ELECTRON TUNNELING MEASUREMENT OF A SMALL ENERGY GAP IN LANTHANUM

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This Letter reports the first electron tunneling measurements of an energy gap in lanthanum, La. The measured value for $2\Delta_0/kT_c$ of 1.65 ± 0.15 is considerably lower than the value predicted by the Bardeen-Cooper-Schrieffer (BCS)[1] theory, 3.52. At voltages above that at which the gap is observed, an increase in conductance is also observed. This might be due to the f-band quasiparticle excitations predicted by the model of Kuper, Jensen, and Hamilton.[2]

It is surprising that La is a superconductor at around 5°K, while other Group-IIIB elements, such as lutetium, yttrium, and scandium, are not superconducting down to 0.2°K. Above T_c the Knight shift[3] and electron susceptibility[4] of La increase rapidly with decreasing temperature. These facts led to speculation that the superconductivity of La is not due solely to an effective, attractive interaction caused by the phonons.[5] Kuper, Jensen, and Hamilton[2] have suggested that the existence of a narrow f band above and close to the Fermi level could assist the BCS condensation of the conduction electrons. The predictions of Kuper's theory are that (1) the energy gap for the conduction electrons $2\Delta_s$ is proportional to $\sqrt{n_f}$, where n_f is the occupation number of pairs in the f band; (2) the ratio $2\Delta_s/kT_c$ is smaller than the BCS value of 3.52; (3) there should also be quasiparticle excitations in the f band. This would give rise to an increase in tunneling current at voltages high enough to produce these excitations. A similar theory by Kondo[6] leads to an enhancement of T_c even without the f band being populated.

Leslie et al.[7] have made infrared-absorption measurements on face-centered cubic La which resulted in values for $T_c = 6.06$°K, $2\Delta_0/kT_c = 2.85 \pm 0.24$, and the possibility of a second gap at twice the energy of the first one. Gardner and Smith,[8] on the other hand, interpreted an increase in T_c with pressure as evidence against the above theories.

The tunneling diodes were formed from an evaporated 0.38-mm-wide film of either magnesium or aluminum, its oxide, and an evaporated La film on a glass substrate. The background pressures during the different La evaporations varied from 10^{-5} to 10^{-6} mm Hg. The magnesium or aluminum films were thicker than 5000 Å, and all the La films were approximately 14 000 Å thick. X-ray analysis showed that at most 5% of the La was in the hexagonal phase. The remainder was, of course, face-centered cubic. Analysis of the La films indicated that the concentration of paramagnetic impurities was approximately 300 ppm. The diode I-V characteristics were measured using a constant-current source and a crossed-strip geometry which permitted a four-point measurement. The resistance of the diodes increased[9] in going from room temperature to 4.2°K. This indicates the absence of metallic shorts. Table I shows values for the energy gap $2\Delta_0$, T_c, and $2\Delta_0/kT_c$, and the residual-resistance ratio for several La diodes. The last sample in the table, La37b, was a La-MgO_x-Mg diode. The values for $2\Delta_0/kT_c$ are approximately one half of the BCS value of 3.52.

The T_c's were taken to be the temperatures at which the resistance of the La strip vanished. These values for T_c are consistent with the temperature at which the gap extrapolates to zero. The transition widths were about 0.1°K. The energy gaps for La, $2\Delta(T)$, and for the Al in the La-AlO_x-Al diodes were determined from the I-V characteristics by the method of Douglass and Meservey.[10] For the La-MgO_x-Mg diodes, $2\Delta(T)$ was determined from the voltage at which the conductance was equal to its limiting value g_0. The values of energy gap obtained by fitting the I-V curves agree with those obtained by this method.[11] The values of $2\Delta_0$ quoted in Table I are extrapolations of $2\Delta(T)$ to $T = 0$°K.

Table I. Experimental results for several diodes.

	$2\Delta_0$ (meV)	T_c (°K)	$2\Delta_0/kT_c$	Residual resistance ratio
La31a	0.662 ± 0.02	4.95	1.55	2.87
La31b	0.684 ± 0.03	5.09	1.56	2.43
La34a	0.780 ± 0.03	5.12	1.77	4.09
La37b	0.756 ± 0.03	5.14	1.71	...

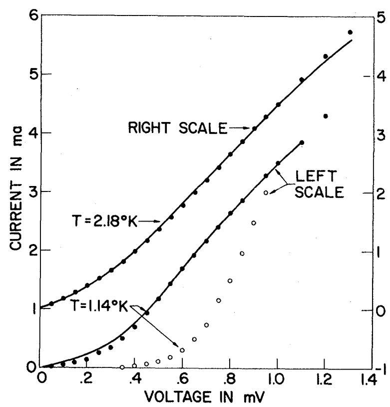

FIG. 1. I-V characteristics for a La-MgO_x-Mg diode, diode 37b, at 1.14 and 2.18°K. The points represent the calculated curves at these temperatures based upon the BCS density of states. The points at the temperatures 1.14 and 2.18°K are based upon energy gaps $2\Delta(T)$ of 1.71 and $1.68kT_c$, respectively. The current scale for the 2.18°K data is on the right. The open circles represent the calculated data at 1.14°K for $2\Delta = 3.52kT_c$.

