the unperturbed host metal and also about the matrix elements of the perturbation. In the "strongly localized" approximation there is only one matrix element V. which can be conveniently treated as a parameter, and the band structure of the host metal enters only through the density of states. For the "moderately localized" case, Mann found it useful to use the tight-binding approximation to describe the band structure. However, this is unnecessarily restrictive. The Green's function method offers the possibility of performing calculations for energy bands of arbitrary form. Unfortunately, because of difficulties connected with the calculation of certain principal value integrals, these have not yet been performed.

Finally it is worth mentioning that the Green's function approach described here can be used in studying the phenomenon of localized magnetic moments associated with iron atoms dissolved in various 4delements and alloys.¹⁸⁻²⁰ For example, Wolff's "selfconsistent equations" for the existence of a localized moment [Eqs. (18) and (19) of Ref. 19] follow at once from (18), introducing a simple spin dependence into the matrix element V. As Wolff does not consider the case in which a bound state separates from the band. the second term of (18) does not appear in his equations.

This study was stimulated by a series of lectures on the lattice impurity problem by Professor Waller, to whom we are grateful for many interesting discussions.

¹⁸ A. M. Clogston, B. T. Matthias, M. Peter, H. J. Williams,
 E. Corenzwit, and R. C. Sherwood, Phys. Rev. **125**, 541 (1962).
 ¹⁹ P. W. Anderson, Phys. Rev. **124**, 41 (1961).

²⁰ P. A. Wolff, Phys. Rev. 124, 1030 (1961).

PHYSICAL REVIEW

VOLUME 136, NUMBER 4A

16 NOVEMBER 1964

Ultrasonic Investigation of Open Orbits in Cadmium and Zinc*

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An experimental investigation of the frequency and temperature variation of ultrasonic resonance absorption by open-orbit electrons moving parallel to [0001] in Cd and Zn is presented. The observations indicate conclusively that the Fermi surfaces of Cd and Zn are open parallel to [0001]. The Brillouin zone dimensions along [0001] calculated from the experimental data are $1.20\pm0.005\times10^{-19}$ g cm/sec for Cd and 1.36 ± 0.01 $\times 10^{-19}$ g cm/sec for Zn. These values agree very well with x-ray data and provide experimental evidence against the possibility of there being an effective charge carrier e^* different from the electronic charge e. The frequency dependence of the resonance is found to agree quite well with theory, and no evidence for magnetic breakdown is seen up to 2000 G. The width of the open-orbit resonance is directly related to the electron mean free path l, thus allowing a determination of l for the open-orbit electrons from sample to sample or as the temperature varies in a particular sample.

I. INTRODUCTION

HE effects of open-orbit electrons on the various transport properties of metals are well recognized.¹ In a preliminary communication, a resonant absorption of ultrasonic waves by conduction electrons moving along open orbits in cadmium was reported.² The present study is concerned with a detailed analysis of the absorption of ultrasonic waves by open-orbit electrons in cadmium and zinc, the phenomena having been investigated experimentally with compressional and shear waves as a function of temperature from 1.0 to 4.2°K at frequencies from 10 to 110 Mc/sec.

The possibility of resonant absorption of ultrasound by open-orbit electrons was first discussed by Galkin, Kaner, and Korolyuk³ who showed that the open-orbit electrons would absorb energy resonantly from the sound field when the period of the open orbit is a multiple of the sound wavelength. Initial observations on a tin single crystal allowed the pertinent Brillouin zone dimension corresponding to the open orbit electrons to be selected.

The Fermi surfaces for cadmium and zinc proposed by Harrison⁴ and corrected by Cohen and Falicov⁵ to include spin-orbit coupling effects are connected in the

^{*} This work was supported by the General Dynamics Corporation, the National Science Foundation, and the U.S. Office of Naval Research.

¹ The Fermi Surface, edited by W. A. Harrison and M. B. Webb

⁽John Wiley & Sons, Inc., New York, 1960). ² J. D. Gavenda and B. C. Deaton, Phys. Rev. Letters 8, 208 (1962).

