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Far-infrared absorptivity of superconducting Pb-Bi alloys

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Absolute values of the far-infrared (FIR) absorption of Pb, $Pb_{0.9}Bi_{0.1}$, $Pb_{0.8}Bi_{0.2}$, and $Au_{0.9}Cu_{0.1}$ have been obtained at 4.2 K using a calorimetric technique. Measurements were made at discrete frequencies over the range 20–150 cm^{-1} (0.6–4.5 THz or 500–70 μm) using an optically pumped FIR laser as the source of radiation, and with a typical absolute error in the absorptivity of approximately 0.1%. The absorption in pure Pb and Pb-Bi alloys increases sharply at the superconducting energy gap and shows structure at frequencies that can be associated with peaks in the phonon density of states, and which is ascribed to the Holstein photon-phonon-electron process. However, it appears from both the magnitude and the enhanced structure of the absorption in the alloys that the process is enhanced in the presence of impurity scattering, suggesting that existing theories are incomplete.

I. INTRODUCTION

When an electromagnetic wave of sufficiently low frequency, in the infrared region and below, is incident on a metallic sample, the absorption of radiation is determined by the electron scattering processes within the conduction band.[1] In metallic alloys the dominant temperature-independent impurity scattering usually leads to an electron mean free path smaller than the penetration depth of the radiation in the metal, but in pure metals at low temperatures the situation can be reversed. This is the regime of the anomalous skin effect, where energy transfer from the electron to the lattice occurs mainly at the metal surface. There is, however, a quantum-mechanical volume absorption known as the Holstein process,[2] in which an electron absorbs an incident photon and emits a phonon. For incident radiation in the near infrared, phonons of all frequencies may be generated and the effective scattering time is frequency independent. At lower frequencies, in the far infrared, this quantum-mechanical process is still important but the radiation energy is sufficient to generate only part of the phonon spectrum. In this case the absorption is frequency dependent, proportional to a weighted integral over the phonon density of states up to a cutoff determined by the photon frequency.

The far-infrared (FIR) absorption of Pb at low temperatures has been the subject of a number of investigations. Early measurements were mostly concerned with determinations of the superconducting energy gap,[3] which lies in the FIR or submillimeter regions for most elemental superconductors. Joyce and Richards[4] were the first to observe a phonon contribution to the FIR absorption, in Pb. Their data revealed a rise in absorption at frequencies corresponding to peaks in the phonon density of states, an increase associated with the onset of the Holstein process. When the metal is in the superconducting state, this onset occurs at the frequencies of the phonon modes added to the energy-gap frequency, since only the difference between the photon and gap energy is available for phonon emission. Subsequently, Brandli and Sievers[5] provided absolute results of FIR absorption at low temperatures by measuring the surface resistance of Pb films. Other experimental investigations were able to probe only the ratio of absorption in the superconducting and normal states.

This paper presents measurements of low-temperature FIR absorptivity in superconducting Pb-Bi alloys. Lead-bismuth alloys have an fcc structure up to a Bi concentration of 20 at %,[6] and superconducting transition temperatures slightly greater than in pure Pb. Electron tunneling studies[7] of these alloys show that the spectral function $\alpha^2F(\omega)$ [the phonon density of states $F(\omega)$ weighted by the electron-phonon coupling parameter α^2] increases slowly with Bi concentration through the alloy series. The aim of this investigation is to probe the Holstein phonon-emission process in the FIR absorption of superconducting alloys that have a strong electron-phonon interaction.

The experimental apparatus used in the measurements provides absolute absorptivity results (percentage of radiation absorbed) at low temperatures, using a calorimetric technique to detect both the incident power and the power dissipated in the metallic films. Similar methods have previously been used at infrared frequencies,[8,9] but to our knowledge this is the first time that this procedure has been extended down to the FIR region. The initial part of the paper gives a description of this experimental technique and is followed by details of sample preparation, results and an analysis of the absorption data on Pb and Pb-Bi alloys.

II. EXPERIMENTAL

A. Apparatus

The optical source used in the experiment was a FIR molecular gas laser,[10] pumped by an acousto-optically stabilized CO_2 laser, and providing a large number of discrete laser frequencies in the range of 20–150 cm^{-1}.

