where  $\Delta$  is a nearest-neighbor lattice vector. Since we are interested in the scattering length at zero energy, we take the limit of (A14) as  $\mu \rightarrow 0$  and use the fact that in this limit the  $B_{\delta}$  cannot depend upon the direction of **δ**. Thus, one finds that

$$\sum_{\delta} B_{\delta} = -\gamma_0 A / [1 + A (\gamma_0 M)^{-1} \\ \times \sum_{\mathbf{k}} \gamma_{\mathbf{k}}^2 (\gamma_0 - \gamma_{\mathbf{k}})^{-1}].$$
(A15)

Replacing the sum over  $\mathbf{k}$  by an integral and remembering (1.18'), this becomes

$$\sum_{\delta} B_{\delta} = -\gamma_0 A / [1 + A |C_2|], \qquad (A15')$$

where

$$-C_2 = \frac{1}{(2\pi)^3} \int \int \int \Gamma(1-\Gamma)^{-1} du dv dw = 0.516 \,, \quad (A6)$$

as in Appendix I. Inserting (A15') into the asymptotic wave function, one obtains for the scattering length at zero energy,

$$f_0 = A \gamma_0 d [4\pi (1 + A | C_2|)]^{-1} = 3A d [2\pi (1 + A | C_2|)]^{-1}, \quad (A16)$$

which is the expression given in the text, Eq. (3.33).

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# Magnetoacoustic Effects in Longitudinal Fields\*

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The absorption of transverse and longitudinal ultrasonic waves has been studied as a function of the magnetic field applied along the direction of propagation in pure tin and lead crystals at liquid-helium temperatures. At low fields, the attenuation of both transverse and longitudinal waves exhibits oscillations approximately periodic in reciprocal field, which are ascribed to electron orbits which execute a periodic motion along the field direction. The attenuation of transverse waves in tin shows regions of rapid decrease with magnetic field, which are interpreted as the absorption edges first predicted by Kjeldaas. In higher fields, the absorption of longitudinal waves appears to saturate at a nonzero value, while that of the transverse waves in tin appears generally still to be decreasing with field at fields of about 10 kG.

## 1. INTRODUCTION

LARGE number of experiments have been carried out on the effect of a transverse magnetic field on the absorption of ultrasonic waves in pure metals at low temperatures, and the study of the angular variation of the magnetoacoustic oscillations has contributed significantly to the knowledge of the Fermi surfaces of many metals. Few results have so far been obtained on the dependence of the attenuation on a longitudinal magnetic field, however, partly because the results cannot be so readily interpreted in terms of the geometrical parameters of the Fermi surface, and partly on account of the experimental difficulties involved. These measurements do have a certain intrinsic interest, however, and the present work represents an attempt to understand the coupling between acoustic waves and the conduction electrons in metals in the presence of a longitudinal magnetic field, while simultaneously obtaining some information about the Fermi surfaces of the metals studied.

In the following sections the experimental technique used in these measurements is described briefly and the experimental results are presented. The theory of the

attenuation of ultrasonic waves in longitudinal magnetic fields is then discussed, and finally the results are interpreted in the light of this theory. A brief account of some of the results of this work has already been published.1

#### 2. EXPERIMENTAL METHOD

The absorption of 80-Mc/sec transverse and longitudinal ultrasonic waves in pure lead and tin crystals in a longitudinal magnetic field was measured by means of a "pulse-echo" technique, the details of which have been described elsewhere.<sup>2</sup>

The longitudinal and shear waves were generated by applying a high-frequency electromagnetic pulse across X- and Y-cut quartz crystals, respectively, exciting them on their fifth harmonic. Ultrasonic reflections from the free end of the specimen were reconverted by the transducer into electrical signals which were amplified, demodulated, and displayed on a cathode-ray oscilloscope. In practice, because of the high attenuation in the pure crystals used in these experiments, only one reflection could be observed, in the normal state. The

<sup>\*</sup> Work was performed in part at the Ames Laboratory of the U. S. Atomic Energy Commission.

<sup>&</sup>lt;sup>1</sup> A. R. Mackintosh, in Proceedings of the Seventh International Conference on Low-Temperature Physics (University of Toronto Press, Toronto, 1960), p. 12. <sup>2</sup> A. R. Mackintosh, Proc. Roy. Soc. (London) A271, 88 (1963).