⁸ A. A. Galkin, E. A. Kaner, and A. P. Korolyuk, Dokl. Akad. Nauk SSSR 134, 74 (1960) [English transl.: Soviet Phys.— Doklady 5, 1002 (1961)]; Zh. Eksperim. i Teor. Fiz. 39, 1517 (1960) [English transl.: Soviet Phys.—JETP 12, 1055 (1961)]. ⁴ W. A. Harrison, Phys. Rev. 118, 1190 (1960); 126, 497 (1962). ⁵ M. H. Cohen and L. M. Falicov, Phys. Rev. Letters 5, 544 (1960)

^{(1960).}

[0001] direction in the second band so that open orbits can occur when a magnetic field **H** is applied perpendicular to this direction. We have observed the ultrasonic resonance phenomena in transverse fields for sound propagation q along $\lceil 12\overline{1}0 \rceil$ and $\lceil 10\overline{1}0 \rceil$ for both cadmium and zinc, but have seen no ultrasonic resonance corresponding to open orbits perpendicular to $\lceil 0001 \rceil$ for either metal. Our measurements thus indicate conclusively that cadmium and zinc have open Fermi surfaces parallel to [0001], but we are unable to offer evidence as to the possibility of open orbits perpendicular to [0001], since for this configuration the ultrasonic attenuation is extremely large and might obscure the resonance effect. Alekseevskii and Gaidukov,⁶ using magnetoresistance measurements, found that cadmium and zinc possess open Fermi surfaces parallel to [0001] and, in addition, found the zinc surface to be open in certain directions perpendicular to [0001].

The height and width of the ultrasonic open-orbit resonance are related to the electronic mean free path land provide a convenient means for observing variations in l from sample to sample or the variation of l with temperature for a particular sample. As an example, this technique has been used to corroborate the presence of a mean-free-path maximum in cadmium.7 The period of the open orbits, i.e., the magnetic field at which the ultrasonic resonance occurs at a particular frequency, is found to be a direct measure of the Brillouin zone dimension and gives experimental results in accord with values calculated from x-ray measurements. It appears possible, in addition, to determine the thermal expansion of the lattice in the open-orbit direction by a precise measurement of the period of resonance as a function of temperature.

II. THEORY

Resonant absorption of ultrasonic waves in a magnetic field was first studied in the work of Galkin et al.,3 and extended by Kaner, Peschanskii, and Privorotskii.8 The effect predicted is quite different from the regular magnetoacoustic nonresonant oscillations for which the relative widths of the maxima and the general form of the curves are essentially unchanged as $l \rightarrow \infty$. The mechanism of resonant absorption is similar to cyclotron resonance in metals, but is related to the spatial rather than the temporal periodicity of the field in the metal.

Resonant ultrasonic absorption is possible when the average value of the electron velocity (over a period of motion in H) along the sound-wave vector **q** differs from zero. For closed orbits, this requires that q not be

perpendicular to H. For open orbits, resonance is possible for the case $\mathbf{q} \perp \mathbf{H}$, and we consider here only the theory applicable to this case. If the external magnetic field is directed such that some electrons traverse periodic open orbits, the resonance occurs when the open-orbit periodicity is a multiple of the sound wavelength. Open-orbit electrons cause a resonant type of attenuation maximum because all of the open orbits must have the same period in a given crystallographic direction, determined by the dimensions of the reciprocal lattice. For closed surfaces the dimensions of orbits in the direction of sound propagation generally vary as a function of $\mathbf{k}_{\mathbf{H}}$, where $\mathbf{k}_{\mathbf{H}}$ is the component of electron momentum in the direction of the magnetic field. Thus, for closed orbits, the value of attenuation near an absorption maximum involves an average over $k_{\rm H}$ and is inherently broad. Although the particular shapes of various open orbits may vary as a function of $\mathbf{k}_{\rm H}$, they all must have the same fundamental period in the open direction, that determined by the reciprocal lattice. Thus, when the sound wave propagates parallel to the open orbits in real space, sharp maxima are observed in the attenuation.

