with a chemically polished {111} silicon surface we have found the remarkable result that for *the same surface* the transmission into helium was *greater* than into solid neon. This is surprising considering that solid neon has a density more than 10 times that of helium and an average sound velocity at least 3 times larger. The smallest reflection coefficient we have so far observed is 0.3—this being for transverse phonons incident on a {100} silicon-helium interface.

In a more detailed paper we hope to discuss these results in the context of the various theories of the Kapitza resistance.[1] We thank A. C. Anderson, C. H. Anderson, V. Narayanamurti, and H. Kinder for a number of stimulating conversations at the recent heat-pulse conference at St. Maxime.

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# Phonon Spectrum of La†

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Observed phonon structure in the tunneling density of states of superconducting La films ($T_c = 4.9$°K, $2\Delta/kT_c = 3.8$) contains resolvable detail not reported previously, with maximum deviations from the BCS prediction amounting to 1.7%. The McMillan-Rowell method of analysis produces a phonon spectrum $\alpha^2F(\omega)$ characterized by parameters which predict $T_c = 5.0$°K via the McMillan equation. Implications of this agreement are discussed.

Tunneling studies of La have assumed added significance in view of suggestions that superconductivity in La may be significantly affected by a narrow band of $f$ states just above the Fermi level.[1] Although sample preparation problems persist, La tunneling data have continued to improve in reliability with improvements in diode quality. For example, $2\Delta/kT_c$ obtained with films[2-6] has increased from an early value of 1.6 to the full bulk value (this work) of 3.7–3.8.[7,8] Nevertheless, tunneling studies continue to indicate an absence of strong structure[4-6,8] directly attributable to $f$-band effects, revealing instead only modest deviations from the BCS tunneling density of states (TDS) reminiscent of phonon structure[4,6,8] described by strong-coupling theory. This suggests that strong-coupling theory may provide an adequate description of La, and that the tunneling phonon spectrum $\alpha^2F(\omega)$ may be obtained by the method of McMillan and Rowell.[9] Any effects attributable to $f$ levels would presumably be reflected in parameters such as $\lambda$ (electron-phonon coupling strength) and $\mu^*$ (effective Coulomb pseudopotential) obtained in the course of computing $\alpha^2F(\omega)$. These parameters can then be used to calculate $T_c$ via McMillan's approximate solution of the Eliashberg equations.[10] Failure to obtain reasonable agreement with an independent tunneling measurement of $T_c$ would suggest difficulties with either the tunneling data or the applicability of strong-coupling theory. The significance of obtaining agreement will be discussed.

The critical components of an ideal film diode are (1) a low-leakage barrier in contact with (2) a pure, defect-free, single-phase metal film. Since tunneling results are sensitive to conditions

quite near the barrier, good metallic properties must extend to this region. A high chemical reactivity complicates preparation of pure La films, while rapid deterioration of junction characteristics at 300°K implies a continued reaction between metal and barrier. Considerations involving phase coexistence are also important.

Diodes of the form Al-$AlO_x$-La were fabricated by rapidly evaporating (350 Å/sec) micrometer thick films ($1\times10^{-7}$ Torr) over conventional Al-$AlO_x$ electrode-barrier strips held near 77°K. These were then covered with an Al film (300–1000 Å), warmed to room temperature, transferred, cooled to 0.9°K, and examined with a stable bridge spectrometer. Several massive evaporations of La prior to film production were routinely employed. Low substrate temperatures and protective Al coatings appear to improve junction quality. As anticipated, x-ray results indicated only minor amounts of $d$-hcp La,[2] the remainder being metastable fcc.[11] Diodes formed at 300°K almost always exhibit structure just above $\Delta^*(\mathrm{La})+\Delta(\mathrm{Al})$, where $2\Delta^*(\mathrm{La})$ is the depressed (or induced) energy gap near the barrier.[12] Such diodes also exhibit smeared phonon structure which may be attenuated (relative to better diodes formed at ~77°K) by a factor of 3 or more at higher biases, resembling effects seen in Ta.[6] As a minimum requirement, diodes used for phonon studies in La should be free of structure in the second derivative for about 1 mV above $\Delta(\mathrm{La})+\Delta(\mathrm{Al})$. Even so, La diodes fabricated to date are not as good as those commonly used in phonon studies of less troublesome metals.[9] Zero-bias ac conductances (0.9–1°K) vary from less than 1% to several percent of the normal-state value. Zero-bias anomalies (~7°K) of roughly the same magnitude also occur, poorer phonon structure tending to correlate with larger anomalies. One suspects that the present data may still contain a certain amount of residual smearing and attenuation, especially at higher biases.