The laser light enters the apparatus through a light pipe connected to an evacuated can placed in a liquid-helium cryostat. The radiation is focused onto the samples using a condenser cone that contains a cold crystalline-quartz window to remove room-temperature blackbody radiation. Samples are mounted on a rotating disk and can be moved in and out of the incident beam. With the metal sample rotated away from the beam, the FIR radiation shines through a clear aperture onto a black absorber, referred to as the black cone. A schematic diagram of the low-temperature apparatus is given in Fig. 1.

The black cone is a novel device, initially developed by Martin and Quinn,[11] designed to be a total absorber for electromagnetic radiation in the FIR region. A black absorbing surface cannot be used for this purpose because standard paints (like carbon black) reflect more than 50% of the incident radiation at submillimeter wavelengths. The most efficient black paint for this frequency region is 3M Nextel black,[12] which contains a mixture of silica spheres with a range of diameters from 5 to 100 μm. The optical properties of this paint are quite well known;[11] the reflectance at normal incidence varies from 10% at 100 cm^{-1} to 30% at 20 cm^{-1}. The black cone is made of a thin copper foil, covered on the inside with several layers of 3M black paint. Care must be taken not to have an excessive amount of paint at the end of the cone, to avoid retroreflectance. The temperature rise of the black cone is measured with a carbon resistor and a Eureka wire provides a heater with a resistance of 100 Ω. The support is a brass rod, which acts as a thermal link to the helium bath. A simple geometric sketch[13] can be used to show that the radiation suffers approximately six reflections inside the cone, and so it should have a reflectance of the order of 1%. Test measurements at room temperature confirmed that the amount of radiation reflected from the black cone was always less than 2% at the low-frequency end of the range.

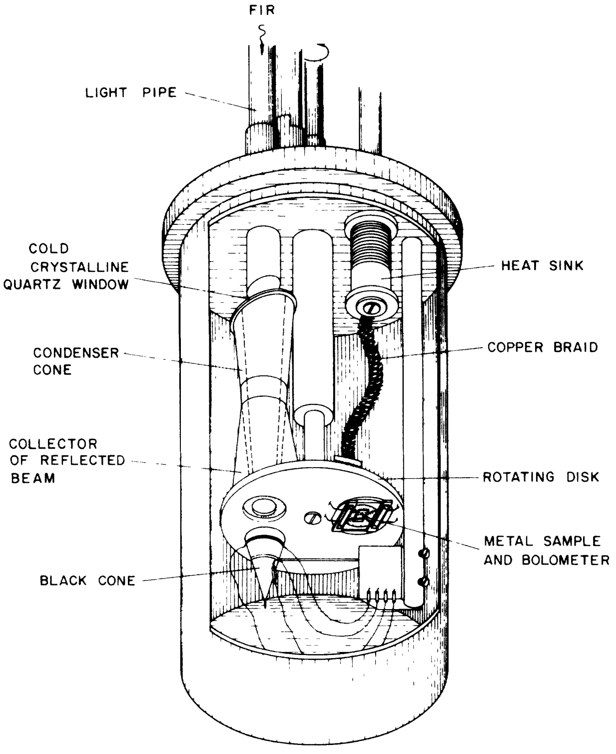

FIG. 1. Schematic diagram showing the low-temperature insert for absorptivity measurements in the FIR.

The substrate was attached with GE varnish to a silicon-on-sapphire bolometer,[14] which measures the FIR radiation absorbed in the sample. The bolometer is supported by two alumina rods and mounted on a copper frame attached to the rotating disk (see Fig. 1). The total heat capacity of the bolometer and metal sample is of the order of a few μJ K^{-1}. The supporting rods provide a thermal conductance greater than 10^{-4} W K^{-1}, which gives an external relaxation time of the order of 5 ms. This response time allows the measurement of the temperature rise of the sample at a chopping frequency of the incident radiation of approximately 20 Hz. The bolometer is capable of accurately measuring an incident power below 10^{-8} W, which corresponds to a temperature rise of only a few millikelvins.

