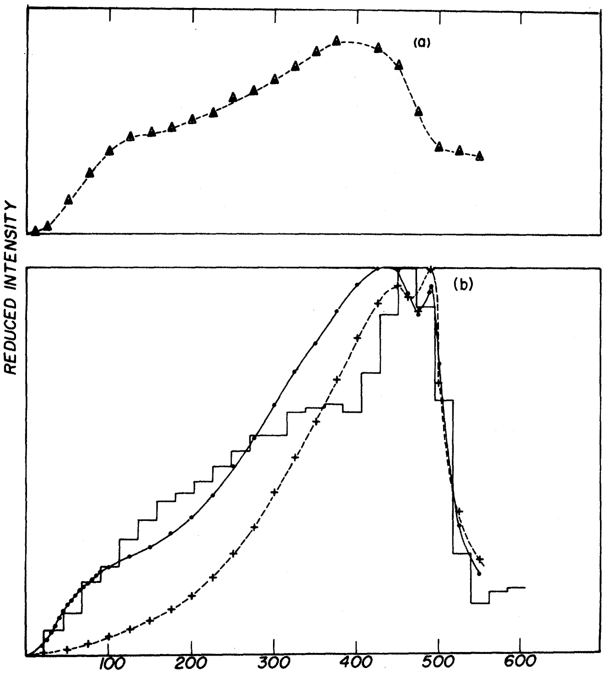

FIG. 1. Fused silica. (a) VH polarized spectrum reduced by $[1+n(\omega)]/\omega$ (b) Dashed line, VV polarized spectrum reduced as in (a); line with dots, VV polarized spectrum reduced by $[1+n(\omega)]$. The histogram is the density of states from the calculations of Bell, Bird, and Dean (Ref. 6).

but this is misleading. In fact, a large number of modes contribute at low frequencies but are most easily detected in the VH spectrum.

The fully reduced VV spectral data by themselves do not agree well with Dean's calculation. We think this is due to the different coupling constants C_b.

The low-frequency part of the spectrum contains the modes dominating the thermodynamic properties. We have used our data to obtain a shape for the low-frequency density of states which gives a calculated heat capacity temperature dependence in agreement[8] with the measured anomaly.[1]

We are pleased to acknowledge the stimulation and encouragement given to us during this work by T. A. Litovitz and P. B. Macedo.

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*Research sponsored by the Office of Naval Research under Grant No. N00014-68-A-0506-0002.

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FREQUENCY DEPENDENCE OF THE CYCLOTRON MASS AND OF THE RELAXATION TIME IN LEAD AND MERCURY

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(Received 20 April 1970)

We report a series of Azbel'-Kaner cyclotron resonance experiments in lead and mercury at wavelengths varying from 9 to 1 mm. We observe that in both metals the electron-phonon relaxation time is frequency dependent ($\tau \propto \omega^{-2}$ in lead), and that the effective mass increases slightly for the highest frequency in mercury ($3 \mp 1\,\%$ at $\lambda = 1$ mm).

The electron-phonon interaction theory predicts a change of the electron effective mass and relaxation time when the electron is excited far from the Fermi energy. In a cyclotron resonance experiment this excitation above the Fermi level can be obtained either by an increase of frequency[1] or by an increase of temperature.[2,3] The temperature effect has already been observed in zinc[4] and lead.[5] The present work is the first experimental evidence of the frequency dependence of the effective mass m^* and of the relaxation time τ in metals.

The theoretical predictions of Scher and Holstein[1] are the following: When the microwave frequency becomes of the same order of magnitude as the Debye frequency, the effective mass of the electron should increase slightly and the relaxation time should decrease as ω^{-3}. We have chosen to work with the lowest Debye temperature metals available in a pure state, lead and mercury, whose first phonon peaks correspond, respectively, to $\lambda_p(\mathrm{Pb}) \simeq 0.3$ mm and $\lambda_p(\mathrm{Hg}) \simeq 0.7$ mm in wavelengths.[6]

Experiments.—Our microwave sources are carcinotrons[7] whose wavelengths are centered at $\lambda = 9$, 4, 2, and 1 mm with a maximum output power of 40 W, 500 mW, 2 W, and 1 W, respectively.