Although bulk values of $2\Delta/kT_c$ are obtainable with La films, energy gaps ($\Delta\approx0.83$ meV) and $T_c$ values ($T_c\approx4.9$°K) observed by *tunneling*[3,5] are commonly suitable not for fcc ($T_c=6.00$°K)[7] as suggested by x-ray evidence, but rather more nearly for $d$-hcp ($T_c=4.87$°K).[7,8] Surface contamination seems an unlikely explanation on at least two counts. First, the observed value of $T_c$ (by tunneling) is almost always approximately 4.9°K.[3,5] Secondly, contamination reduces both $\Delta$ and $2\Delta/kT_c$ below their bulk values, as is easily demonstrated with diodes having strong structure just above $\Delta^*(\mathrm{La})+\Delta(\mathrm{Al})$.

This apparent conflict can be explained in terms of the martensitic nature of the transformation fcc → $d$-hcp. Below ~500°K, large amounts of metastable fcc La can be retained indefinitely.[11] If material is *scraped* from such a specimen and x rayed, a virtually pure $d$-hcp pattern results.[11] Mechanical strain efficiently converts the fcc phase into $d$-hcp. If La films are not produced in a stressed state, they almost certainly become so upon cooling to 0.9°K. We propose that the region near the barrier becomes preferentially stressed, driven into the $d$-hcp phase, thereby relieving the driving stress.

Support for this mechanism can be found in published data of Hauser.[3] For thick La films, $T_c(\Delta=0)\approx4.9$°K obtained by tunneling is smaller than $T_c(R=0)$ determined resistively, $T_c(R=0)$ converging to $T_c(\Delta=0)$ with decreasing film thickness. As was pointed out,[3] tunneling measures $T_c$ near the barrier, whereas $T_c(R=0)$ corresponds to the highest $T_c$ involved. Interpreted in terms of a stress-induced $d$-hcp layer near the barrier, Hauser's data suggest a layer thickness of ~1000 Å.

Figure 1 presents second-derivative data and a computed spectrum $\alpha^2F(\omega)$ for a La film char-

