and earlier observations

of giant anomalies<sup>1,2</sup> probably represent impurity effects or low quality junctions.

Samples were prepared by electron-beam evaporation of high purity<sup>7</sup> 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 minutes. A few samples were oxidized for several months at room temperature in a small desiccator. Previous investigations<sup>8,9</sup> 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  $\approx 50$  Å. Preliminary junction capacitance measurements, using a value of 12 for  $\epsilon(\text{Cr}_2\text{O}_3)$ ,<sup>10</sup> 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.

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.<sup>11</sup> One of these Al-Cr<sub>2</sub>O<sub>3</sub>-M junctions is shown as A of Fig. 1. The shape of the characteristic is the same as for Cr-Cr<sub>2</sub>O<sub>3</sub>-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, 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.

Cr<sub>2</sub>O<sub>3</sub> is the only common oxide<sup>12</sup> which grows on pure Cr under oxidation conditions similar to those we used.<sup>8,9,13</sup>  $\alpha$ -Cr<sub>2</sub>O<sub>3</sub> is chemically and structurally similar to Al<sub>2</sub>O<sub>3</sub>, having the  $\alpha$ -corundum structure and a static dielectric constant  $(\epsilon/\epsilon_0) \approx 12$ , but it is antiferromagnetic with a transition temperature of  $\sim 310\text{K}$ .

The magnon dispersion relations and density of states have recently been determined by neutron diffraction.<sup>14</sup> The differences between the "ordinary" behavior of Al-Al<sub>2</sub>O<sub>3</sub>-M junctions and the remarkable behavior of Cr-Cr<sub>2</sub>O<sub>3</sub>-M junctions are evidently a consequence of either the antiferromagnetism of Cr<sub>2</sub>O<sub>3</sub> or exchange scattering from the localized d-orbitals of the Cr<sup>+++</sup> ions.

According to the theory of inelastic tunneling developed by Duke, Silverstein, and Bennett<sup>15,16</sup> (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

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

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

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

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  $k_B T / \hbar \omega_m$ , 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  $k_B T \approx 0.1 \hbar \omega_m$ , reduced by ~70% when  $k_B T \approx 0.3 \hbar \omega_m$ , and almost totally gone for  $k_B T \geq 0.5 \hbar \omega_m$ .

Fig. 2 shows  $dG_e/dV$  as a function of  $V$  and  $T$  for a typical Cr-Cr<sub>2</sub>O<sub>3</sub>-M junction; at 1.2K there are peaks at 28, 44, 62, and 82 meV. The progressive dis-

appearance of the lower bias structure as  $T$  is increased is characteristic of the DSB theory; ordinary thermal smearing would reduce all peaks equally. At 77K,  $k_B T/eV$  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 200K the  $k_B T/eV$  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 200K curve (cf. the rise in  $dG/dV$  for  $V > 82$  mV at 200K). The change in background with temperature and bias precludes a direct measurement of the peak height, particularly at the higher temperatures and voltages.

Although qualitative agreement seems to be good, we cannot obtain a quantitative lineshape fit for our data. The linear dependence of  $G_e(V)$  on  $V$  at low biases, although due to non-anomalous 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<sup>15-17</sup> 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 on 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 lineshapes, 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 therefore attempted to identify the peaks in  $dG_e/dV$  with known excitations in  $\text{Cr}_2\text{O}_3$ . Infrared reflectivity experiments<sup>10</sup> have shown that there are strong optical modes in bulk single-crystal  $\text{Cr}_2\text{O}_3$  at 66 and 74 meV, with other weaker modes distributed between 35 and 90 meV; this determines the  $k=0$  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<sup>14</sup> in  $\text{Cr}_2\text{O}_3$  rises quadratically to a sharp peak at 53 meV, falling rapidly to zero at 56 meV; although DSB predict<sup>17</sup> that  $dG_e(V)/dV \propto N_b(\text{eV})$  for such magnons, we observe no structure in the vicinity of the measured  $\text{Cr}_2\text{O}_3$  magnon peak. The acoustic phonon spectrum is presently unknown. The 28 meV peak may be due to acoustic phonons, while the 28 meV 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.<sup>18</sup>

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 [ $\text{\AA}(\text{eV})^{3/2}$ ], where  $s$  is the oxide thickness and  $\bar{\phi}$  the mean barrier height. Using the previous estimate of 50  $\text{\AA}$  for  $s$ ,  $\bar{\phi} \gtrsim 0.3$  eV. This indicates that all of our data is "true" tunneling at energies below the mean barrier height. We also estimate from the above that  $s\bar{\phi}^{1/2} \approx 20$  [ $\text{\AA}(\text{eV})^{1/2}$ ] for  $\text{Cr}_2\text{O}_3$ , which is quite close to the commonly

accepted value for  $\text{Al}_2\text{O}_3$ ; for these high values of  $\phi^{-1/2}$ , the WKB approximation used in the theory is sufficiently valid for computing the tunneling matrix elements.