The problem was to perform a series of cyclotron resonance experiments at different frequencies while the other parameters (especially the sample orientation) remained fixed. We used an original spectrometer[8] based on a Perot-Fabry cavity. The sample is horizontal and its surface is a plane mirror; opposed to it, a copper spherical mirror has a coupling hole for the microwave input. The spherical mirror can be translated along a vertical axis to tune the cavity and to measure the wavelength of the incident microwave. Each time we change the frequency band by using another carcinotron, we have to change the spherical mirror designed to work in a narrow frequency region. This is possible while the sample remains in its place in liquid helium. We used a low-Q cavity ($Q \simeq 1000$) because of the absence of any feedback to lock the microwave frequency to the cavity resonance.

The classical dc magnet (0-27 kG) can be rotated in a horizontal plane, in good parallelism with the sample surface, in order to choose a convenient crystallographic direction. A classical field modulation technique allows the plotting of the derivative of the surface impedance dR/dH versus the magnetic field, which is linearly recorded by a rotating coil gaussmeter with 0.2% total accuracy. We use a thermal detection: A thin carbon bolometer is glued on the sample surface. Although the whole cavity is immersed in superfluid helium at 1.5°K, the Kapitza resistance between the sample and the helium bath allows us to measure the temperature variations related to the resistive part of the surface impedance.

Sample preparation.—Lead single crystals are grown in a quartz and stainless steel mold.[9] The orientation of the crystal is determined by a seed grown in a capillary tube and placed in contact with molten lead in the mold. The dimensions of the sample are diameter 19 mm and thickness 2 mm. The quality of the surface depends on the carbon layer deposed on the optically polished quartz plate which is in contact with the plane face of the disk; to the eye it appears to be good. The lead purity[10] is 99.9999% and the residual resistivity ratio (RRR) is $R(300°\mathrm{K})/R(1.5°\mathrm{K}) \simeq 2 \times 10^5$. This RRR has been deduced from the low-frequency relaxation time $\tau = 4.5 \times 10^{-10}$ sec at 1.5°K.

Table I. Experimental results: measured cyclotron masses and relaxation times as functions of frequency for mercury and lead.

Microwave wavelength λ [a] (mm)	Frequency[a] (GHz)	m^*/m_0 [b]	$\omega\tau$ [c]	τ [c] (10^{-11} sec)
		Pb		
8.95	33.40	0.544	95	45.3
4.10	73.05	0.542	183	40
2.18	135.5	0.541	230	27
0.957	310	0.542	212	10.9
		Hg		
4.10	73.05	0.760	12	2.6
2.187	135.5	0.755	18	2.1
1.085	277	0.783	16	0.92

[a] Accuracy ∓0.3%.
[b] Accuracy ∓0.7%.
[c] Accuracy ∓8% for Pb, ∓20% for Hg.

Mercury single crystals (diameter, 12 mm; thickness, 1 mm) are grown in situ in a Kel F mold. The upper surface is limited by a glass plate of thickness 0.2 mm which gives a plane surface but might create some dislocations. The crystals are grown and cooled down to liquid nitrogen in a primary vacuum at a rate of 15°/h. A temperature gradient is imposed between the tail and the surface of the sample by heating with a lamp. The purity of the mercury[11] is 99.99999%. The low-frequency extrapolated relaxation time is 3×10^{-11} sec at 1.5°K.

Experimental results (see Table I).—Lead: We have chosen a crystallographic orientation such that two masses only appear. The one giving the largest resonance signals corresponds to a ζ orbit[12] of the third zone, $m^* = 0.542 m_0$ (m_0 is the free electron mass); the second one corresponds to a hole orbit in the second zone, ψ type, $m^* = 1.155 m_0$. Within the experimental accuracy these two measured effective masses are constant in the wavelength band 9 mm $\geqslant \lambda \geqslant 0.95$ mm as is theoretically predicted for $\lambda > 3\lambda_p$. We have measured the relaxation time only for the ζ orbit. In the case of lead, because of the high $\omega_0\tau$ value and because of the small number of resonant electrons, one observes Chambers's resonance line shapes[13] (see Fig. 1). So we measure the relaxation time with a good relative accuracy