A detailed working of the theory of resonant ultrasonic absorption by open-orbit electrons shows that the attenuation is the product of two terms, one giving the resonance character, and the other being a slowly varying integral term involving the detailed shape of the open orbit on the Fermi surface as well as the deformation potential. The shape of the open orbits apparently determines the amplitude of the subharmonics of the fundamental resonance.9 The resonance character can be found, however, without a detailed knowledge of the shape of the open orbits. Near resonance, the absorption is found to be³

$$\alpha \sim \frac{\alpha_0 \gamma}{\gamma^2 + (Gqc/2\pi eH - n)^2} = \frac{\alpha_0 \gamma}{\gamma^2 + n^2 (1 - H_n/H)^2}, \quad (1)$$

where

$$H_n = Gqc/2\pi ne \tag{2}$$

is the field at which the nth-order resonance occurs, $n=1, 2, 3, \cdots$ is the resonance order, $\gamma = \pi n/q$, e/c is the electronic charge, G is the period of the open orbit in momentum space, and α_0 is the absorption in zero magnetic field. The resonance line thus has a Lorentz shape and its relative width is

$$\Delta H/H = \gamma/n = \pi/ql, \qquad (3)$$

which is independent of n. At the resonance maximum, we find

$$\alpha_n = \alpha_0 / \gamma = \alpha_0 q l / \pi n. \qquad (4)$$

For the case of $ql \gg 1$, the zero-field attenuation¹⁰ α_0 is

⁶N. E. Alekseevskii and Yu. P. Gaidukov, Zh. Eksperim. i Teor. Fiz. 43, 2094 (1962) [English transl.: Soviet Phys.—JETP 16, 1481 (1963)]. ⁷ B. C. Deaton, Phys. Letters 7, 7 (1963). ⁸ E. A. Kaner, V. G. Peschanskii, and I. A. Privorotskii, Zh. Eksperim. i Teor. Fiz. 40, 214 (1961) [English transl.: Soviet Phys.—JETP 13, 147 (1961)].

<sup>A. B. Pippard, in Low Temperature Physics, edited by C. DeWitt, B. Dreyfus, and P. G. de Gennes (Gordon and Breach Publishers, London, 1962), p. 126.
¹⁰ A. B. Pippard, Phil. Mag. 46, 1104 (1955).</sup>

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proportional to q and independent of l so that α_n is proportional to q^2l . Equations (3) and (4) thus indicate that the relative width of the resonance line is inversely proportional to the product of mean free path and ultrasonic frequency while the resonance height is proportional to the product of the mean free path and the square of the frequency.

III. EXPERIMENTAL

The experiments were performed at temperatures from 4.2 to 1.05°K, the temperature being determined by measuring the vapor pressure of the liquid helium. Several single crystals of cadmium and zinc grown from 99.999% pure (or better) starting materials were used, and measurements on three of these will be reported, Cd I, Cd II, and Zn. Cd I is of greater purity than Cd II which has approximately the same purity as the Zn sample used in the measurements. Each crystal was cut so that sound can be progapated between a pair of $(\overline{1}2\overline{1}0)$, $(10\overline{1}0)$, or (0001) faces. The electron mean free path in each of the samples of cadmium and zinc is thermal phonon limited at 4.2°K.

A pulse technique was employed to excite 10-Mc/sec fundamental quartz transducers, a pair of which were bonded to each sample with Nonaq stopcock grease. X-cut transducers were used for compressional waves and AC-cut for shear waves. Ultrasonic frequencies from 10 to 110 Mc/sec were utilized at magnetic fields up to several thousand gauss. All ultrasonic attenuation data were recorded automatically; data analysis consisted of analyzing the X-Y recorder curves, which were traces of relative ultrasonic attenuation as a function of external magnetic field. Some of the data were also punched on paper tape and analyzed on a CDC-1604 computer. Magnetic field values were obtained from a rotating-coil gaussmeter which was calibrated frequently by nuclear magnetic resonance (NMR) equipment. The attenuation values were calibrated relative to the H=0 values by a precise voltage measurement.

