contains references to earlier work on the tunneling states in KCl:Li.

[2]Previous work in this field has emphasized paramagnetic impurities. Their long spin-lattice relaxation times prevent generation of ballistic pulses of phonons and the low saturation-power levels, and weak microwave absorption compared with paraelectric systems reduces the maximum power available. See C. H. Anderson and E. S. Sabisky, Phys. Rev. Letters 21, 987 (1968), and W. J. Brya and D. E. Wagner, Phys. Rev. 157, 400 (1967), for recent progress and reference to earlier work.

[3]Such bolometers can be used to detect both thermal pulses and monochromatic ultrasonic pulses. See John M. Andrews, Jr., and M. W. P. Strandberg, J. Appl. Phys. 38, 2660 (1967).

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[7]The original intent of this experiment was to demonstrate the monochromatic nature of the phonons by transmitting them through a scattering medium of resonant lithium ions and observing the signal to increase on application of a field that tunes the scatterers out of resonance with the phonons. Weak scattering and microwave leakage produced the opposite effect, namely a decrease of signal with electric field.

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PHONON SPECTRUM OF SUPERCONDUCTING AMORPHOUS BISMUTH AND GALLIUM BY ELECTRON TUNNELING*

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The phonon spectra for amorphous Bi and Ga are derived by using McMillan's inversion program on our tunneling data. The results indicate an extreme "softening of the phonon spectrum" from what is found for crystalline superconductors. Parameters derived from our phonon spectra are used to test recent theories of the transition temperature of amorphous and strong-coupling superconductors, and also to test the McMillan equation for the maximum possible transition temperature in the limit of extremely strong coupling.

In this paper we present results on the phonon spectrum of superconducting amorphous Bi and Ga derived from tunneling measurements. The results are in the form of plots of $\alpha^2(\omega)F(\omega)$, where $\alpha^2(\omega)$ is the energy-dependent electron-phonon coupling parameter and $F(\omega)$ is the phonon density of states, with associated values of μ^*, the Coulomb pseudopotential. These results were obtained by inverting the strong-coupling gap equation, using the computer program of McMillan[1] which employs the experimental tunneling density of states $N(\omega)$ and the superconducting energy-gap parameter Δ_0 as input data. The resulting $\alpha^2(\omega)F(\omega)$ gives some insight into why the amorphous phases of Bi and Ga are such strong-coupling superconductors.

The tunnel junctions used in this investigation were Al-Al_xO_y-Bi and Al-Al_xO_y-Ga, and were prepared in situ in an evaporator cryostat. The Bi and Ga films were 1000 Å thick and were condensed onto a substrate held at 1.5°K. A brief description of the preparation of the tunnel junctions and of the method of measuring transition temperatures and of obtaining Δ_0 and $N(\omega)$ from the tunneling measurements have been given in an earlier publication.[2] A more detailed description of the experimental method will be included in a later article.

The values of the transition temperature T_C, twice the superconducting energy-gap parameter at zero temperature $2\Delta_0$, and the ratio $2\Delta_0/k_BT_C$ obtained for amorphous Bi and Ga in the present investigation are given in Table I, along with other values of these quantities obtained by some previous investigators. We have found that to obtain reproducible values of T_C and Δ_0 for amorphous Bi and Ga the substrate temperature during the condensation of the film has to be kept at a very low value (e.g., 1.5°K in the present investigation) compared with the temperature at which the amorphous phase converts to the crystalline phase (approximately 20°K for Bi and 15°K

Table I. A comparison of the transition temperature T_c, energy-gap parameter Δ_0, and the ratio $2\Delta_0/k_BT_c$ obtained for amorphous Bi and Ga in this experiment with values of these parameters obtained by previous investigators.

Source of data	Amorphous bismuth T_c (°K)	Amorphous bismuth $2\Delta_0$ (meV)	Amorphous bismuth $2\Delta_0/k_BT_c$	Amorphous gallium T_c (°K)	Amorphous gallium $2\Delta_0$ (meV)	Amorphous gallium $2\Delta_0/k_BT_c$
This experiment	6.11 ± 0.03	2.42 ± 0.02	4.59 ± 0.06	8.56 ± 0.02	3.32 ± 0.02	4.51 ± 0.04
Shier and Ginzburg[a]	6.17 ± 0.03	...	...			
Zavaritskii[b]	6.0	2.37	4.6			
Reif and Woolf[c]	...	2.15	...			
Minnigerode and Rothenberg[d]	5.93	2.33	4.56	8.47	3.29-3.30	4.50-4.52
Wühl, Jackson, and Briscoe[e]				8.4 ± 0.1	3.30 ± 0.06	4.5

[a]J. S. Shier and D. M. Ginzburg, Phys Rev. 147, 384 (1966).