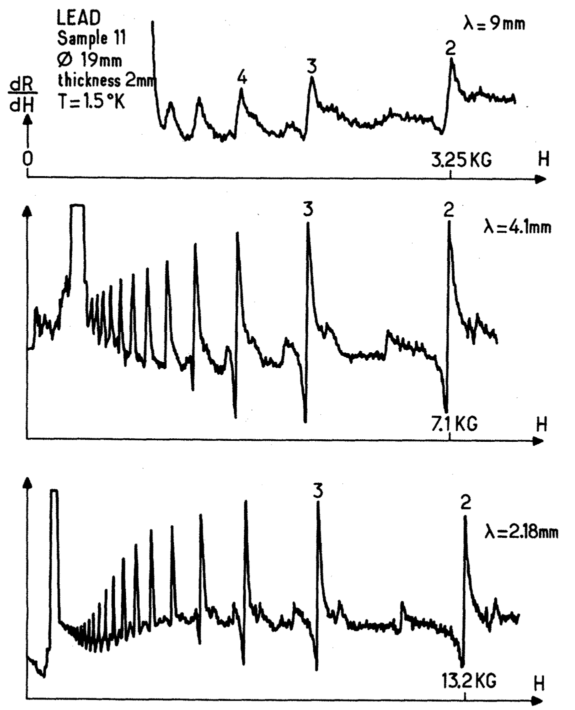

FIG. 1. Azbel'-Kaner cyclotron resonance in lead. The traces show a Chambers's line shape in the case of a minimum mass (Ref. 13). One observes that $\omega\tau$ is not proportional to the frequency, in the high-frequency region. Near 800 G we observe a large signal as a result of the superconducting transition.

using Chambers's formula: $\omega\tau = 1.55H/\Delta H$, where ΔH, the linewidth of the resonance, is the field difference between the maximum and the minimum of dR/dH. The measured relaxation time τ depends on frequency by the following law:

$$1/\tau = 1/\tau_{\text{imp}} + a(\omega/\omega_p)^\alpha,$$

where $\tau_{\text{imp}} = (4.5 \mp 0.4)\times 10^{-10}$ sec, $a = (8.3 \mp 0.3)\times 10^{10}$ sec^{-1}, $\omega_p = 2\pi c/\lambda_p = 6.71\times 10^{12}$ sec^{-1}, and $\alpha = 1.9 \mp 0.3$. The first term corresponds to the impurity-limited relaxation time, the second term to electron-phonon interaction (EPI). The order of magnitude of the electron-phonon relaxation time can be compared with numerical predictions of Scher and Holstein for cesium. They give $\tau_{\text{EPI}} = 1.4\times 10^{-11}$ sec for $\omega = 0.4\omega_{\text{D}}$, where ω_{D} is the Debye frequency. Nevertheless the phonon-limited relaxation time decreases as ω^{-2}, slower than the theoretically predicted law ω^{-3}. The frequency dependence of m^* and τ can be compared with their experimental[5] dependence in temperature T: m^* increases as T^2 (in good agreement with the theory[2,3]), and τ decreases classically as T^{-3} (instead of $T^{-4.4}$ as predicted by Grimvall[2]).

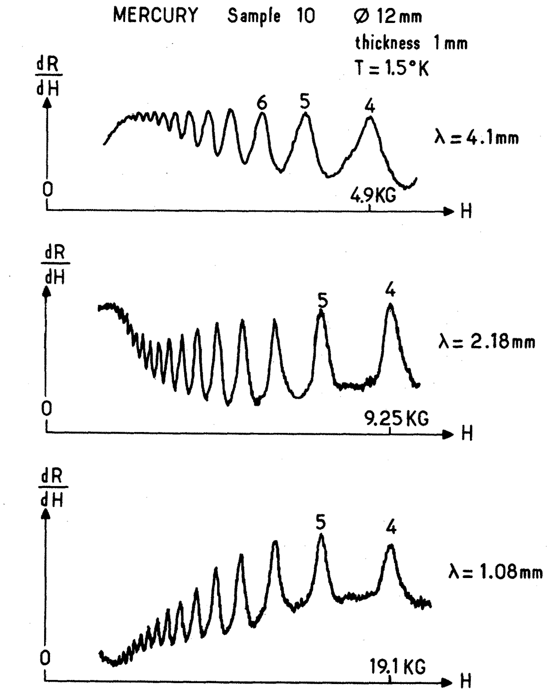

FIG. 2. Azbel'-Kaner cyclotron resonance in mercury. For the high-order harmonics, the line shape is the Azbel'-Kaner type. As in lead, $\omega\tau$ is not proportional to the frequency.