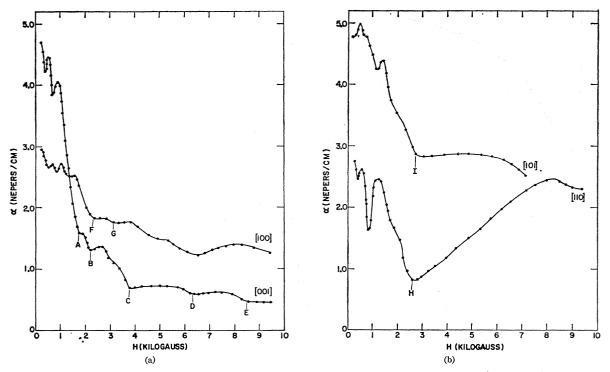


FIG. 1. Longitudinal field dependence of the attenuation of transverse waves in tin at 80 Mc/sec and 1.2°K.

attenuation was measured by comparison with a pulse from a high-frequency oscillator, which was fed into the receiver through a calibrated piston attenuator, thus eliminating the effect of nonlinearity of the receiver.

The specimen was immersed in liquid helium in a conventional nitrogen-shielded cryostat and the temperature could be further reduced to about 1.2°K by pumping on the helium bath. The longitudinal magnetic fields were provided by water-cooled solenoids. Most of the measurements were made in a solenoid which was capable of producing fields up to 10 kG, but a few experiments were carried out in a larger coil, in which higher fields could be attained. The signal received in a magnetic field could be compared to that in the superconducting state, and since the electronic attenuation is very small in superconducting lead and tin at the temperatures used, this allowed an absolute value of the ultrasonic absorption by the electrons to be determined.

The crystals were cast in the form of cylinders 1 cm in diameter in graphite crucibles, using a seeding technique to obtain the required orientations. For the longitudinal wave experiments specimens 1 cm in length were used but, since the ultrasonic velocity of shear waves is less and the attenuation greater, the specimen length was reduced to 0.5 cm for the shear wave measurements. The lead crystals had a resistivity ratio  $R_{300^{\circ}\text{K}}/R_{4.2^{\circ}\text{K}}$  of about  $1.5 \times 10^4$ , while the tin crystals had a resistivity ratio  $R_{300^{\circ}\text{K}}/R_{1.2^{\circ}\text{K}}$  of about  $5 \times 10^4$ . The product of the acoustic wave number and the electronic free path, ql, was deduced from the results of Chambers<sup>3</sup> to be about 15 for the longitudinal waves in lead at  $4.2^{\circ}$ K, and about 100 and 60 for transverse and longitudinal waves, respectively, in tin at  $1.2^{\circ}$ K.

#### 3. THE EXPERIMENTAL RESULTS

## A. Transverse Waves

The dependence of the attenuation of shear waves on longitudinal magnetic field at  $1.2^{\circ}$ K was studied in four tin crystals whose axes were oriented within about  $1^{\circ}$  of the symmetry directions [001], [100], and [110], and within  $3^{\circ}$  or  $4^{\circ}$  of [101]. The results of these measurements are shown in Fig. 1.

The variation of attenuation with field has a number of noteworthy features. At magnetic fields of about 2 kG and less the ultrasonic absorption exhibits oscillations which are approximately, though not exactly, periodic in reciprocal field. These oscillations are also present in a less pronounced form in measurements at 4.2°K, where the electronic mean free path is shorter, and can be followed to lower magnetic fields, since there is no superconducting transition at this temperature.

There are, in addition, regions in which the absorption decreases rapidly with magnetic field. The most striking example occurs in the [001] crystal where the attenuation falls by a factor of about 4 in a range of 500 G. A number of other absorption edges can also be observed in the results, however, and since an attenuation change

<sup>&</sup>lt;sup>3</sup> R. G. Chambers, Proc. Roy. Soc. (London) A215, 481 (1952).

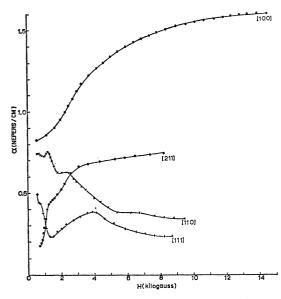


FIG. 2. Dependence of the attenuation of longitudinal waves in lead on longitudinal magnetic field at 80 Mc/sec and 4.2°K.

of about  $10^{-2}$  Np/cm could be detected in this work, they generally lie well outside the experimental error. The experimental results were reproducible, furthermore, in different runs at 1.2°K and the larger absorption edges persisted at 4.2°K, although some of the smaller ones became much less distinct. In some cases, notably in the  $\lceil 110 \rceil$  specimen, the attenuation rises at intermediate fields before beginning to fall again at high fields.