In operation, radiation of the desired wavelength is allowed to fall on the sample, and the temperature rise measured with a phase-sensitive detector (PSD). The sample is then rotated away from the beam and the dc temperature rise of the black cone measured using a differential resistance bridge with a PSD operating at 1 kHz. With the laser blocked off, electrical power is applied to the heater of each detector in order to reproduce the temperature rise previously recorded with the radiation. The absorptivity of the sample is obtained by simply dividing the total power dissipated in the metal sample and in the black cone. This method of measuring does not require absolute values of the temperature rise or previous calibration of the apparatus. The output of the laser is continuously monitored with a Gollay detector to ensure that it remains constant during the sequential procedure.

Initial measurements revealed the existence of a stray absorption due to leakage of radiation through the gaps around the metal sample, a consequence of using an optical type of arrangement in the submillimeter region of the spectrum. The leak was considerably reduced by introducing a graphite washer in the rotating disk, but nevertheless a small part of the sample signal was still spurious. This residual stray absorption was measured independently using a dummy sample thermally isolated from the bolometer, giving an additional absorption of less than 0.1% at frequencies above 50 cm^{-1}, increasing to 0.3% at 30 cm^{-1}. The absorptivity of the metal under investigation is corrected by subtracting the spurious contribution from the total measured absorption, a procedure that gives zero absorption below the energy gap. The system is therefore capable of measuring absorptivities with an absolute error of about 0.1%. More details of the experimental apparatus are given elsewhere.[15]

B. Samples

The measurements were carried out on metal films of superconducting Pb and Pb-Bi alloys prepared by vacu-

TABLE I. Measured and calculated parameters for Pb, Pb-Bi and Au-Cu alloys. The first two columns give the resistivity measured at 300 and 4.2 K. The parameters $\omega\tau_0$ and l_0/δ_0 are calculated using the resistivity $\rho(\omega)$ determined by impurity scattering, while $\omega\tau$ and l/δ are calculated using $\rho(\omega)$, which includes the contribution from the phonon-emission process.

	ρ_{300} (10^{-8} Ω m)	ρ_0 (10^{-8} Ω m)	$\omega\tau_0$	l_0/δ_0	$\rho(\omega)$ at 100cm^{-1} (10^{-8} Ω m)	$\omega\tau$	l/δ
Pb	21	0.075	21	180	2.2	0.7	1.1
$Pb_{0.9}Bi_{0.1}$	26	6.5	0.25	0.22	8.4	0.2	0.15
$Pb_{0.8}Bi_{0.2}$	39	16	0.1	0.06	18	0.1	0.05
$Au_{0.9}Cu_{0.1}$	23	21	0.05	0.03	22	0.05	0.03

um thermal evaporation. These films are quite easy to make, with the desired bulk material evaporated from a single heating source. The evaporation was carried out at pressures just below 10^{-6} torr and with a growing rate of 20 nm s^{-1}. The substrates were thin disks of optically polished crystalline quartz (diameter 7 mm, thickness 0.16 mm), and the film thickness varied around 800 nm. The samples were placed in the apparatus soon after evaporation to reduce surface contamination.

The resistivity of the metal films was measured at 300 and 4.2 K, the latter by quenching the superconductivity in a magnetic field, and the results are presented in Table I. The superconducting transition temperature T_c was also determined using a calibrated Ge thermometer, and increased from 7.15±0.05 K in pure Pb to 7.97±0.05 K in $Pb_{0.8}Bi_{0.2}$. These measurements were carried out on long strips of the metal, evaporated simultaneously with the films for optical studies. A sample of $Pb_{0.65}Bi_{0.35}$, known to have a mixed phase structure,[6] was used for measurements of stray radiation at low frequencies, making use of its greater superconducting energy gap.

The agreement between these values of T_c and previously published data[7] indicated that the alloy films had the desired concentration. This was confirmed using x-ray analysis in an electron microscope. The room-temperature resistivity agrees with tabulated results[16] within 10%, a typical error resulting from the uncertainty in measuring the film thickness. The large value of the resistance ratio r ($r \neq \rho_{300}/\rho_0$) in Pb is an indication of the good quality of the sample. The low values of r in the alloy films are due to impurity scattering. The width of the superconducting transition temperature in all the samples was less than 0.1 K.