Mercury: We have chosen a crystallographic orientation such that two main resonance lines due to the lenses of the second zone[14] merge into one unique mass $m^* = 0.75m_0$. A smaller signal corresponds to a mass of $0.66m_0$ (see Fig. 2). The masses are calculated from the slope of a least-square line fitted to a plot of H_n^{-1} versus n, where H_n is the field at which the nth maximum occurs.[15] Within the experimental accuracy the effective mass is constant for $\lambda = 4$ mm and $\lambda = 2$ mm, but it increases for $\lambda = 1$ mm by $(3 \pm 1)\%$ (the 1% accuracy is the addition of a 0.5% uncertainty on the wavelength). This result is in good agreement with the theoretically predicted increase for $\lambda = 1.4\lambda_p$.

In the case of mercury we observe an Azbel'-Kaner line shape due to the low value of $\omega_c\tau$ and the large number of resonant electrons. We thus have measured $\omega\tau$ by the amplitude method,[16] valid for low $\omega_c\tau$ values ($\omega_c\tau < 2\pi$),

$$A_n \propto n^2 \exp(-2\pi n/\omega\tau),$$

where A_n is the amplitude of the resonance order n.

The same law as for lead can be verified for mercury:

$$1/\tau = 1/\tau_{\text{imp}} + a(\omega/\omega_p)^\beta,$$

where $\beta = 2.7 \mp 1$, $\omega_p = 2.73 \times 10^{12}$ sec^{-1}, and, if we take $\beta = 2$, $a = (1.8 \mp 0.4) \times 10^{11}$ sec^{-1}, $\tau_{\rm imp} = (3 \mp 0.5) \times 10^{-11}$ sec.

Let us point out that our experiment has been tested with copper samples[17] from 4- to 0.6-mm wavelength. We have observed there an effective mass and a relaxation time independent of frequency, as would be expected from the high Debye temperature of copper.

Conclusion.—Our experiments on mercury give evidence of the change of the electron effective mass in the vicinity of the Debye frequency. The related decrease of the relaxation time in this region has also been put in evidence in lead and mercury. The fact that we observe an electron-phonon–limited relaxation time proportional to the inverse of the square of the frequency does not agree with the previous theories.

It is a great pleasure to express appreciation to Professor A. Libchaber, Professor P. Nozieres, and Professor Y. Sharvin for helpful discussions, to Mr. J. Brochard for his exceptional skill in mechanical design, and to Mr. H. Thome for his technical assistance.

Note added in proof.—Experiments on cyclotron linewidth dependence in frequency and temperature have been performed on bismuth by V. S. Edel'mann and J. M. Tcheremicin, Pis'ma Zh. Eksp. Teor. Fiz. 11, 373 (1970). The observed relaxation time τ varies as $\tau^{-1} = \tau_0^{-1} + \tau^{-1}(F, T)$, where $\tau^{-1}(F) \propto F^{2.5}$ and $\tau^{-1}(T) \propto T^2$. These variations are attributed mainly to electron-electron interaction.

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RAMAN SCATTERING IN RESONANCE WITH THE EXCITON TRANSITION IN PURE POLAR CRYSTALS*

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A study of the Raman scattering near resonance with the exciton transition in pure polar crystals is presented. The following conclusions are obtained, independently of the crystal symmetry: (I) The resonant Raman spectra should show multiphonon structures at energy multiples of the first-order peak. The repetition of the peaks depends on the strength of the exciton-phonon coupling. (II) For the case of large-radius excitons, these spectra should show the same peaks for any polarization of the light.

In pure crystals, Raman scattering spectra far from resonance with an electronic transition have been always interpreted by following the usual selection rules.[1] Here we show that for the Raman scattering in resonance with the exciton transition in a pure polar crystal, the usual selection rules are no longer applicable. Rather, the following conclusions are reached: (I) Resonant Raman spectra should show multiphonon structures at energy multiples of the first-order peak. The repetition of the