yield $\Theta_D \simeq 120°K$ at 10°K for hcp or fcc La.

In conclusion, we have observed structure in the tunneling characteristics of La thin-film diodes which may be attributed to a broad phonon spectrum in the material sampled by the tunneling measurement, but we do not expect this spectrum to be a good representation of pure bulk La.

Thus, while our results are in accord with the present theories of superconductivity which are based on an electron-phonon interaction, the resolution obtained is not sufficient to rule out the possibility that some other mechanism may be responsible for the superconductivity of La. It would appear, however, that any alternative theory must predict a departure (or departures) in the tunneling density of states near the Debye energy which is not much different in amplitude from those given by the present theories.

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PHOTOSENSITIVE TUNNELING AND SUPERCONDUCTIVITY

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If two conductors are separated by a sufficiently thin, evaporated CdS film, the observed tunnel current through the CdS film may be modulated by exposing the sample to a light source. If both conductors are metals in the superconducting state, it is possible to switch the CdS into a resistanceless state, the Josephson state, by exposing it to a light source.

Most experiments involving electron tunneling through a thin insulating region rely either upon a natural-grown oxide layer or upon a space charge region in a semiconductor. Attempts have been made to fabricate an artificial tunneling barrier,[1-4] for example, by simply evaporating a thin, insulating film. The main experimental problem with such an approach is that an evaporated insulating film which is thin enough to pass an appreciable tunnel current will in general not be continuous but will contain small pinholes. When the second electrode is deposited, it will be in direct contact with the metal substrate through the pinholes, and the tunnel junction will be short circuited. The above-mentioned attempts to fabricate tunnel junctions this way have been reported as successful; however, the insulating film has in all cases been deposited onto a metallic substrate already covered by an oxide layer or on a semiconducting crystal. Direct short circuit is then avoided, but in the case of the metal surfaces it seems probable that most of the observed current will flow through the oxide inside the pinholes.

One possible solution to the pinhole problem is to evaporate the insulating film before the substrate metal has been oxidized. After the deposition of the insulating film, the substrate can be allowed to oxidize in the unprotected regions at the pinholes. The two electrodes are then separated at all points by either the insulating film or by the substrate oxide. However, one is still faced with the problem of deciding whether the current through such a junction flows mainly through the insulating film or through the small oxide-covered regions, and whether the conduction mechansim is indeed tunneling. By employing an evaporated, photosensitive, insulating

film as a tunneling barrier between two superconductors these questions can be answered conclusively.

In the present experiment the insulating layer is an evaporated CdS film, and the tunnel junctions are produced in the following manner. First, a metal film is evaporated in a vacuum of 5×10^{-5} mm Hg onto a glass slide as shown in Fig. 1. The metal should be known to oxidize; for example, Al, Sn, or Pb will work nicely while Au does not. Immediately and without breaking the vacuum, a thin CdS film is evaporated over the metal film. The next step consists of exposing the assembly to air for about one hour. If there are pinholes in the CdS film, the underlying metal film will be exposed to air and an insulating oxide layer will be formed inside the pinholes. Finally, a second metal film is deposited across to complete the tunnel junction, and current and voltage leads are attached in the usual manner. During the evaporations the substrate is always kept at, or close to, room temperature.

In the past, I have attempted to make tunnel junctions by evaporating CdS onto Au substrates, but they were inevitably shorted, indicating that the CdS film had pinholes. It seems reasonable to assume that the CdS will contain pinholes when it is deposited on other metals as well. Therefore, when current is passed through a tunnel junction

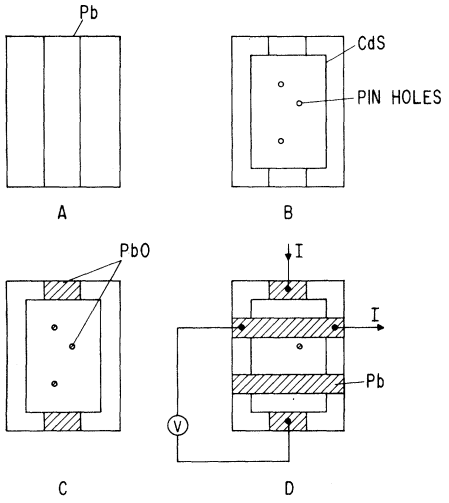

FIG. 1. Sample preparation. (a) An evaporated Pb film on a glass slide. (b) A CdS film has been deposited on top of the Pb film. Normally the CdS film will not be continuous but contain small pinholes. (c) The sample is oxidized such that an insulating layer of PbO can be formed in the pinholes. (d) Cross strips of Pb have been evaporated to complete the tunnel junctions.

prepared in the above manner, the electrons can pass either through the CdS film or through the small, oxide-covered pinholes. It remains to be established which current predominates.