[b]N. V. Zavaritskii, Zh. Eksperim. i Teor. Fiz.—Pis'ma Redakt. 5, 434 (1967) [translation: JETP Letters 5, 352 (1967)].

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[d]G. V. Minnigerode and J. Rothenberg, Z. Physik 213, 397 (1968).

[e]H. Wühl, J. E. Jackson, and C. V. Briscoe, Phys. Rev. Letters 20, 1496 (1968).

for Ga. Samples prepared at higher substrate temperatures (e.g., 4.2°K) had slightly smaller values of T_C and $2\Delta_0$ than the samples prepared at 1.5°K. This substrate temperature effect might account for some of the variation in T_C and $2\Delta_0$ observed in Table I. We believe that our Bi and Ga films are almost completely amorphous; however, our phonon spectrum for Bi suggests that there might be a little of another phase present in our Bi film, which might account for the slightly lower T_C that we observe compared with the value obtained by Shier and Ginsberg.[3]

The solid curves in Figs. 1(a) and 2(a) show the ratio of the tunneling density of states $N(\omega)$ to the BCS density of states $N_{BCS}(\omega)$ for amorphous Bi and Ga, respectively, as derived from our experimental tunneling data. The maximum deviation of $N(\omega)$ from 1 is 1.8% for amorphous Bi and 0.9% for amorphous Ga. [The maximum deviation of $N(\omega)$ from $N_{BCS}(\omega)$ is slightly larger and is 2.2 and 1.3% for amorphous Bi and Ga, respectively.] The maximum deviation of $N(\omega)$ from 1 that we observe for amorphous Bi is substantially larger than the value of ≈1% obtained by Zavaritskii,[4] whereas the corresponding value that we obtain for amorphous Ga is only slightly larger than the value of 0.8% obtained by Wühl, Jackson, and Briscoe.[5] We have found that the strength of the deviation shows the same substrate temperature effect as T_C and Δ_0, i.e., samples with a lower T_C show a smaller percentage deviation, and we believe that this is the cause of the differences in the percentage deviations noted above. The general shape of the tunneling data published by Zavaritskii on amorphous Bi and by Wühl, Jackson and Briscoe on amorphous Ga is very similar to the correspond-

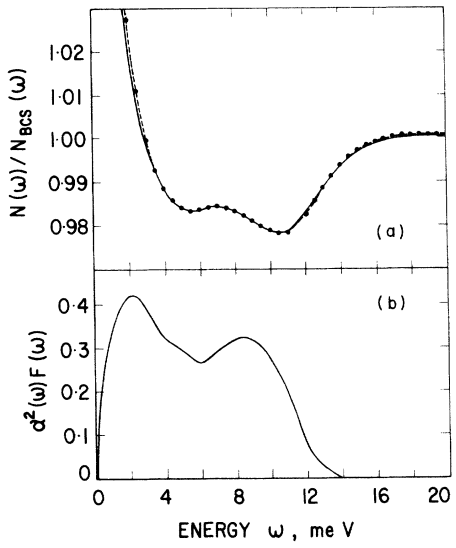

FIG. 1. Tunneling results for amorphous bismuth. (a) The solid line is the plot of the experimental $N(\omega)/N_{BCS}(\omega)$ data. The dashed line through the solid circles is $N(\omega)/N_{BCS}(\omega)$ calculated from the gap equations using the phonon spectrum shown in (b). (b) The phonon spectrum $\alpha^2(\omega)F(\omega)$ derived by using the McMillan program to invert the experimental $N(\omega)/N_{BCS}(\omega)$ data shown in (a).

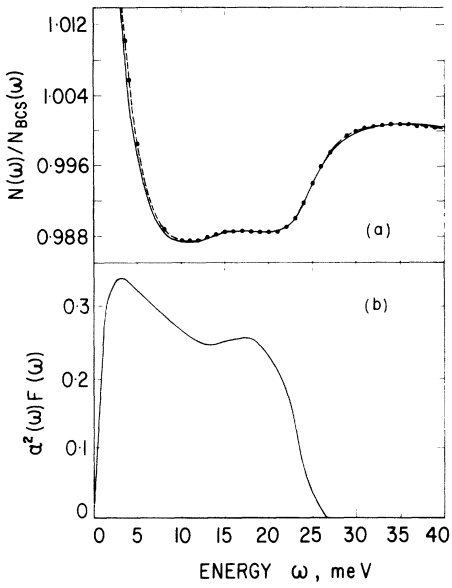

FIG. 2. Tunneling results for amorphous gallium. (a) The solid line is the plot of the experimental $N(\omega)/N_{BCS}(\omega)$ data. The dashed line through the solid circles is $N(\omega)/N_{BCS}(\omega)$ calculated from the gap equations using the phonon spectrum shown in (b). (b) The phonon spectrum $\alpha^2(\omega)F(\omega)$ derived by using the McMillan program to invert the experimental $N(\omega)/N_{BCS}(\omega)$ data shown in (a).