IV. RESULTS

A. Compressional Waves

The compressional wave open-orbit resonance phenomena in cadmium and zinc are observed as single sharp maxima (n=1) at fields determined for a particular frequency ν only by the Brillouin-zone dimension corresponding to the periodicity of the open orbits. In cadmium and zinc the resonance is observed for the configurations \mathbf{q} | [1210], \mathbf{H} | [1010] and \mathbf{q} | [1010], **H**|[1210] which corresponds to open orbits moving in the $\lceil 0001 \rceil$ direction in momentum space. As Onsager¹¹ showed, it follows that the real-space paths of the open orbits will be perpendicular to H and parallel to the sound-wave vector q. The absence of submultiples of the resonance in the compressionalwave case is probably due to the following reasons: (1) Using Pippard's argument⁹ relating the amplitudes of the subharmonics to the Fourier components of the force acting parallel to the open-orbit electron's motion, one would expect only a single resonance line if the force component along the electron path is a simple harmonic function of position, and (2) the extremely strong magnetoacoustic oscillations observed simultaneously with the open-orbit resonance could very well obscure any weak subharmonics.

In Fig. 1 is shown the relative attenuation as a function of ν/H in Cd I for **q**|[1010], **H**|[1210] at 4.2°K illustrating the sharpness of the open-orbit resonance in comparison to the first magnetoacoustic oscillation. Also shown in Fig. 1 is the frequency variation of the resonance line for this sample, indicating the resonance nature of the phenomenon, i.e., the relative width of the absorption line decreases with increasing frequency. Determination of the magnetic field H_n at which the resonance occurs for a particular frequency allows a calculation of the period G of the open orbits responsible for the resonance [see Eq. (2)]. This period should, in the cases of cadmium and zinc, correspond to the Brillouin-zone dimension in the $\lceil 0001 \rceil$ direction. The averages of our experimental data for this dimension in cadmium and zinc are

Cadmium:
$$G_{[0001]} = 1.20 \pm 0.005 \times 10^{-19} \text{ g cm/sec}$$
;
Zinc: $G_{[0001]} = 1.36 \pm 0.01 \times 10^{-19} \text{ g cm/sec}$.

These values represent an average of about 20 runs for cadmium samples Cd I and Cd II and about 15 runs for the zinc sample. They are found to agree extremely well with those calculated from room temperature x-ray data which are corrected for thermal contraction^{12,13}: Cd, $1.19(7) \times 10^{-19}$ g cm/sec and Zn, $1.36(2) \times 10^{-19}$ g cm/sec. The major uncertainty in our experimentally determined values is the ultrasonic frequency which



¹² N. Madaiah and G. M. Graham, Can. J. Phys. 42, 221 (1964); we would also like to acknowledge helpful correspondence with G. K. White on this matter.

magneto-

¹³ R. W. Meyerhoff and J. F. Smith, J. Appl. Phys. 33, 219 (1962).

¹¹ L. Onsager, Phil. Mag. 43, 1006 (1952).

4.20°K

3.81°K 3.40°K

3.00°K

2.60°K

2.20°K

1.81 K

1.40°K

1.06 K

1500

I.5db/cm RELATIVE ATTENUATION

800

900 1000

H (gauss)

700

FIG. 2. Temperature variation of the openorbit resonance line for Cd I at 50 Mc/sec with q along [1010], H along [1210].



From Eq. (3), it is seen that the width of the resonance line is inversely proportional to the electron mean free path l of the open-orbit electrons. Since l is thermal phonon limited at 4.2°K for each of the samples used, decreasing the temperature should increase l, and the resonance should become sharper. A set of temperature measurements on Cd I at 50 Mc/sec is shown in Fig. 2 in which is plotted α as a function of H on a reciprocal scale. The resonance width ΔH decreases with temperature, showing an approximate T^4 dependence¹⁷ down to about 3°K where anomalous behavior is seen.⁷ An investigation of the temperature variation of l for the open-orbit electrons is thus possible by making a careful study of the resonance width as the temperature varies. The present data on Cd II and Zn also show a marked resonance width variation with temperature,

TABLE I. Mean-free-path values calculated from open-orbit resonance widths for q [[1010]. An average background was subtracted from the raw data as shown in Fig. 3.