The tunnel current in our junction is the sum of two currents flowing in parallel; and at low applied voltage V, it can be written as[5]

$$I \sim V\{A_c \exp(-2t_c/\hbar)(2m\varphi_c)^{1/2} + A_0 \exp(-2t_0/\hbar)(2m\varphi_0)^{1/2}\}, \quad (1)$$

where A_c and A_0 are the areas of CdS and oxide, respectively; t_c and t_0 are the barrier thicknesses; φ_c and φ_0 are the barrier heights; and m is the electron mass. Because the effective barrier height for the evaporated CdS happens to be very low compared with that for an oxide, and because the areas of the pinholes are so small, we expect the main part of the current to flow through the CdS.

Figure 2 shows a current-voltage characteristic of a Pb-CdS-Pb sample at 2.2°K. Except for the basic nonlinearity, the behavior is very similar to the ordinary Pb-PbO-Pb characteristic.[6] Because the superconducting energy gap is readily visible in the curves, we can say with confidence that we are observing mainly a tunnel cur-

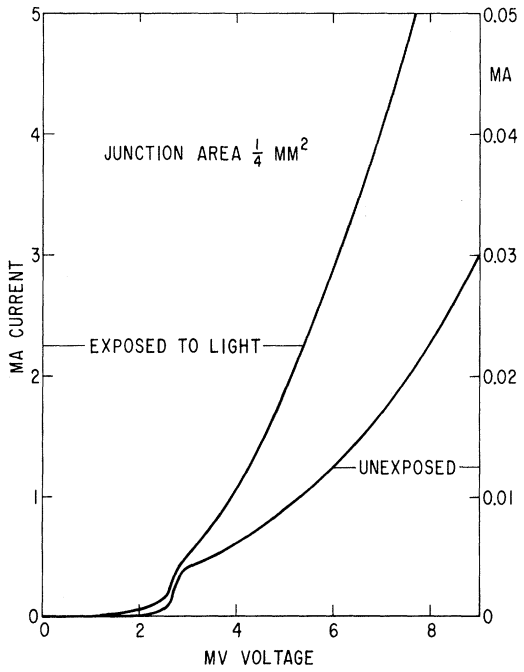

FIG. 2. A typical Pb-CdS-Pb sample characteristic at 2.2°K. The CdS layer is approximately 200 Å thick. Note the current onset at approximately half the energy gap in the exposed curve.

rent.

The metal electrodes were made thin enough to transmit light, and Fig. 2 also shows the current-voltage characteristic after the sample has been exposed to light. Basically, the only change is an increase in the current; the shape of the characteristic is the same. Since the oxide is not affected by light, we conclude that the current flows through the CdS. Because the superconducting energy gap appears in the current-voltage characteristic, the main current flow is still due to tunneling.

It is curious that the sample remains in the low-resistance state after the light source has been removed, which in essence means that the decay time is very long. Such an effect is known from work on specially prepared single crystals at low temperature,[7] and it is believed that the mechanism responsible for the long time constant is a trapping of the holes such that the electron-hole recombination is nearly forbidden. The trapping of the holes changes the position of the Fermi level in the CdS, which in turn is directly related to the effective barrier height. By heating the sample to approximately 100°K the high-resistance state is recovered. The sample may also be switched back to the high resistance state by applying a few volts across the junction; however, whether this is caused by the electric field or simply by Joule heating is not known at present. There is also the possibility of quenching the photoconductivity by using infrared light, as is done in bulk CdS.[8]

A certain fraction of the current flowing between the metal films will be due to conduction mechanisms other than tunneling; for example, part of the current will be carried by photoexcited electrons in the CdS. The part that is tunneling current can readily be established from the experimental data. For two Pb films separated by a CdS film of about 300 Å average thickness, we find that tunneling accounts for about one-half the current. This is equivalent to an effective barrier height (ignoring the uneven thickness of the barrier) of order of magnitude 25 mV if the effective electron mass is taken as unity. Such a low barrier height can also be inferred from the temperature behavior of the samples. At room temperature the resistance is too low to be measured because of the lack of an exact four-probe measurement.[9] The tunnel current will begin to dominate when the temperature is too low for an appreciable number of carriers to go over the barrier. The temperature at which this happens is, of course, a strong function of thickness. A nonlinear current-voltage characteristic is also typical of a low barrier height. Equation (1) is valid only when the applied voltage is much smaller than the effective barrier height φ; when they are of the same order, the equation must be modified.[5]

It is known that when two superconductors are separated by a sufficiently thin insulating barrier, the so-called Josephson state will become observable.[10] The Josephson state manifests itself by the fact that it becomes possible to pass a small current through the insulating region without any voltage drop across it. In other words, the barrier in some respects appears as a superconducting short. By using evaporated CdS films of about 50 Å thickness, I have been able to switch the CdS from a high- to a zero-resistance state by exposing it to light, as seen in Fig. 3. When the effective barrier height is lowered by light exposure, the strength of the coupling between the superconductors increases, and the Josephson effect becomes observable.