Measurements were also made with a nonsuperconducting metal film of Au Cu alloy. This sample was also evaporated from a single heating source, with Au and Cu in the ratio of 0.9:0.1 by weight. The final concentration of the alloy film may, however, have a slightly higher amount of Cu, because of its lower vapor pressure and boiling point. This implies that the film thickness, and consequently the resistivity, are less accurately known. The measured resistivities of this alloy at 300 and 4.2 K are also shown in Table I.

III. RESULTS

FIR absorptivities of Pb, $Pb_{0.9}Bi_{0.1}$ and $Pb_{0.8}Bi_{0.2}$ at 4.2 K are shown in Fig. 2. Results on pure Pb are in satisfactory agreement with surface resistance measurements at 1.2 K by Brandli and Sievers,[5] although our results are up to 20% higher at high frequencies. The samples differ in that ours have a larger resistance ratio, but those of Brandli and Sievers are annealed so no direct comparison is possible. The difference is, however, consistent with that observed at room temperature between annealed and nonannealed samples. Attempts to anneal the Pb samples were unsuccessful: annealing in an argon atmosphere produced samples with a transition temperature of 6 K, possibly as a result of the diffusion of impurities from the substrate. Both sets of data, however, show a superconducting energy gap 2Δ at approximately 21 cm^{-1}, leading to a ratio $2\Delta/k_BT_c$ of 4.2±0.2, and structure arising from the Holstein phonon-emission process at about 60 and 85 cm^{-1}. These frequencies correspond to peaks in the phonon density of states in Pb, shifted upwards by the superconducting energy gap. The values obtained from tunnelling measurements[7] are 55 and 89 cm^{-1} respectively.

The FIR absorptivity of Pb-Bi alloy samples is greater

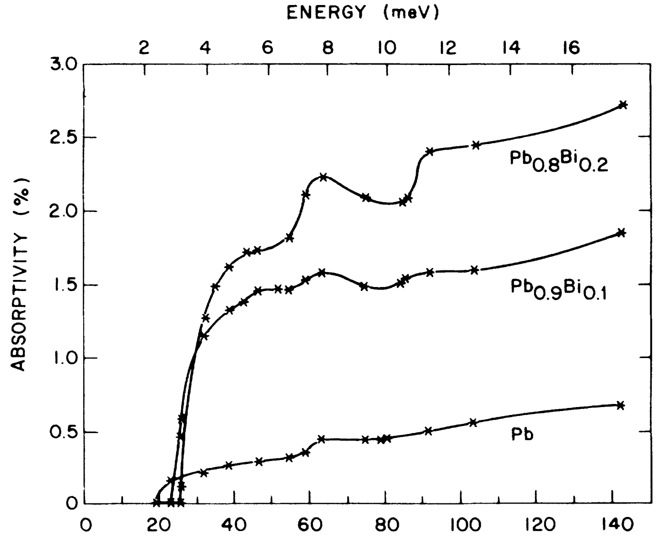

FIG. 2. Low-temperature FIR absorptivity of superconducting Pb and Pb-Bi alloys, showing the energy gap at low frequencies and the steps of the Holstein process. The lines are hand drawn between the experimental points.

than that of pure Pb. The sharp onset of absorption at low frequencies defines a superconducting energy gap of 24 ± 1 cm^{-1} in $Pb_{0.9}Bi_{0.1}$ and 26 ± 1 cm^{-1} in $Pb_{0.8}Bi_{0.2}$, increasing with increasing Bi concentration as observed in tunnelling measurements.[7] The ratios $2\Delta/k_BT_c$ are 4.5 and 4.7 ± 0.2, respectively. By far the most interesting feature of the alloy data is the enhancement of the phonon structure seen below 100 cm^{-1} relative to that seen in pure Pb. The absorption shows not only a strong rise at frequencies corresponding to peaks in the phonon spectrum, but also a decrease at slightly higher frequencies. The data on $Pb_{0.8}Bi_{0.2}$ is shown separately in Fig. 3 in order to emphasize the agreement between the rise in the absorptivity and the frequencies of the transverse and longitudinal phonon peaks obtained from tunneling measurements,[7] increased by the superconducting gap frequency. The Drude theory curve[21] was calculated from the dc resistivity at 4.2 K, ρ_0, and therefore includes only the contribution from impurity scattering.