### **B.** Longitudinal Waves

The magnetic-field dependence of the attenuation of longitudinal ultrasonic waves was investigated at 4.2°K in four lead crystals whose axes were oriented within about  $1^{\circ}$  of the symmetry directions  $\lceil 100 \rceil$ ,  $\lceil 110 \rceil$ , and [111], and within 3° or 4° of [211]. The results are shown in Fig. 2. In the [110] and [111] crystal measurements there are oscillations at low fields, although these are not so pronounced as the tin oscillations. In view of the considerably smaller value of ql in lead, this is not perhaps surprising. In each crystal, the absorption appeared to approach a constant value at high fields.

In addition a few measurements were made on tin crystals at 1.2°K. In all cases, distinct oscillations were observed at low fields and the ultrasonic attenuation appeared to approach a constant value at high fields.

#### 4. THEORY OF ULTRASONIC ATTENUATION IN LONGITUDINAL FIELDS

The theory of the interaction between acoustic waves and the electrons in real metals has been considered by

Gurevich,<sup>4</sup> Pippard,<sup>5</sup> Kaner,<sup>6</sup> Chambers,<sup>7</sup> and Mackintosh.<sup>8</sup> In particular, the first two authors have given detailed discussions of magnetoacoustic effects in a transverse field.

Although the details of the various theories differ, in each case the attenuation coefficient can be written in the form

$$\alpha = (4\pi^3 \hbar M s u^2)^{-1} \int \frac{dS}{l} \left[ \int_{-\infty}^0 \mathbf{F} \cdot \mathbf{v} \exp\left(-\int_t^0 \frac{dt'}{\tau}\right) dt \right]^2, \quad (1)$$

where M is the ionic mass of the metal, s is the sound wave velocity, u the amplitude of the particle velocity in the lattice, and l and  $\tau$  are the mean free path and relaxation time of an electron with a velocity v on an element dS of the Fermi surface. The effective force **F** which acts on the electrons is composed of contributions from the electric fields set up by the sound wave, the effect of the moving lattice, and the change of the equilibrium Fermi surface due to lattice distortion. This force, which is a function of the wave vector of the electron, and has the periodic character of the sound wave itself, can be calculated self-consistently from the condition that the electron current effectively cancels that due to the lattice, in the frequency range of these experiments. The integral in the square brackets is evaluated over the trajectory of each electron, and it is the oscillatory character of this integral which leads to the magnetoacoustic oscillations in a transverse field.

Equation (1) can also be used to calculate the attenuation in a longitudinal magnetic field, provided that the integral is taken over the appropriate electron trajectories. In the free electron model of a metal, the component of the electronic velocity in the direction of a longitudinal force is unaffected by a magnetic field and, if the relaxation time is constant, the trajectory integral remains constant. The absorption of a longitudinal ultrasonic wave by a free electron metal is therefore independent of the longitudinal magnetic field, as was shown first by Rodriguez.9 In the case of transverse waves, however, Kjeldaas<sup>10</sup> showed that the cyclotron motion of the electron can resonate with one of the circularly polarized components of the sound wave and absorb energy from it, provided that the cyclotron frequency is equal to the Doppler shifted frequency of the sound wave, i.e.,

$$\omega_c = eH/mc = (v_z/s)\omega, \qquad (2)$$

where  $v_z$  is the velocity of the electron along the direc-

<sup>4</sup> V. L. Gurevich, Zh. Eksperim. i Teor. Fiz. 37, 71 (1959) [translation: Soviet Phys.—JETP 10, 51 (1960)].
<sup>5</sup> A. B. Pippard, Proc. Roy. Soc. (London) A257, 165 (1960).
<sup>6</sup> E. A. Kaner, Zh. Eksperim. i Teor. Fiz. 38, 212 (1960) [translation: Soviet Phys.—JETP 11, 154 (1960)].
<sup>7</sup> R. G. Chambers, in *Proceedings of the Seventh International* Conference on Low Teoreties.

Conference on Low-Temperature Physics (University of Toronto Press, Toronto, 1960), p. 11.

<sup>8</sup> A. R. Mackintosh, Ph.D. thesis, University of Cambridge, 1960 (unpublished). <sup>9</sup> S. Rodriguez, Phys. Rev. 112, 80 (1958).

