The emission at the complementary frequency ω_2 is located 10 cm^{-1} above the $5P_{3/2}$-$4S$ resonance line in potassium (Fig. 2). For this frequency, the coefficient α in Eq. (1) is close to resonance. The enhanced emission at $\omega_2 = 24\,730$ cm^{-1} satisfies the equation $\hbar(\omega_1+\omega_2)=E_{6S}-E_{4S}$ to within one wave number.

A Polaroid plate showing this emission from the potassium vapor cell is shown in Fig. 2(b). The lines are placed parallel to the corresponding emitting levels in Fig. 2(a). Within each of the $5P$-$4S$ resonance lines there is a black strip which matches exactly the position of the $5P \rightarrow 4S$ resonance emission from a potassium spectral lamp. The resulting doublet structure was observed by Lumpkin et al.[7] and was attributed to wave-function modulation. In our setup there is evidence that at high vapor pressure the emission takes place predominantly at the front of the 1-m-long vapor cell, and the black strips are due to self-reversal by resonant absorption along the cell. The doublet structure in the two lines is not observed when the potassium vapor pressure is sufficiently low.

When nitrobenzene is replaced by bromonaphthalene, the requirement for two-photon excitation of the $6S$ state is not satisfied. Correspondingly, the blue emission at the complementary frequency ω_2 was not observed even though the atomic Raman line appears as usual.[6] This observation is a further evidence for our assignment.

Enhanced two-photon emission is a method for amplifying laser radiation.[8] The virtue of such amplification is that it does not require inversion of population. Enhancement is particularly favorable when the coefficient α in (2) is resonant.

An alternative decay, in which the incident photon ω_1 is absorbed and an anti-Stokes Raman photon $\omega_2=\omega_1+(E_3-E_1)/\hbar$ is simultaneously emitted, can also take place. Such emission is favorable when the "virtual" level E_2 happens to be outside the interval E_2-E_1.

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STRUCTURE IN THE TUNNELING DENSITY OF STATES OF SUPERCONDUCTING La†

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Structure has been observed in the tunneling characteristics of La thin-film diodes which may be attributed to a poorly developed phonon spectrum in the portion of the La film sampled by the experiment.

It has frequently been suggested that a magnetic interaction may be primarily responsible for the superconductivity of some of the transition metals. Such ideas would gain considerable impetus if experimental data were available which were at variance with existing formalisms of superconductivity,[1] and it would help considerably if the experiments were ones which portrayed the electron-phonon interaction in a fairly direct manner so that any variance would be readily recognized.

The electron-tunneling experiment is one of this type,[2] and Wyatt[3] has demonstrated phonon effects in Ta and Nb in this manner. The position of La is less certain. Levinstein, Chirba, and Kunzler[4] have reported seeing phonon effects of amplitudes intermediate between those for Sn and Pb during the course of preliminary point-contact tunneling measurements with La, but Edelstein[5] has reported seeing no such effects with La thin-film tunnel diodes. The lack of sharp phonon effects in thin films may be attributed to lattice disorder, but in view of the results of Chen et al.,[6] who observed phonon effects in amorphous Bi, or of Zavaritskii,[7] who observed phonon effects in Pb films having a deliberately distorted lattice, one would not expect phonon effects to be totally absent in La thin films. This conjecture is confirmed by the results reported here.

The diodes were formed by evaporating La from a Ta boat onto an Al film which had previously been subjected to a glow discharge in oxygen at ~0.1-Torr pressure. The La deposition rates were ~500 Å/sec, the substrates were glass at 300°K, and the system vacuum prior to La deposition was ~10^{-7} Torr. Masking definition and film widths were such that we believe over 90% of the tunneling was into La film regions of thickness $\gtrsim 1\ \mu$. The resulting residual resistivity ratios for the La films were only 5 or 6 however, corresponding to an electron free path of ~50 Å. Since the bulk starting material had a resistivity ratio of 20, we assign this short free-path value to lattice defects.

