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tion-metal compounds which are unstable at room temperature, but which can be prepared at high temperatures. Stability at high temperatures is promoted by entropy contributions to the free energy if the material is ternary or quaternary rather than binary. Here we use these terms in a structural sense and not a chemical one. For example, in $Li_x Ti_{1+y}S_2$ compounds, TiS_2 is one element, while Li_x and Ti_y are the second and third elements. In this sense the intercalated materials such as pyridine-TaS₂ are binary, while the intercalated bridge compound $Li_x Ti_{1+y}$ - S_2 is a ternary system. Values of T_s above 20°K have been found⁹ in the system $Nb_3Al_{1-x}Ge_x$, but again this system is pseudobinary, as both Nb₃Al and Nb₃Ge are stable and form continuous solid solutions with the same crystal structure. It may be correct to say that the high value of T_s in the $Li_{x}Ti_{1+y}S_{2}$ intercalated bridge system is the first example to be found of a new class of ternary materials, and that the values of T_s attainable in true ternary structures may exceed those so far attained in binary structures by as much as $T_s(\text{Li}_x \text{Ti}_{1+y} S_2)$ exceeds $T_s(\text{NbS}_2)$ —i.e., about a factor of 2.

In summary, the microscopic model presented here supports the conclusion already emphasized by Barz et al.⁵ that for purposes of superconductivity the compound $\operatorname{Li}_{x}\operatorname{Ti}_{1+y}S_{2}$ should not be described as an intercalation compound. Rather it is primarily a bridge compound, with intercalation of Li atoms making possible a random distribution of bridge Ti atoms and hence a very large density of states at the Fermi energy. The Ti bridge atoms behave as a two-dimensional gas at 600°K, and are therefore "soft" at low temperatures, which is another factor contributing to the very high values of T_s observed.

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¹J. A. Wilson and A. D. Yoffe, Advan. Phys. 18, 193 (1969).

²M. L. Cohen and C. S. Koonce, J. Phys. Soc. Jap. Suppl. 21, 633 (1966).

³F. R. Gamble *et al.*, Science <u>168</u>, 568 (1970); T. H. Geballe et al., Phys. Rev. Lett. 27, 314 (1971).

⁴A. D. Wadsley, Acta Crystallogr. <u>10</u>, 715 (1957).

⁵H. E. Barz *et al.*, Science <u>175</u>, 884 (1972).

⁶R. B. Murray, R. A. Bromley, and A. D. Yoffe, to be published.

⁷L. Ramqvist, J. Appl. Phys. 12, 2113 (1971). ESCA electron spectroscopy for chemical analysis.

⁸See Fig. 10 of W. L. McMillan, Phys. Rev. <u>167</u>, 331 (1968).

⁹G. Arrhenius et al., Proc. Nat. Acad. Sci. U. S. <u>61</u>, 621 (1968).

Phonon-Assisted Tunneling through Amorphous Germanium

F. R. Ladan and A. Zylbersztejn

Groupe de Physique des Solides de l'Ecole Normale Supérieure,* Tour 23, Paris 5e, France (Received 13 March 1972)

We report the observation of electron tunneling between two metal electrodes separated by an amorphous germanium layer. Measurements of the derivative of the conductance with respect to the applied voltage yield the tunneling phonon density of states for amorphous germanium.

Electron tunneling has proved to be a valuable technique for studying the phonon density of states in solids.¹ For example, tunneling through II-VIcompound films has been used by Giaever and Zeller² to determine the longitudinal optical phonons of the compounds. They also reported observation of the LO phonon in a germanium barrier believed to be amorphous. In the present work, we have studied electron tunneling through amorphous germanium. We obtain from the data the tunneling phonon density of states of amorphous germanium. Its general structure is found to be reminiscent of the phonon density of states