In order to check the results on Pb and Pb-Bi, measurements were carried out with a nonsuperconducting alloy sample of $Au_{0.9}Cu_{0.1}$ and the results are shown in Fig. 4. The data show no anomalous features, which confirms that the structure seen in the spectra of Pb-Bi is not experimental in origin. The Drude theory curve[21] in Fig. 4 was also obtained from the low-temperature dc resistivity, and predicts values approximately 20% lower than the experimental data. This cannot be due to the Holstein phonon process, which has a negligible contribution in this alloy. A similar discrepancy has previously been observed in room temperature FIR measurements on nonannealed samples,[5] and has also been reported in connection with near infrared measurements on noble metals,[9] which always show a higher absorption in metal films than in bulk samples.

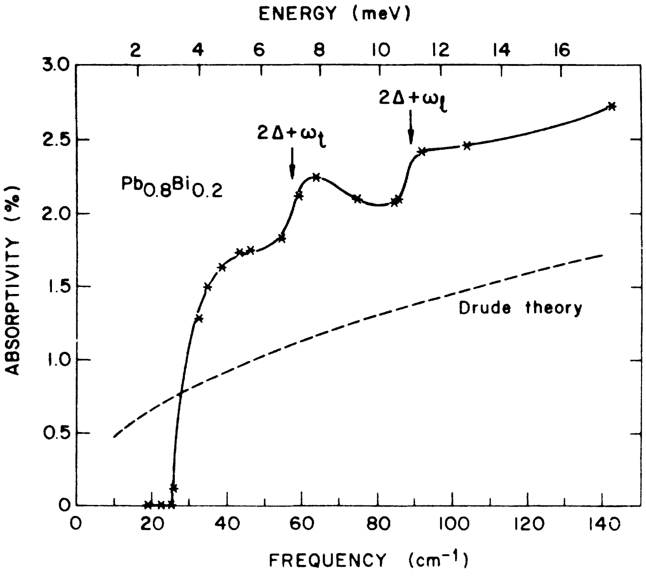

FIG. 3. Low-temperature FIR absorptivity of $Pb_{0.8}Bi_{0.2}$. The arrows indicate the position of the transverse and longitudinal phonon peaks,[7] shifted upwards by the energy gap. The theoretical Drude curve is calculated using the dc resistivity at 4.2 K, ρ_0, which gives only the contribution from impurity scattering.

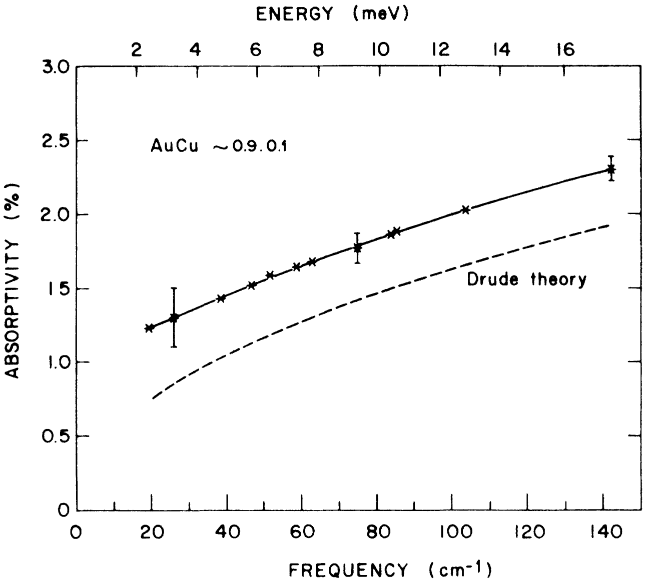

FIG. 4. The low-temperature FIR absorptivity of $Au_{0.9}Cu_{0.1}$ alloy. The theoretical Drude curve is calculated using the dc resistivity at 4.2 K.