Attempts to anneal the films by allowing the fabricated diodes to remain at 300°K in a vacuum or a pure He atmosphere for even a few hours caused a marked degradation of all parameters measured by tunneling. In particular, the energy gap $2\Delta_0$, the transition temperature T_c, and the ratio $2\Delta_0/kT_c$ all became smaller, while positive zero-bias conductance anomalies of ~1% amplitude became larger and the conductance at high bias voltages became erratic. The annealing attempts did not cause any appreciable change in the film resistivity ratios or the transition temperatures determined by film resistance measurements.

Taken collectively, these results suggest that thermal energy promotes a degradation of the oxide-La interface, and that the degradation influences the superconducting state of the tunneling-sampled La material immediately behind this interface.

The fabrication technique which we have adopted is accordingly a compromise between deposition onto a cold substrate,[8] which would smear the phonon spectrum, and deposition onto a hot substrate, which would destroy the tunneling barrier. Since this fabrication method has resulted in reasonably reproducible tunneling results on three successive attempts, only the results obtained from one diode are presented.

The energy gap value $2\Delta_0 = 1.4$ meV was obtained by fitting the Bermon calculations to the experimental data. The fit was not good in the sense that the same difficulties were encountered as those reported by Edelstein.[5] Our assignment of a single energy-gap value to the tunneling results is therefore only an approximation, but it is quite adequate in view of the extreme variability of results which may be obtained with these diodes if fabrication parameters are altered. In this sense, our values for the transition temperature and gap ratio, $T_c \simeq 5.0$°K and $2\Delta_0/kT_c \simeq 3.2$, are in reasonable accord with those obtained by other workers, but they are not representative of bulk hcp La ($T_c = 4.9$°K, $2\Delta_0/kT_c = 3.7$), or bulk fcc La ($T_c = 6.0$°K, $2\Delta_0/kT_c = 3.7$).[9]

Results which have been obtained at higher energies are shown in Fig. 1. The dynamic conductance $g(v) = di/dv$ was measured with an ac bridge technique, due care having been taken with regard to modulation levels and normalization procedures. The normal-state first-derivative characteristic $g_n(v)$ which enters Fig. 1 was obtained with the aid of a magnetic field rather than an increase in temperature. This was done because the zero-bias anomalies present were observed to exhibit some temperature dependence but negligible magnetic field dependence at high bias values.

While it is true that sharp structure of amplitude ≃0.1% is not present in the first-derivative results, the overall results do show some resemblance to the phonon structure for In.[10] The normalized results were also independent of bias polarity, the gross first-derivative departure from BCS scaled approximately as $\Delta(T)^2$, and the amplitude of the gross structure is of the order of magnitude (~1%) which one would expect if La were a phonon-mediated superconductor.

The first- and second-derivative results are thus suggestive of a phonon spectrum consisting of transverse and longitudinal peaks at ~4.5 and 10 meV, respectively. The Debye temperature Θ_D (at Θ_D) affords an approximate (±20%) cross check on the longitudinal energy in that this energy is usually $(1.1\text{-}1.4)\kappa\Theta_D$. Our results would therefore suggest $\Theta_D \simeq 100$°K at 100°K; the specific-heat results of Johnson and Finnemore[9]

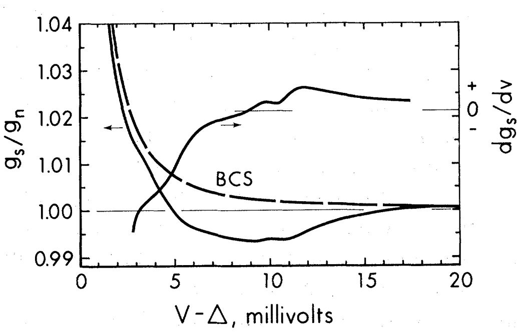

FIG. 1. Normalized first-derivative ($g = di/dv$) and second-derivative results for an Al-Al_2O_3-La tunnel diode at 2.05°K.

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