ing data that we have obtained.

Figures 1(b) and 2(b) show the plots of $\alpha^2(\omega)F(\omega)$ for amorphous Bi and Ga, respectively, that we have derived from our tunneling data using the inversion program of McMillan. The shapes of $\alpha^2(\omega)F(\omega)$ for amorphous Bi and Ga are strikingly similar, i.e., a high peak at low energies and a lower peak at higher energy. The maximum of the low-energy peak is located at 2.2 meV for amorphous Bi and at 3.0 meV for amorphous Ga. The maximum of the higher energy peak, which is broader and more difficult to locate exactly, is at 8.5 meV for amorphous Bi and at 17.5 meV for amorphous Ga. The two peaks are rather distorted and the wings of the peaks merge together so that the exact location of the maximum of a peak is probably not as important a physical quantity as the distribution of the strength in that peak. Zavaritskii attempted to fit his tunneling data for amorphous Bi by assuming that $\alpha^2(\omega)F(\omega)$ consisted of two symmetrically shaped peaks located at 3.5 and 8.5 meV, and his fitting procedure[6] consisted of varying the height and width of these peaks until he obtained an $\alpha^2(\omega)F(\omega)$ that yielded a calculated $N(\omega)$ that was close to his experimental $N(\omega)$. The location of our high-energy peak in amorphous Bi agrees exactly with the value of 8.5 meV found by Zavaritskii, and this peak occurred in the same position for all our samples. The location of our low-energy peak at 2.2 meV is significantly lower than the value of 3.5 meV that Zavaritskii assumed for his fitting procedure. However, we have found that the location of the low-energy peak in amorphous Bi shifts to higher energy for a sample with a lower T_c, and this may be the cause for the difference. The $\alpha^2(\omega)F(\omega)$ plots in Figs. 1(b) and 2(b) correspond to the samples characterized by the data in Table I; these are the highest T_c samples that we have been able to prepare, and we assume that this means that they are almost completely amorphous. However, Fig. 1(b) shows the trace of another very small peak in the region of 5 meV which we suspect might be due to a small amount of another phase in the junction.

The dashed curve through the solid circles in Figs. 1(a) and 2(a) shows the calculated plot of $N(\omega)/N_{BCS}(\omega)$ that results from the phonon spectrum shown in Figs. 1(b) and 2(b), respectively. The almost exact coincidence between the dashed and solid curves in Figs. 1(a) and 2(a) indicates that our derived $\alpha^2(\omega)F(\omega)$ for amorphous Bi and Ga fit the experimental data very well. The values of μ^* obtained from the inversion procedure are 0.105 ± 0.01 for amorphous Bi and 0.17 ± 0.02 for amorphous Ga. While the value of μ^* for amorphous Bi is quite reasonable, in that it is very close to the value found for Pb, we are somewhat surprised that the value of μ^* for amorphous Ga is so much larger, especially since in their general behavior amorphous Bi and Ga seem to act in the same way. However, all our amorphous Ga samples yielded this same value of μ^*, and if we tried to force the inversion program to fit the tunneling density of states with a lower value of μ^*, i.e., by keeping μ^* fixed at 0.11, the resulting fit was very poor. While a value of μ^* equal to 0.17 is large, it is not completely unreasonable, since values of μ^* as large as this have been found for some other superconductors.[7]

The following parameters were calculated from our $\alpha^2(\omega)F(\omega)$ for amorphous Bi and Ga: (i) the total electron-phonon interaction α_T^2, i.e., the total area under the $\alpha^2(\omega)F(\omega)$ plot:

$$\alpha_T^2 = \int \alpha^2(\omega)F(\omega)d\omega; \quad (1)$$

(ii) the electron-phonon coupling constant λ de-

fined by

$$\lambda = 2\int d\omega\, \alpha^2(\omega)F(\omega)/\omega; \quad (2)$$

(iii) the average phonon energy $\langle\omega\rangle$ and the average squared phonon energy $\langle\omega^2\rangle$, both introduced by McMillan[9]:

$$\langle\omega\rangle = \int\alpha^2(\omega)F(\omega)d\omega/\int\alpha^2(\omega)F(\omega)\omega^{-1}d\omega, \quad (3)$$

$$\langle\omega^2\rangle = \int\omega\alpha^2(\omega)F(\omega)d\omega/\int\alpha^2(\omega)F(\omega)\omega^{-1}d\omega. \quad (4)$$