of crystalline germanium as deduced from neutron-scattering experiments.³

The geometry of the samples, which allows four-probe conductance measurements, is shown in the inset of Fig. 1. The metal electrodes and the germanium layer are evaporated by Joule heating in an oil diffusion pumped vacuum system, equipped with a liquid-nitrogen cold trap and a water-cooled baffle. The pressure is always lower than 10⁻⁶ Torr before evaporation, rising to 2×10^{-6} Torr at most during the germanium deposition. The substrate (microscope glass plate) is kept at low temperature during the aluminum

and germanium depositions by thermal contact with a copper block cooled to 77 K. The distance from the source to the substrate is 36 cm. The deposition rates and the final thicknesses are monitored and measured with a guartz crystal oscillator. The aluminum electrode is evaporated at 10 Å/sec with a thickness ranging from 200 to 700 Å. A mask-changing system subsequently allows us to deposit the germanium (99.9999% purity) without destroying the vacuum. For evaporating the germanium, we use either a graphite crucible or an alumina-coated tantalum boat: a very slow deposition rate is used (1 to 3 Å/sec) and the final film thickness is nominally 30 Å. The glass plate is brought back to room temperature before evaporating the 3000-Å-thick tin electrodes at a rate of 100 Å/sec.

An electron diffraction study shows that the germanium patterns consist only of broad halos characteristic of the amorphous state.

Immediately after preparation, the samples are introduced into the cryostat. Their conductance σ is measured as a function of the applied voltage V using a conventional modulation technique. The quantity $\sigma^{-1} d\sigma/dV$ is also plotted using a second-harmonic detection scheme. The



FIG. 1. (a) Conductance versus applied voltage and (b) $\sigma^{-1} d\sigma/dV$ versus applied voltage, both plotted for the same junction (note that voltage scales are different). Inset shows the geometry of the sample.

zero-bias impedances of the samples at 77 K are in the 200- to 2000- Ω range for a cross section of 10^{-4} cm². There is no noticeable impedance change when the samples are immersed in liquid helium. Conduction in thick amorphous germanium layers is temperature dependent, and would result in impedances larger than a hundred kilohms at 77 K.⁴ By lowering the temperature below the superconducting transition of the tin electrode, we always observe the characteristic BCS density-of-states structure at small biases. All this proves that the main transport mechanism in our samples is due to tunneling.

A conductance-versus-voltage curve taken at 4.2 K is shown in Fig. 1(a). It is parabolic up to about 250 mV with its minimum shifted a few millivolts from the origin. From sample to sample, this shift varies erratically, but is always small. From this, we infer that the tunnel barrier is symmetrical with respect to the metal electrodes.⁵ Therefore, although a monolayer of oxygen atoms is almost certainly adsorbed on the aluminum surface before it is covered with germanium, we conclude that the effective tunneling barrier is due to the amorphous germanium layer. This is further supported by the fact that we never observed the structure at ± 115 mV, which on the $\sigma^{-1} d\sigma/dV$ curves [see Fig. 1(b)] is associated with the bending mode of the Al-O-H bond, and which is always present in Al-oxide-metal junctions.⁶ It has been demonstrated⁷ that amorphous germanium prepared in the way described above has a well-defined gap, i.e., the electron density of states drops by at least several orders of magnitude at the valence and conduction band edges. From our zero-bias conductances, we can try to estimate the distance between the Fermi level and the conduction band (mean barrier height). In the case of a simple square barrier with an electron mass equal to the free-electron mass, one finds a value in the 0.3- to 0.5-eV range. Recent photoemission measurements on amorphous germanium films locate the valence band edge 0.31 eV below the Fermi level.⁸ By adding this number to the above estimate, one obtains a value for the forbidden gap of amorphous germanium in the 0.6–0.8-eV range, roughly consistent with optical absorption data.⁹

We present the quantity $\sigma^{-1} d\sigma/dV$ versus applied voltage in Fig. 1(b). The observed peaks correspond to a relative increase in conductance with increasing voltage, and exhibit a general antisymmetry with respect to zero bias. This is characteristic of the opening up of new channels

for electron tunneling, due to assisted tunneling processes.¹ These occur when the difference in energy between the Fermi levels of the two metals becomes large enough for the tunneling electron to emit an excitation of the junction, such as a phonon. Two groups of structures are present: (a) a group in the 0-40-mV range, with two broad peaks at 8 and 34 mV; (b) a group centered at 70 mV. We shall first focus our attention on group (a).