Clearly, the only significant difference between  $\text{Cr}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  is the magnetic behavior of the former, which must be responsible for the enormous enhancement of the inelastic tunneling in  $\text{Cr}_2\text{O}_3$  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,<sup>6</sup> if impurity mechanisms dominated. The coherent scattering mechanism couples the electrons to magnons via the highly localized d-orbitals on the  $\text{Cr}^{+++}$  ion sites by s-d exchange. Such a model explains why  $\text{Al}_2\text{O}_3$  shows so little structure and predicts the amplitude of the effect to be very large in  $\text{Cr}_2\text{O}_3$ . 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  $\text{Cr}^{+++}$  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  $\text{Cr}_2\text{O}_3$  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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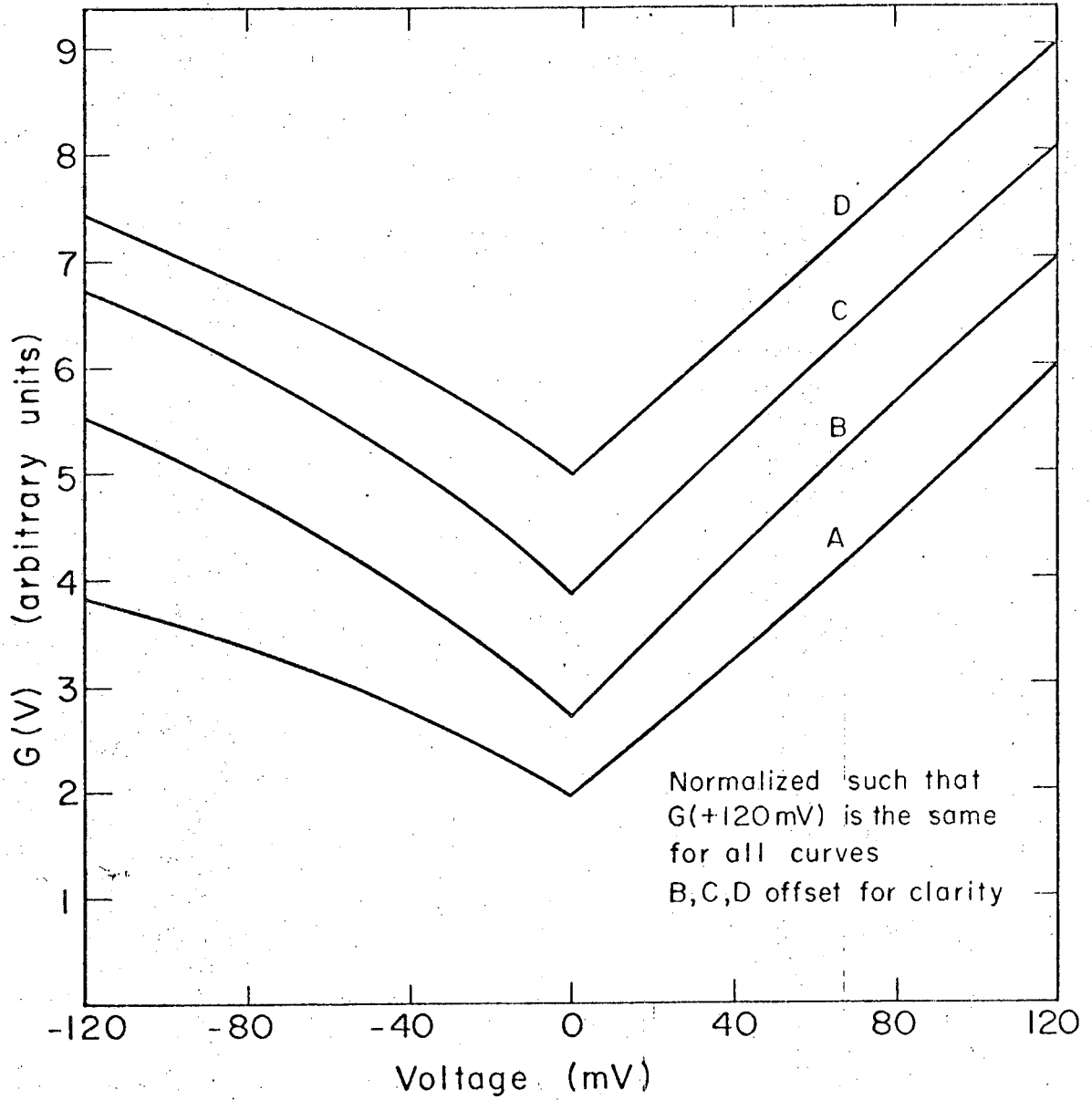
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## FIGURE CAPTIONS

Fig. 1. Conductance vs bias voltage for several different junctions at  $\leq 4.2\text{K}$ , normalized at  $V=+120\text{ mV}$ ; positive bias corresponds to Cr positive. (A)