In view of the consistently smaller calculated values of the absorption it is important to examine the possibility of a systematic error in the measurements. Two possible sources of error suggest themselves: The presence of the sample changes the effective intensity of the incident radiation and leads to a constant fractional error in A, or an incorrect subtraction of other sources of absorption arising from the thermometer or heater gives a direct error in A. If the first of these were important, the measured absorption should go to zero for frequencies below the gap frequency, which is not the case, and the measured absorption should go to zero when the sample is thermally distanced from the bolometer, again in disagreement with experiment. It is unlikely that the second possibility leads to serious errors in the case of $Pb_{0.9}Bi_{0.1}$ and $Pb_{0.8}Bi_{0.2}$ because to judge from the data in Pb the absolute error is unlikely to be more than 0.1%. Furthermore, the subtraction of a larger background would give a negative absorption below the gap frequency. It appears, therefore, that the enhanced phonon structure seen in the Pb alloy films is a real effect.

IV. DISCUSSION

Any discussion of the FIR absorption in metals requires an initial evaluation of two parameters, $\omega\tau$, where ω is the angular frequency of the radiation and τ the electron relaxation (scattering) time, and δ/l, where l is the electron mean free path and δ the classical skin depth. In the regime $\omega\tau<1$ and $\delta/l>1$, the motion of electrons is determined by collisions, and neither the spatial nor the temporal variations of the electric field needs to be considered. For $\omega\tau>1$, however, the inertia of the electrons is important while for $\delta/l < 1$ the electric field cannot be assumed uniform over an electron mean free path. (Of course, for a given metal both parameters are linked through the relaxation time.)

Values of these two parameters are given in Table I for a frequency of 100 cm^{-1}, well above the superconducting gap energy in Pb and Pb-Bi alloys, and also above the maximum phonon frequency in these compounds. The skin depth is calculated as

$$\delta_0=(\omega\mu_0/2\rho_0)^{-1/2} \tag{1}$$

where ρ_0 is the low-temperature limiting dc resistivity, given in Table I. The mean free path l_0 was calculated using the value of ρl given by Chambers,[17] close to that expected for a free electron metal. A Fermi velocity of 1.24×10^6 $\mathrm{m\,s^{-1}}$, approximately two thirds of the free electron value, was used[18] to give τ_0. It appears from the values of $\omega\tau_0$ and l_0/δ_0 that pure Pb is firmly in the anomalous regime at 100 cm^{-1}, as has been assumed previously.[18,19] We believe, however, that this analysis is incomplete because of the neglect of the phonon emission process, first suggested by Holstein.[2] It is the total scattering time of electrons that is responsible for determining the extent to which spatial and temporal variations of the electric field are important, and so phonon emission processes must be included in the evaluation of the skin depth by using an effective resistivity.

An appropriate expression for the resistivity $\rho(\omega)$ can be derived from the high-temperature "ideal" phonon resistivity, $\rho_{\mathrm{ph}}(T)=\rho(T)-\rho_0$, by making use of an analysis given by Allen[19] to obtain

$$\rho(\omega)=\rho_0+\rho_{\mathrm{ph}}(T)\hbar\langle\omega_{\mathrm{ph}}\rangle/2k_BT \tag{2}$$

where $\langle\omega_{\mathrm{ph}}\rangle$ is an average phonon frequency. This expression is valid above the maximum phonon frequency. In the Debye approximation $\hbar\langle\omega_{\mathrm{ph}}\rangle=\frac{4}{5}k_B\vartheta$, where ϑ is the Debye temperature, giving a value of 9.5 meV. However, this parameter can be more realistically estimated from tunneling data,[7] which yield values of 5.2, 4.8, and 4.4 meV for $\hbar\langle\omega_{\mathrm{ph}}\rangle$ in Pb, $\mathrm{Pb_{0.9}Bi_{0.1}}$ and $\mathrm{Pb_{0.8}Bi_{0.2}}$ respectively. Calculated values of $\rho(\omega)$ and the corresponding values of $\omega\tau$ and l/δ are also given in Table I, where the results for Pb-Bi alloys assume the same value for $\rho_{\mathrm{ph}}(T)$ as used in pure Pb. Comparison of the parameters $\omega\tau$ and l/δ with the results given by Pippard[20] shows that the classical Drude theory[21] should be a reasonable approximation even for pure Pb, as well as for Pb-Bi and Au-Cu alloys. In Au-Cu there is almost no difference between ρ_0 and $\rho(\omega)$ because the phonon contribution to the high-temperature resistivity is small.