The relative change in conductance $(\Delta\sigma/\sigma)$ from 0 to 40 mV amounts to 2.5% for the particular sample under discussion, and is in the 2 to 3% range for all the samples studied. Conductance changes associated with the phonons of the electrodes are always much smaller (0.1 to 0.3%),¹⁰ and the corresponding structures observed on Aloxide-Sn junctions do not resemble the structures (a).⁵ On the other hand, the entire structure bears a remarkable similarity to the phonon density of states of germanium, as discussed below.

By subtracting the linear background and averaging over both polarities, one obtains the solid curve plotted in Fig. 2(a). In the same figure is plotted the phonon density of states of crystalline germanium deduced from neutron-scattering ex-



FIG. 2. Crystalline phonon density of states (dashed curves) from neutron scattering (Ref. 3) compared with (solid curves) (a) tunneling density of states and (b) tunneling density of states multiplied by energy, for the same junction as in Fig. 1.

periments (dashed curve).³ The two main peaks in our data correspond to the TA and (LO, TO) phonon peaks in the density of states. The peak at 34 mV was also observed by Giaever and Zeller.² The shoulder that we observe at 15 mV is clearly related to the peak at 14.6 mV in crystalline germanium. There is also a good correspondence between the position of the relative minimum in both curves. The experimental curve in Fig. 2(a) looks like a broadened version of the crystalline phonon density of states weighted by an energy-dependent factor, as does the Raman spectrum of amorphous germanium.¹¹

A theory giving the exact relationship between the tunneling spectrum and the phonon density of states of amorphous germanium is not available at present. However, we wish to discuss a few ideas that might lead to it. Stern¹² has calculated the optical absorption and the mobility edge in amorphous silicon by assuming that the potential in the amorphous solid is the crystalline one perturbed by a fluctuating potential with given rootmean-square amplitude and correlation length. The correlation length represents a measure of the distance over which short-range order is observed in the radial distribution function (6 Å for amorphous silicon). Such a model could be used to calculate the tunneling current associated with the presence of these fluctuations of potential inside the barrier. A similar problem has been treated by Bennett, Duke, and Silverstein¹³ for a model crystalline barrier containing impurities. These authors derive expressions for the incoherent electron-phonon coupling via potential fluctuations in the barrier. The momentum-conservation rules are removed, and it is found that the derivative of the conductance, $d\sigma/d\sigma$ dV, as a function of voltage (i.e., energy) is simply proportional to the phonon density of states divided by the energy. Applying this procedure to our experimental results, we obtain the phonon density of states of amorphous germanium shown in Fig. 2(b). We note that there is good agreement between the relative amplitudes of the two main peaks in the amorphous case and in the crystalline case, and that the experimental phonon density of states is parabolic at very low energies.

We have at present no satisfactory explanation for the structure observed at 70 mV [Fig. 1(b)]. It could be due to a two-phonon assisted tunneling process.

In conclusion, we have observed electron tunneling through an amorphous germanium layer. VOLUME 28, NUMBER 18

The samples are believed to be representative of an ideal covalent disordered material.¹⁴ As a matter of fact, conductance changes associated with inelastic tunneling yields a tunneling density of states which is clearly reminiscent of the phonon density of states of crystalline germanium, considerably broadened however. This is related to the short phonon correlation length to be expected in a disordered material.

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*Laboratory associated with the Centre National de la Recherche Scientifique.

¹C. B. Duke, *Tunneling in Solids*, Suppl. No. 10 to *Solid State Physics* (Academic, New York, 1969), p. 279.