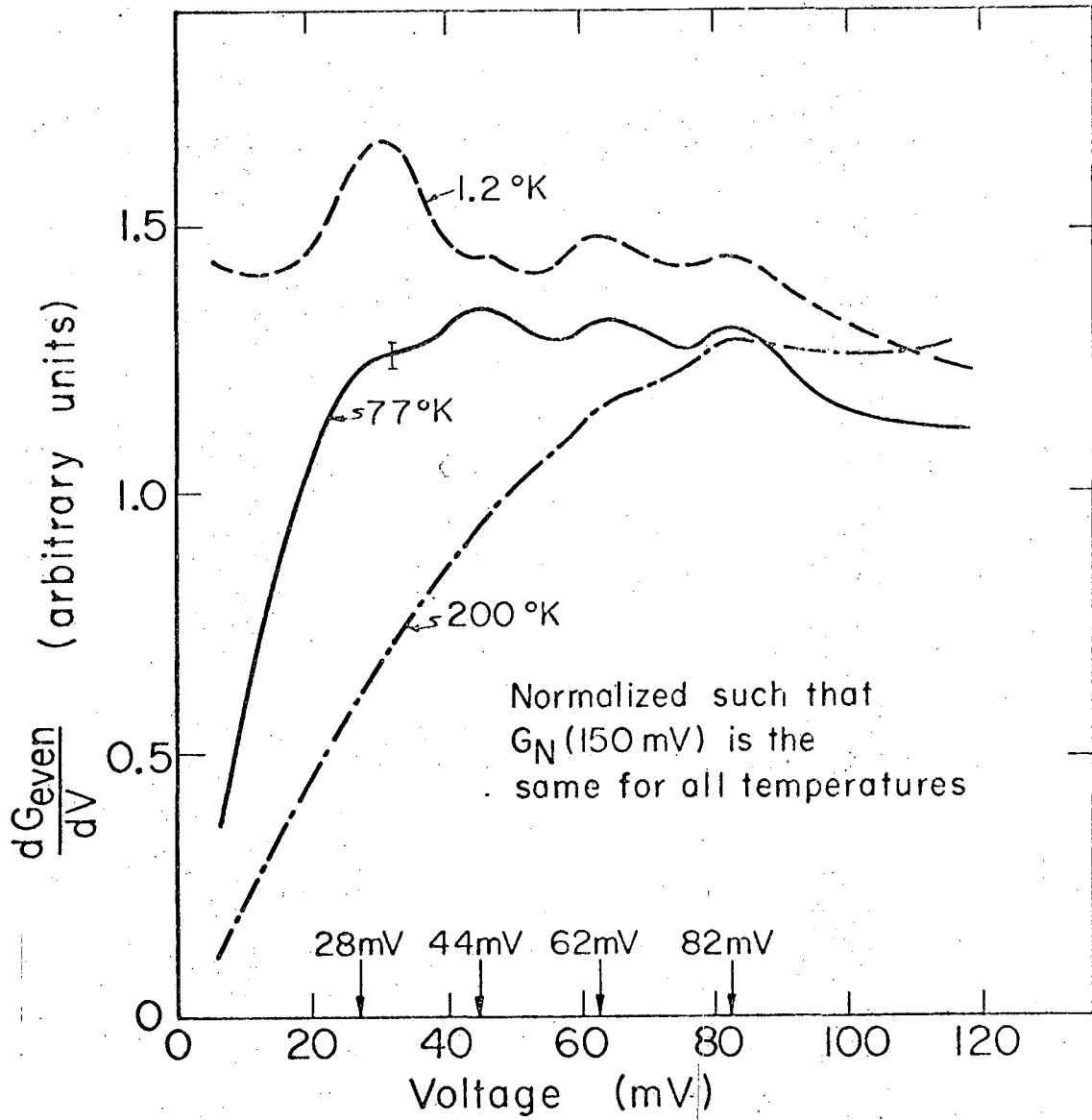
Al-Cr<sub>2</sub>O<sub>3</sub>-Sn, no offset,  $G^{-1}(+120)=22\Omega$ ; (B) Cr-Cr<sub>2</sub>O<sub>3</sub>-Sn, G offset +1 division,  $G^{-1}(+120)=110\Omega$ ; (C) Cr-Cr<sub>2</sub>O<sub>3</sub>-Pb, G offset +2 divisions,  $G^{-1}(+120)=1,750\Omega$ ; (D) Cr-Cr<sub>2</sub>O<sub>3</sub>-Sn, G offset +3 divisions,  $G^{-1}(+120)=25,000\Omega$ .

Fig. 2. The voltage derivative,  $dG_e(V)/dV$ , of the even conductance as a function of bias for a Cr-Cr<sub>2</sub>O<sub>3</sub>-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,  $dG_e/dV$  (77K) should be multiplied by a factor of 1.1 and  $dG_e/dV$  (200K) 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  $\lesssim \pm 3\text{ mV}$ , which approximates the accuracy to which the data may be read.



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Fig. 1



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Fig. 2

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