TABLE II. Calculated and measured values of the absorptivity of Pb, Pb-Bi, and Au-Cu alloys at 100 cm^{-1}.

Sample	$A_{\mathrm{calc}}/\%$	$A_{\mathrm{exp+}}/\%$
Pb	0.39	0.55
$\mathrm{Pb_{0.9}Bi_{0.1}}$	0.97	1.60
$\mathrm{Pb_{0.8}Bi_{0.2}}$	1.47	2.44
$\mathrm{Au_{0.9}Cu_{0.1}}$	1.67	2.00

Calculated values of the absorption A_{calc}, at 100 cm^{-1} were obtained for all samples using the Drude theory with the resistivity $\rho(\omega)$. This is compared to experimental values in Table II. One might expect by reference to Pippard's results that the effect of the surface, ignored in the Drude theory, is important in Pb, increasing the calculated value to 0.5%. Note that in this limit it is not correct to simply add a surface contribution to A. The agreement shown in Table II is then good for pure Pb and Au-Cu, but in general the calculated values while correctly predicting trends consistently underestimate the measured absorption in the Pb alloys.

Application of the sum rule proposed by Brandli[22] implies that the scattering from both impurities and phonons must be stronger in the superconducting state. Allen[19] gives an explicit expression which shows that the impurity scattering time is shorter by a factor that decreases from 1.5 at the gap frequency to 1.2 at 100 cm^{-1} in the alloy samples. These factors have not been included in the tables, but are such as to improve agreement between calculated and experimental values.

It appears, however, that there is a real discrepancy between experiment and theory in Pb-Bi alloy samples at 100 cm^{-1}. In the regime relevant to these alloys absorption processes do not add, so that it is inappropriate simply to ascribe the difference to an additional process. In order to explain the measurements the phonon process would need to be larger than estimated from $\rho_{\mathrm{ph}}(T)$ by a factor of 7 in $\mathrm{Pb_{0.9}Bi_{0.1}}$ and 14 in $\mathrm{Pb_{0.8}Bi_{0.2}}$. These factors imply a major breakdown of Matthiessen's rule, which treats impurity and phonon scattering as separate processes. Of course, in the limiting case of an amorphous solid we know that the rule is invalid because direct phonon-photon processes are possible in the absence of wave-vector conservation. In these alloys, however, k_Fl is greater than 50, so that the Fermi wavevector k_F is a well-defined quantity. Nevertheless, it is clear that impurity scattering plays a role in the Holstein process. As pointed out by Allen,[19] it is impossible to separate impurity and phonon interactions in a strongly coupled superconductor.

V. SUMMARY AND CONCLUSIONS

This paper presents absolute FIR absorptivity measurements in Au-Cu, superconducting Pb and Pb-Bi alloys. The results on Pb are in satisfactory agreement with previously published data,[5] which confirms that direct absorption measurements with the calorimetric technique can be made in the submilleter region of the spectrum. Absorptivity spectra of the alloy films show a sharp rise above the superconducting energy gap, a large background due to impurity scattering and peaks related to structure in the phonon density of states. The frequencies of the transverse and longitudinal phonon modes added to the energy gap frequency coincide with maxima in the derivative of the absorptivity curve.

The most surprising feature of the results is the enhancement of the strength of the Holstein process in the alloy samples. Not only is the magnitude significantly larger than expected on the basis of previous calculations, but the phonon structure is much more clearly defined, again unexpected on the basis of calculations which express the phonon emission process in terms of a weighted integral over the phonon density of states. It is difficult to see how these theories can predict a decrease in the absolute absorptivity. Moreover, the size of the structure appears to increase with decreasing electron mean free path, suggesting that a more complete theory is needed in which impurity and phonon scattering are treated together. Measurements on $Au_{0.9}Cu_{0.1}$ confirm that the structure seen in the superconducting alloys is not the result of a systematic error in the measurement.

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