- ²I. Giaever and H. R. Zeller, Phys. Rev. Lett. <u>21</u>, 1385 (1968).
- $^3G.$ Dolling and R. A. Cowley, Proc. Phys. Soc., London $\underline{88},\ 463\ (1966).$
- ⁴J. Stuke, J. Noncryst. Solids 4, 17 (1970).
- ⁵J. M. Rowell, W. L. McMillan, and W. L. Feldmann, Phys. Rev. 180, 665 (1969).
- ⁶J. Klein and A. Léger, private communication.
- ⁷W. E. Spicer and D. T. Pierce, Bull. Amer. Phys. Soc. <u>17</u>, 115 (1972).

⁸C. G. Ribbing, D. T. Pierce, and W. E. Spicer, Phys. Rev. B 4, 4417 (1971).

- ⁹T. M. Donovan, W. E. Spicer, and J. M. Bennett, Phys. Rev. Lett. 22, 1058 (1969).
- ¹⁰A. Léger, Thèse de doctorat d'Etat (unpublished), p. 35.
- ¹¹J. E. Smith, Jr., M. H. Brodsky, B. L. Crowder,
- and M. I. Nathan, Phys. Rev. Lett. <u>26</u>, 642 (1971). $^{12}{\rm F}.$ Stern, Phys. Rev. B <u>3</u>, 2636 (1971).
- ¹³A. J. Bennett, C. B. Duke, and S. O. Silverstein, Phys. Rev. 176, 969 (1968).
- ¹⁴N. F. Mott, Advan. Phys. <u>16</u>, 49 (1967).

Scattering of Quasiparticles by Thermal Phonons in Copper*

David Nowak and Martin J. G. Lee

The James Franck Institute and the Department of Physics, The University of Chicago, Chicago, Illinois 60637 (Received 13 March 1972)

We present an augmented-plane-wave pseudopotential calculation of the scattering of quasiparticle excitations by thermal phonons in symmetry zones of the Fermi surface of copper. The results provide an interpretation of recent experimental data.

Low-temperature experiments¹⁻³ have yielded for the first time measurements of the relaxation time for quasiparticle excitations averaged over small regions of the Fermi surface. It is convenient to express the experimental relaxation times in the form

$$1/\tau = \Gamma_0 + \gamma T^3,$$

where the coefficient γ measures the rate of scattering of quasiparticles by thermally excited phonons. The data for copper show that γ is strongly anisotropic, varying by factors as large as 30 between different regions of the Fermi surface. In this Letter we report some results of a calculation of the anisotropy of the coefficient γ in copper, based on an augmented-plane-wave (APW) formulation of the matrix element of the electronphonon interaction.

In the rigid-ion approximation, the matrix element of the electron-phonon interaction in a metal can be expressed in terms of pseudoatom phase shifts⁴ that are determined by an analysis of experimental Fermi-surface data. Screening by conduction electrons is treated approximately by choosing the phase shifts so that the Fermisurface average of the low-q limit of the pseudopotential is consistent with the known response to a long-wavelength density fluctuation.⁵ Such a model has proved quite successful in predicting the phonon resistivities and renormalization factors for metals of the alkali series.⁴ As a further and more rigorous test of the model, we have carried out a calculation of the anisotropy of the scattering of quasiparticles by thermal phonons in copper, evaluating the matrix elements of the electron-phonon interaction from an empirical phase-shift pseudopotential.

In the low-temperature limit $T \ll \Theta$, the phonon scattering rate is given by⁶

$$\frac{\hbar}{\tau(\vec{k})} = \frac{1 \cdot 31\Omega k_{\rm B}{}^3 T^3}{M V_{\vec{k}} \hbar^3} \sum_{\sigma} \left\langle \frac{|V_{\sigma}(0,\vec{k})|^2}{C_{\sigma}^4} \right\rangle,$$

where Ω is the volume of the primitive unit cell, *M* is the ion mass, $V_{\vec{k}}$ is the Fermi velocity of