Apart from the rapid increase in tunnel current at a voltage equal to the superconducting energy gap, for some time it has been known that

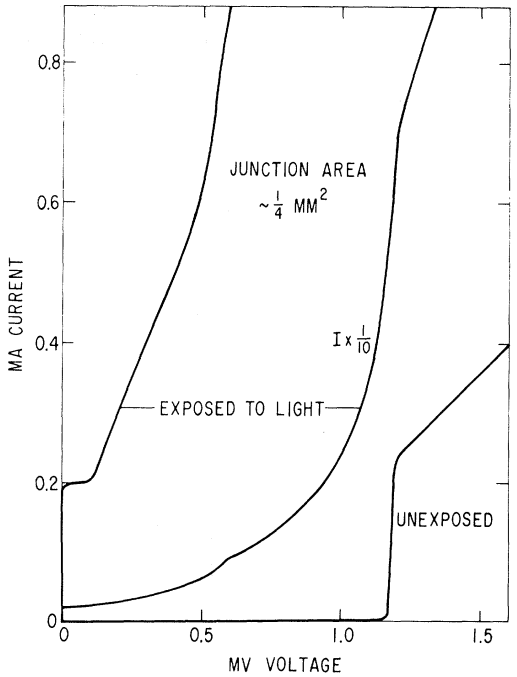

FIG. 3. A typical Sn-CdS-Sn sample characteristic at 2.2°K. The CdS layer is approximately 75 Å thick. The dc Josephson current is clearly visible after the junction has been exposed to light. Note current onset at approximately half the energy gap in the exposed curve.

small increases take place at especially half the energy gap and also at other integer fractions of the gap.[2,11] As can be seen from these curves in Figs. 2 and 3, when the samples have been exposed to light, the so-called "mid-gap bump" becomes clearly visible. The thickness of the evaporated CdS film is probably uneven; and, at least at first sight, the experimental results tend to support the explanation given by Schrieffer and Wilkins of multi-particle tunneling.[12]

In summary, these experiments demonstrate that it is possible to tunnel through a properly prepared artificial barrier and that both ordinary tunneling and supercurrent tunneling can be made photosensitive.

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ESR OF A [111] DEFECT IN X-RAYED LiF†

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A new defect center that is believed to be the equivalent of the interstitial halide atom is observed in x-rayed pure LiF. It has the form of a negatively charged diatomic halide molecule situated on a single halide site and orientated along a [111] axis. The ESR constants are $g_x = g_y = 2.0105$, $g_z = 2.0017$, $T_x = T_y = 19.0$ G, and $T_z = 1005.9$ G.

This Letter reports the results of measurements and analysis of an ESR spectrum of a new defect that is produced by x irradiation of LiF at low temperatures. This new defect has [111] symmetry and appears to be the interstitial fluorine defect for pure LiF.

Interstitials are important in several phenomena of solid-state physics. There are many examples of interstitial impurities and interstitials associated with impurities, but interstitials in pure materials have been very elusive. Until recently, it was generally believed that the interstitial halide atom in pure alkali halides was a defect with [110] symmetry. This [110] defect has the form of a negatively charged diatomic halide molecule (e.g., F_2^-) centered on a lattice site and is the result of the combination of an interstitial halide atom with a halide lattice ion. The [110] defect in LiF, KCl, and KBr was studied by Känzig and Woodruff[1] by ESR, and was called the H center since it appeared to correspond[2] to the optical H band which was first studied by Duerig and Markham[3] after x irradiation of KCl and KBr at liquid-helium temperature. However, a recent electron-nuclear double-resonance (ENDOR) study by Dakss and Mieher[4] has shown that in LiF the [110] defect is associated with a sodium impurity which is located on a nearest-neighbor lithium site. We believe that the new [111] ESR defect[5] is also an F_2^- molecule that is centered on one negative-ion lattice site with the molecular axis in a [111] direction.

The observed angular dependence of the ESR of the [111] defect is shown in Fig. 1 for a rotation of the magnetic field in a $(1\bar{1}0)$ plane. For comparison the angular dependence of the ESR of the self-trapped hole (V_K center), which has [110] symmetry, is also shown. It is well established that the V_K center in the alkali halides has the form of a negatively charged diatomic halide molecule (e.g., F_2^-) located on two lattice sites and is the equivalent of a hole shared by two negative ions in a [110] direction.[6,7] The ESR spectra of all F_2^- (and the other halides) defects are characterized by a large anisotropic hyperfine interaction between the unpaired electron and the two