T (°K)	Cd I l (cm)	Cd 11 l (cm)	Zn l (cm)
4.20	0.047	0.030	0.031
1.10	0.10	0.046	0.039

but it is not nearly so pronounced as that seen with the much purer sample, Cd I. If values of l are calculated using Eq. (3), the results in Table I are found for the case \mathbf{q} [[1010], \mathbf{H} [[1210]. The variation in l from sample to sample is evident, as is the temperature variation. The mean free path values for $\mathbf{q} | [\bar{1}2\bar{1}0]$ are of the same order of magnitude as for $\mathbf{q} \mid [10\overline{1}0]$ even though the total attenuation at the resonance α_n is much larger for $\mathbf{q} \mid [1210]$. For these calculations, ΔH was taken to be the resonance width at A/2 where A is the height of the resonance determined from curves where an average background attenuation has been subtracted as is shown in Fig. 3. This gives the resonance a true Lorentz shape and this half-width possibly has more meaning than that measured from the raw data. Values of l determined from the raw data are found to be about 50% higher than those with the background subtracted. The mean free path values obtained are of the same order of magnitude as those measured using a high-field attenuation analysis.^{7,17} The apparent width of the resonance is increased somewhat by the use of the pulse technique. The packet of ultrasonic waves is typically about 0.3 cm in length so that some of the open-orbit electrons do not stay in the sound field throughout their free paths. This becomes an increasingly important effect as l approaches the length of the wave packet, and experimental results using very pure specimens must be corrected for it.

It is seen from Eqs. (3) and (4) that the width and height of the resonance depend on the ultrasonic frequency ν since $q = 2\pi\nu/v_s$, where v_s is the sound velocity. The width is inversely proportional to ν , while the resonance height α_n varies as the frequency squared. Our experimental data are found to vary approximately

FIG. 3. Illustration of method of determining resonance half-width ΔII after subtracting an average background.



 ¹⁴ C. W. Garland and J. Silverman, Phys. Rev. 119, 1218 (1960).
 ¹⁵ G. A. Alers and J. R. Neighbours, Phys. Chem. Solids 7, 58 (1958).

 ¹⁶ L. M. Falicov, *The Fermi Surface*, edited by W. A. Harrison and M. B. Webb (John Wiley & Sons, Inc., New York, 1960).
 ¹⁷ B. C. Deaton (unpublished).



FIG. 4. Frequency variation of the open-orbit resonance for Cd II.

as expected in both cadmium and zinc. The frequency variation of the open orbit resonance is shown in Fig. 4 for Cd II at 4.2 and 1.05°K, and in Fig. 5 for Zn and Cd I at 4.2°K. In Fig. 6 is shown the height α_n of the resonance (relative to H=0) as a function of ν^2 for the data of Figs. 4 and 5. It is seen that α_n is much larger for q along $[12\overline{1}0]$ than $[10\overline{1}0]$ indicating a larger density of states of open-orbit electrons for the former configuration. This is just what would be expected from consideration of the Fermi surfaces of Cd and Zn. As the frequency (and thus the field at which the resonance occurs) increases, an approximate ν^2 dependence is observed for cadmium and zinc. Thus we find no evidence of magnetic breakdown^{18,19} at fields up to about 2000 G. If magnetic breakdown occurs, the band structure will revert to the original double-zone scheme⁴ in which open orbits parallel to [0001] are not possible. There would be a range of fields, however, for which both band structures exist. The number of open-orbit electrons would thus decrease with field, and the resonance height would decrease. An investigation of the present type, if carried to higher frequencies (thus



FIG. 5. Frequency variation of the open-orbit resonance for Zn and Cd I at 4.2°K.

¹⁸ M. H. Cohen and L. M. Falicov, Phys. Rev. Letters 7, 231 (1961).
 ¹⁹ W. A. Reed and G. F. Brennert, Phys. Rev. 130, 565 (1963).

TABLE II. Approximate momentum values corresponding to elongated closed orbits obtained when H is tilted slightly away from the open orbit direction.

Angle of tilt	Associated
from (0001)	momentum (radius)
1.0° 1.4° 1.8° 2.2° 2.6°	$\begin{array}{c} (g \text{ cm/sec}) \\ 8 \times 10^{-19} \\ 8 \times 10^{-19} \\ 8 \times 10^{-19} \\ 5 \times 10^{-19} \\ 4 \times 10^{-19} \end{array}$

higher magnetic fields), would allow a determination of the number of open-orbit electrons as a function of magnetic field.