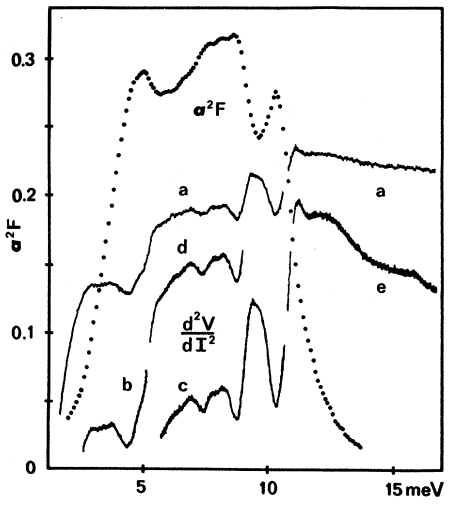


FIG. 1. Second-derivative data (curves $a$ through $e$, arbitrary units) and calculated phonon spectrum (solid circles) $\alpha^2F(\omega)$ for La as a function of energy $\omega$. Energies for $d^2V/dI^2$ correspond to $\omega=eV-\Delta(\mathrm{La})-\Delta(\mathrm{Al})$. Curves $b$ through $e$ represent higher gains and are offset for clarity. The La film is characterized by $\Delta=0.81$ meV, $T_c=4.9$°K, $2\Delta/kT_c=3.8$, and thickness $\approx1$ $\mu$m. Peaks in $\alpha^2F(\omega)$ occur at $\omega=5.0$, 6.0, 6.6, 7.7, 8.1, 8.6, and 10.3 meV, with additional structure at $\omega=3.5$, 4.6, and 11.8 meV. For bulk La ($d$-hcp), $k\Theta=12.2$ meV.

acterized by the indicated parameters, $T_c$ having been determined from $dV/dI$ near zero bias. These data correspond to a maximum deviation from the BCS density of states of 1.7%, a value significantly larger than previously observed,[4,6] and of the magnitude anticipated (~2%) from $T_c/\Theta$.[9] A modified version of McMillan's program[9,13] used to compute $\alpha^2F(\omega)$ yields parameter values $\lambda = 0.77$, $\langle\omega\rangle = 6.1$ meV, and $\mu^* = 0.018$. The value $\mu^* = 0.018$ is approximately $\frac{1}{5}$ that commonly obtained for other strong-coupling superconductors ($\mu^* \approx 0.1$).[10,14] Differences between the experimental TDS and that calculated from the computed $\alpha^2F(\omega)$ are as large as 2 parts per thousand for $\omega \approx 5$ meV, but do not exceed 1 part per thousand at higher energies. As anticipated, structural features of $d^2V/dI^2$ are reproduced by $\alpha^2F(\omega)$, with a rapid drop in amplitude near $k\Theta$(bulk). When inserted into the McMillan formula,[10,15]

$$T_c = \frac{\langle\omega\rangle}{1.20} \exp\left[\frac{-1.04(1+\lambda)}{\lambda - \mu^* - 0.62\lambda\mu^*}\right], \qquad (1)$$

the above parameters yield $T_c = 5.0$°K.

One notes that $\alpha^2F(\omega)$ does not resemble the spectrum anticipated for a fcc structure.[14] As mentioned earlier, there is some evidence suggesting a $d$-hcp layer adjoining the barrier. Since the spectra of fcc structures ($ABC\cdots$) differ markedly from those of hcp ($ABAB\cdots$),[14] even though both are close-packed structures, there appears to be no *a priori* reason for $d$-hcp ($ABAC\cdots$) to resemble either fcc or hcp.

Other issues of concern include (1) the significance of agreement between observed and calculated values of $T_c$, (2) the anomalously small value of $\mu^*$, and (3) the general influence of attenuated derivative data. These issues are interrelated and must be considered together. An initial attempt to discover the influence of attenuation can be made by artificially enhancing the observed TDS structure in the region in which it has been observed, namely, for higher values of $\omega$. To this end we arbitrarily adopt an amplifying function $f = a(\omega/10.9)^2 + 1$. For $a = 0.3$, a 30% enhancement at 10.9 meV, one obtains $\lambda = 0.83$, $\langle\omega\rangle = 6.2$ meV, $\mu^* = 0.04$, and $T_c = 5.1$°K. Below about 9 meV, $\alpha^2F(\omega)$ is increased by at most 10% without changing its basic functional character, i.e., without shifting the energies at which specific structural features occur. Although the peak at 10.3 meV is not shifted in energy, its magnitude doubles and $\alpha^2F(\omega)$ approaches zero more rapidly thereafter. These results suggest that the major effects of modest ($\lesssim 30\%$) attenuations are to depress the peak height at 10.3 meV and extend the tail to higher $\omega$. They also indicate that $T_c$ is insensitive to attenuation at higher values of $\omega$. This could permit rather good agreement between calculated and measured values of $T_c$ despite a certain amount of residual attenuation.