The resulting values of these parameters for amorphous Bi and Ga are α_T^2(Bi) = 3.50 meV, α_T^2(Ga) = 6.15 meV; $\lambda_{Bi} = 2.46$, $\lambda_{Ga} = 2.25$; $\langle\omega\rangle_{Bi} = 2.86$ meV, $\langle\omega\rangle_{Ga} = 5.47$ meV; $\langle\omega^2\rangle_{Bi} = 16.3$ meV^2, $\langle\omega^2\rangle_{Ga} = 61.1$ meV^2. The estimated accuracy on these quantities is ±10% for α_T^2 and λ and ±20% for $\langle\omega^2\rangle$.

Since our experiment has determined the parameters λ, μ^*, $\langle\omega\rangle$, and $\langle\omega^2\rangle$ for the strong-coupling superconductors amorphous Bi and Ga, it is possible to use our results to make a quantitative test of the calculations of Garland, Bennemann, and Mueller[8] on the transition temperature of disordered or amorphous superconductors and the calculations of McMillan[7] on the transition temperature of strong-coupling superconductors, since both of these papers give expressions for T_c in terms of these parameters.

The theory of Garland, Bennemann, and Mueller is based on the assumption that the average amplitude of ionic vibration is larger in a disordered lattice than a perfect crystal, and they conclude that this results in a decrease in $\langle\omega\rangle$, an increase in λ, and a broadening of the peaks in $F(\omega)$ in a disordered or amorphous superconductor in comparison with a crystalline one. Qualitatively our results agree with these conclusions. First, the $\alpha^2(\omega)F(\omega)$ for amorphous Bi and Ga do show broadened peaks compared with what is typically found for crystalline superconductors.[9] Secondly, the ratio of $\langle\omega\rangle$ to ω_0, the phonon energy at the end point of the phonon spectrum, is approximately 0.2 for both amorphous Bi and Ga, and this indicates an enormous decrease in $\langle\omega\rangle$ compared with the case of crystalline superconductors. For example, McMillan uses a value of 0.62 for $\langle\omega\rangle/\omega_0$ for crystalline Nb. Thirdly, the decrease in $\langle\omega\rangle$ does result in a large increase in λ over what is typically found for crystalline superconductors. For example, the largest λ found for a crystalline superconductor is 1.6 in the case of Hg, whereas we find a λ of 2.46 and 2.25 for amorphous Bi and Ga, respectively, which makes them superconductors with the largest electron-phonon coupling constants yet found.

Garland, Bennemann, and Mueller have derived the relation[10]

$$\ln\left(\frac{\langle\omega^2\rangle^{1/2}\omega_{0c}}{1.26T_c\langle\omega_c^2\rangle^{1/2}}\right) = \frac{1+\lambda}{A(1-0.5\mu^*)\lambda-\mu^*} \quad (5)$$

for disordered or amorphous superconductors, where λ, μ^*, ω_0, $\langle\omega^2\rangle$, and T_c have been defined previously, the subscript c denotes that the value of the quantity should be for the crystalline state, and A is a constant of order unity which depends on the functional form of $\alpha^2(\omega)F(\omega)$. Unfortunately, it is difficult to compare our results with the theory of Garland, Bennemann, and Mueller in the form of Eq. (5) because of the uncertainty in what to choose for A and $\langle\omega_c^2\rangle$. However, Garland has informed us that Eq. (5) can be written in a more explicit form where A and $\langle\omega_c^2\rangle$ are approximated in terms of measureable parameters. The resulting expression for T_c is

$$\ln\left(\frac{\langle\omega^2\rangle^{1/2}}{T_c}\right) = \frac{1+\lambda}{0.52\lambda(1+\langle\omega^2\rangle^{1/2}/\omega_0)(1-\langle\omega\rangle\mu^*/\omega_0)-\mu^*}. \quad (6)$$

If we use our values of μ^*, λ, $\langle\omega^2\rangle$, and $\langle\omega\rangle$, and if we neglect the slight tails in the phonon spectra and take ω_0 to be 12 and 25 meV for amorphous Bi and Ga, respectively, Eq. (6) predicts that T_c should be 5.1°K for amorphous Bi (~18% lower than the experimental value of 6.11°K) and 7.6°K for amorphous Ga (~11% lower than the experimental value of 8.56°K). The values of T_c predicted by Eq. (6) represent reasonable quantitative agreement of the theory of Garland, Bennemann, and Mueller with our experimental results.