When the magnetic field is tilted slightly from the (0001) plane, the resonance line broadens and a series of maxima corresponding to initially large but rapidly decreasing momentum values appears as can be seen in Fig. 7 for Cd I at 64 Mc/sec. The maxima around the resonance are thought to be caused by electrons moving in elongated closed orbits passing through several Brillouin zones. These maxima begin to appear when **H** is tilted about 0.5° from the (0001) plane. They continue to appear until **H** is tilted by about 3° at which point these maxima as well as the open-orbit resonance disappear. Several of the approximate momentum values derived from the periods of the high-field maxima are shown in Table II.

B. Shear Waves

The shear-wave open-orbit resonance in cadmium and zinc is observed for the same sound and field configurations as in the compressional case. We have observed the shear resonance with **q** along [1010] and [1210] for polarization ε along [0001], [1010], and [1210]. In cadmium and zinc, resonances corresponding to n=1, 2, 3 have been observed for **q**||[1210], **H**||[1010], and ε ||[0001]. When the shear polarization is along [1210] or [1010] the resonance is quite weak; in these cases, **H** is parallel to ε and all magnetoacoustic oscillations tend to wash out.

In Fig. 8 is shown the attenuation of shear waves with $\mathbf{q} | [10\overline{10}], \mathbf{H} | [\overline{12}\overline{10}], \text{ and } \boldsymbol{\varepsilon} | [0001]$ for three frequencies in Cd II. The open orbit resonance is some-



FIG. 6. Attenuation α_n at the openorbit resonance (relative to H=0) as a function of the square of the ultrasonic frequency. FIG. 7. Variation of the open-orbit resonance at 64 Mc/sec as the magnetic field is tilted out of the (0001) plane toward the [0001] axis. The sound propagation is along [1010] and $H_{\perp}q$.



what enhanced by use of shear waves as is expected since ql is about a factor of 2 larger than in the compressional case as a result of the small sound velocity of shear waves. In the shear run at 50 Mc/sec, the resonances for n=1, 2, 3 are quite clear, but the n=2resonance line does not appear to be as large relative to that for n=1 as that seen in copper.²⁰

The temperature dependence of the fundamental resonance line for shear waves is very similar to that of compressional waves, i.e., it appears that each reflects the same temperature variation of the electron mean free path. Again, it is found that the height of the resonance varies as the square of the frequency. Our data (Fig. 8) show that the height of the fundamental resonance for shear waves varies as $\alpha_n = -2.0 + 0.01\nu^2$ where α_n (dB/cm) is measured relative to the zero-field value and ν is the sound frequency in Mc/sec.

V. CONCLUSIONS

The existence of open-orbit resonance absorption for the various configurations studied provides conclusive evidence that the Fermi surfaces of cadmium and zinc are open in the [0001] direction. No evidence for magnetic breakdown is observed at fields up to 2000 G. It would be of interest to carry the open-orbit resonance studies to much higher frequencies (fields) so that the deterioration of the resonance could be determined if magnetic breakdown occurs.

The investigation of the open-orbit resonance phenomena allows a direct measure of the Brillouin zone



FIG. 8. The open orbit resonance for shear waves in Cd II at several frequencies; n is the resonance order.

dimension in the [0001] direction for cadmium and zinc, and our data are found to agree quite well with values taken from x-ray measurements. It should be possible, with careful field and frequency measurements, to determine the thermal expansion of the lattice in an open-orbit direction with studies of the present type.

Since the width and height of the open-orbit resonance line are related to the electron mean free path, a measure of the relative purity of various samples is possible; a determination of the temperature variation of l for a particular sample and a particular group of electrons can also be made. In the present data it was found that l varies approximately as T^{-4} . Experimentally we find that the resonance height is proportional to the square of the ultrasonic frequency, in agreement with theory.

Shear waves are found to enhance the open-orbit attenuation phenomena and should be very useful for studying this effect in materials where very high purity is not possible. The shear wave data are found to give essentially the same information as is found in the compressional case.

ACKNOWLEDGMENTS

The authors would like to thank J. R. Miller, J. R. Boyd, K. B. Ward, Jr., F. A. Blum, Jr., and D. B. Doan for their assistance in making the measurements.

 $^{^{20}}$ C. W. Burmeister, D. B. Doan, and J. D. Gavenda, Phys. Letters 7, 112 (1963).