Can enhancement continue until $\mu^*$ approaches 0.1 without changing $T_c$ by an objectionable amount? Although computing problems have been encountered for $a > 0.3$, tentative results indicate that $a \approx 1$ may succeed with $\lambda = 0.96$, $\langle\omega\rangle = 6.4$ meV, and $T_c \approx 4.9$°K. This would imply that a factor-of-2 increase in observed first-derivative structure at higher biases (~10 mV) could remedy an anomalously low $\mu^*$ without spoiling agreement between observed and calculated values of $T_c$.[16] The continued implication is that agreement between observed and calculated values of $T_c$ is a minimal requirement, not a sufficient condition assuring a reliable value of $\mu^*$.

The values $\lambda = 0.77$ and $\langle\omega\rangle = 6.1$ meV obtained ($a = 0$) are within 15% of those of In,[17] further supporting the view that strong-coupling theory applies to La. Assuming these values are essentially correct ($a \lesssim 0.3$), then small values of $\mu^*$ (0.02–0.04) are unavoidable if one is to obtain agreement between calculated and observed values of $T_c$. If the high value $T_c$(La) = 4.9°K [versus $T_c$(In) = 3.40°K] is to be attributed to $f$-band effects, then small values of $\mu^*$ must also reflect $f$-band effects, even if only in a phenomenological sense. Interpretations of this sort would gain in stature if one could independently assert that only modest amounts of attenuation ($a \lesssim 0.3$) were involved in the data presented. Failing this, the significance of the present result $\mu^* = 0.018$ remains an open issue.

In summary, phonon-induced structure of considerable complexity has been observed with La films exhibiting bulk values of $2\Delta/kT_c$. A phonon spectrum has been extracted and is probably to be associated with $d$-hcp La. Any subsequent improvements in diode quality will most likely cause a relative enhancement of the phonon peak at 10.3 meV without drastically changing matters at lower energies. Agreement between $T_c$ calculated from $\alpha^2F(\omega)$ via the Eliashberg equations and values measured independently by tunneling would appear to be an insensitive measure of the reliability of $\mu^*$ or the amplitude of $\alpha^2F(\omega)$ at higher energies. The anomalously low value of $\mu^* = 0.018$ remains an open issue in that it could either represent a genuine $f$-band effect or be accounted for by substantial amounts of residual

attenuation.

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# $F$ and $F^+$ Centers and Free-Carrier Absorption in BaO†

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The $F$ and $F^+$ bands in BaO at 77°K are observed to be at 2.3 and 2.0 eV, respectively. The ground state for the $F$ centers is about 0.1 eV below the conduction band. Above 77°K the $F$ centers are partially ionized so that the observed band is composite. The released electrons give rise to a free-carrier absorption in the near infrared. The configuration-coordinate diagram shows a barrier to recombination, and recombination by tunneling is observed. These $F$ centers are believed to be the long sought-after donors in oxide-coated cathodes.

The alkaline-earth oxides are divalent structural analogs of the alkali halides. Because they are divalent they open a new dimension to the study of color centers. For example, excited states exist for anion vacancies containing both one electron ($F^+$ centers) and two electrons ($F$ centers).[1] Recently, numerous papers have appeared on the $F$ and $F^+$ centers in MgO and CaO and to a lesser extent in SrO.[2] However, the literature on BaO still reflects considerable uncertainty regarding even the identification of the $F$ and $F^+$ absorption bands. We have now resolved this uncertainty and have observed these color centers to possess some quite unique properties of unusual interest. In this Letter we present a brief account of our initial findings.

Early work by Sproull, Bever, and Libowitz[3] on additively colored crystals of BaO placed the $F$-center optical absorption band at 2.0 eV. Support for this identification was obtained by Carson, Holcomb, and Rüchardt[4] who found no $F^+$-center ESR which could be associated with the center responsible for the 2.0-eV band. However these ESR measurements were severly hampered