The measured energy gaps for the aluminum films varied from 0.334 to 0.380 mV and are close to previously measured values.[10] Figure 1 shows the I-V characteristics for a La-MgO_x-Mg diode, diode 37b, at 1.14 and 2.18°K. The curve for $T = 2.18$°K has been displaced upward 1 mA for clarity. The points represent the calculated values at these temperatures based upon the BCS density of states. The values for the energy gap, $2\Delta(T)$, used in the calculation were $1.71kT_c$ (or 0.756 meV) at 1.14°K and $1.68kT_c$ (or 0.741 meV) at 2.18°K. The vertical scale of the theoretical points has been adjusted so that they agree with the experimental curve at 1 mV. The agreement is good. There is a small discrepancy in the low-voltage portion of the I-V characteristics obtained at the very lowest temperatures. This may be due to a small "leakage current" or a small departure from the BCS density of states. At higher temperatures (where the conductance is higher) the zero-voltage conductance is within a few percent of that predicted by the BCS theory.[12] For comparison the open circles represent the theoretical values at $T = 1.14$°K for an energy gap of $3.52kT_c$, the value predicted by the BCS theory. Clearly, one cannot fit the experimental results with the larger gap value. The energy gap $2\Delta(T)$ for the La-MgO_x-Mg diode is plotted as a function of T in Fig. 2. A BCS temperature dependence is shown based upon the tabulated values of $2\Delta_0$ and T_c.

At applied voltages of approximately 5 mV the conductance increased from g_0 to a higher value g_n. In some cases this transition occurred smoothly and resembled the tunneling characteristics of a superconducting diode. In other cases, there was an abrupt decrease in voltage. The latter transition, but not the increased conductance, was established to be a thermal effect. As stated above, the conductance change might be due to f-band quasiparticle excitations. Another possibility is that the effect is due to a change in current distribution within the diode when one of the films is driven normal. Further investigation of the effect is in progress.

As Table I indicates, the critical temperatures of the La films varied from 4.95 to 5.14°K. More recent work has yielded T_c's up to 5.25°K. While these values are lower than Leslie's value of 6.06°K, they are not too different from the critical temperature of our starting material which was 5.6-5.9°K. An anodized-aluminum substrate was used instead of the glass substrates to investigate the possibility that the difference in thermal contraction between the substrate and film stressed the film, causing the reduction in T_c. However, the film on the aluminum substrate had a T_c of 4.96°K, which falls within the range observed with glass substrates. The reduction in T_c also might be due to hydrostatic stresses, nonmagnetic impurities, or even magnetic impurities. It is likely that hydrostatic stresses or nonmagnetic impurities, if they reduced T_c, would correspondingly reduce Δ_0, leaving $2\Delta_0/kT_c$ unchanged to a first approximation.[13] Accord-

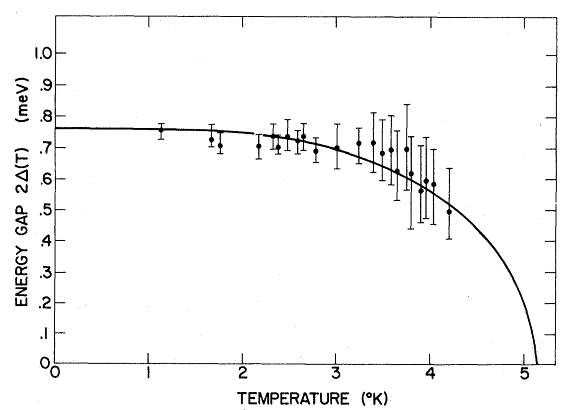

FIG. 2. Plot of the temperature dependence of the energy gap $2\Delta(T)$ of La in the La-MgO_x-Mg diode.

ing to the Abrikosov-Gor'kov theory[14,15] magnetic impurities will reduce both T_c and $2\Delta_0/kT_c$. If the reduction in T_c from 6.06 to 5.1°K is assumed to be due to magnetic impurities, then the Abrikosov-Gor'kov theory predicts that $2\Delta_0/kT_c$ would be reduced from 3.5 to 2.6. If Leslie's value for $2\Delta_0/kT_c$ of 2.85 is used for the pure material instead, then the value predicted for $2\Delta_0/kT_c$ of the impure material is 2.08. Both predictions are larger than the observed value of 1.65 ± 0.15. In fact, it is unlikely that 300 ppm of various magnetic impurities could account for the observed depression of T_c.

On the other hand, the small energy gap is consistent with either Kuper's or Kondo's theory. Thus, superconductivity in lanthanum may be strongly influenced by electronic interactions other than the electron-phonon interaction of the BCS theory.

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STRAIN ALONG c AXIS OF SbSI CAUSED BY ILLUMINATION IN dc ELECTRIC FIELD

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SbSI is an interesting material because of the coexistence of the photoconductivity and ferroelectricity.[1] The present work reports a new phenomenon, which is that the length of an SbSI crystal along the c axis is changed when it is illuminated uniformly by visible light, in the presence of a dc electric field along the c axis.

Needle-shaped single crystals 10-30 mm in length were grown by a transport method, which was similar to those of Kern[2] and Hamano et al.[3] Selected single crystals were cut perpendicular to the needle axis, which is the c axis of SbSI, by embedding them in a mixture of resin and paraffin wax, and then the mixture was removed by dissolving with benzene. Pillared crystals 10 mm in length were thus prepared and evaporated silver on both sides [(001)] was used as electrodes. The area of the (001) faces of the specimens used was about 10^{-2}-10^{-3} mm^2, and the Curie temperature (T_C) was about 19.5°C.

First, the relative change in length along the c axis was measured with an optical lever with an accuracy of 1 part in 10^5. Illumination was provided by an Osram HBO-100W/2 mercury lamp through a Toshiba V-V44 filter and infrared light was excluded with a cupric sulfate solution filter.

Curve A in Fig. 1 shows the temperature dependence of the relative change in length ($\Delta L/L$)