McMillan[7] somewhat prior to Garland, Bennemann, and Mueller derived a similar relationship to Eq. (5) for the transition temperature of strong-coupling superconductors:

$$T_c = \frac{\Theta_D}{1.45}\exp\left[-\frac{1.04(1+\lambda)}{\lambda-\mu^*(1+0.62\lambda)}\right], \quad (7)$$

where Θ_D is the Debye temperature. McMillan derived Eq. (7) in the limit that $\lambda > 1$ and also used the phonon spectrum of Nb. As a result of this, he pointed out that Eq. (7) might be in error for the case of a very strongly coupled su-

perconductor ($\lambda > 1$) with a phonon spectrum wildly different from that of Nb. However, McMillan considered the implications of Eq. (7) for $\lambda > 1$. Using a slightly simplified form of Eq. (7) and arguing that $M\lambda\langle\omega^2\rangle$ should be constant for a given class of materials, where M is the ionic mass, he showed that there should be a maximum possible T_c, $T_c^{\max}$, for a given class of materials, given by

$$T_c^{\max} = (\tfrac{1}{2}\lambda\langle\omega^2\rangle)^{\frac{1}{2}} e^{-\frac{3}{2}}. \quad (8)$$

The λ dependence of T_c is given by

$$T_c/T_c^{\max} = (2/\lambda)^{\frac{1}{2}} e^{(\frac{1}{2}-1/\lambda)}, \quad (9)$$

which gives a broad maximum at $\lambda = 2$ and falls off sharply for $\lambda < 1$. Recently Strongin et al.[11] have reported that the enhanced superconductivity in layered metallic films supports the λ dependence of T_c given by Eq. (9) if they assume that the enhanced T_c's result from a "softening of the phonon spectrum" that decreases $\langle\omega^2\rangle$ and hence increases λ. They suggest that this "soft-phonon" effect might be used to achieve the high T_c's predicted by Eq. (8), e.g., 22 and 40°K for Nb and V_3Si, respectively, by making the superconductor in very thin film or disordered form.

Our results on amorphous Bi and Ga suggest otherwise. First, the phonon spectra in Figs. 1(b) and 2(b) certainly show evidence of "soft phonons." However, if we assume that Θ_D can be approximated by ω_0, which is a good approximation for crystalline superconductors such as Pb and Sn,[11] and if as before we take ω_0 to be 12 and 25 meV for amorphous Bi and Ga, respectively, Eq. (7) predicts that T_c should be 18.4 and 36.6°K for amorphous Bi and Ga, respectively. If we elimate the uncertainty in what to take for Θ_D, and instead use Eq. (8) and the values of λ and $\langle\omega^2\rangle$ derived from our phonon spectra to calculate $T_c^{\max}$, we obtain $T_c^{\max} = 11.6$ and 21.6°K for amorphous Bi and Ga, respectively. With our values of λ, Eq. (9) would predict that $T_c = T_c^{\max}$; however our experimental values of T_c are much lower than the predicted values of $T_c^{\max}$. We would suggest that if our phonon spectra are typical of the extreme softening of the phonon spectra needed to obtain $\lambda \approx 2$, then Eqs. (7), (8), and (9) are invalid in the limit $\lambda \approx 2$, either because of some approximation made in their derivation or because of some additional physical mechanism, which has been neglected in the derivation but becomes important when $\lambda > 1$; and hence suggestions of using the "softening of the phonon spectrum" to achieve T_c's much higher than the current limit near 20°K must be viewed with some caution.

We would like to thank Dr. W. L. McMillan for allowing us to use his inversion program, and Professor D. M. Ginsberg and Mr. W. Hubin for supplying us with their copy of the McMillan program and some of their tunneling data on Hg which were useful in checking out the performance of the program. We would like to thank Dr. J. W. Garland for detailed discussions of his calculations, and we would also like to acknowledge useful discussions with Dr. A. D. Singh.

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[5]H. Wühl, J. E. Jackson, and C. V. Briscoe, Phys. Rev. Letters 20, 1496 (1968).

[6]N. V. Zavaritskii, private communication.

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