<sup>10</sup> T. Kjeldaas, Phys. Rev. 113, 1473 (1959).

tion of the field. Above a certain field, given by

$$H_{\mathbf{A}} = mcv_{F}\omega/es , \qquad (3)$$

where  $v_F$  is the Fermi velocity, no electrons can absorb energy from the sound waves if  $ql \gg 1$  and the attenuation falls to zero. The calculated attenuation as a function of magnetic field according to Kjeldaas is shown for a number of values of ql in Fig. 3.

In a real metal, the electron orbits are more complicated and their complexity is reflected in the trajectory integral. In particular, it is possible for the electrons to execute a periodic motion in the direction of the magnetic field and this can lead to oscillations with field in the ultrasonic absorption. Electrons on a cylindrical Fermi surface, for instance, will execute such orbits unless the field is along or perpendicular to the cylinder axis. For a longitudinal wave, in the simple case where the electron velocity along the field direction is given by

$$v_z = v_0 \cos \omega_c t , \qquad (4)$$

the relaxation time is constant, and the  $\mathbf{k}$  dependence of  $\mathbf{F}$  can be neglected, the trajectory integral has the oscillatory form

$$T = F_0 v_0 \int_{-\infty}^{0} \sin\left(\frac{q v_0}{\omega_c} \sin\omega_c t\right) \cos\omega_c t \ e^{t/\tau} dt$$
$$= \frac{F_0}{q} \left[ 1 - J_0\left(\frac{q v_0}{\omega_c}\right) \right] \quad \text{if} \quad \omega_c \tau \gg 1 , \tag{5}$$

where  $J_0$  is a Bessel function. This function is approximately periodic in  $v_0/\lambda\omega_c$ . Oscillations in the absorption of both longitudinal and shear waves may therefore occur in a longitudinal field, provided that there exist suitable pieces of Fermi surface in the metal.

Kjeldaas<sup>10</sup> has also briefly considered the attenuation of transverse waves in a longitudinal field in a real metal, and has shown that absorption edges can also be expected in this case. It is interesting that his result for the field at which an absorption edge occurs can be obtained by a simple quantum-mechanical argument.<sup>8</sup> If we consider the ultrasonic attenuation as the absorption of phonons of wave vector q and energy  $\hbar\omega$  by the conduction electrons, whose quantum states are specified by the magnetic oscillator quantum number n and  $k_{z_1}$  in a magnetic field, conservation of energy and momentum in the electron scattering process requires that

$$\hbar\omega = \hbar\omega_c \delta n + \frac{\partial \epsilon}{\partial k_z}; \text{ and } \delta k_z = q.$$
 (6)

These conditions imply that

$$\omega_c \delta n = \omega (1 - v_z/s). \tag{7}$$

Since  $v_z$  is much greater than s, the physical process represented by this equation is the scattering of an electron by a phonon into a lower magnetic oscillator

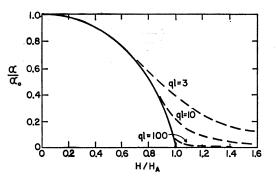


FIG. 3. The longitudinal field dependence of the attenuation of shear waves in a free electron metal, according to Kjeldaas (see Ref. 10).

state, and the taking up of the residual energy by an increase in the kinetic energy of the electron in the direction of the field. The maximum field at which absorption can occur, neglecting s compared with  $v_z$  is given by

$$\omega_c = \omega v_m / s \,, \tag{8}$$

where  $v_m$  is the maximum value of  $v_z$ . Since it can be shown<sup>10</sup> that the cyclotron frequency at the extremal point is given by

$$\omega_c/v_m = H_A e K^{1/2}/c , \qquad (9)$$

where K is the Gaussian curvature of the Fermi surface at that point, the field at the absorption edge is given by

$$K = (\hbar\omega_c/seH_A)^2, \tag{10}$$

which is the result of Kjeldaas.

In a metal in which only closed electron orbits are permitted, the attenuation of longitudinal waves tends to a constant value, which depends upon the variation of velocity and relaxation time over the Fermi surface, at fields such that  $\omega_c \tau \gg 1$  for all electrons. On the other hand, the attenuation of transverse waves goes to zero at a field sufficiently high that it is well beyond the last absorption edge, which corresponds to that section of Fermi surface with the smallest curvature in the direction of the field. The effect of open orbits on the ultrasonic absorption in longitudinal fields has not been considered in detail. A pure longitudinal wave does not interact with electrons executing open orbits confined to the plane normal to the magnetic field, but does if they have a component of velocity along H. On the other hand, a transverse wave will interact with such orbits unless they run in a direction perpendicular to the polarization direction, and the calculations for transverse fields<sup>5,6</sup> suggest that they may modify the high-field behavior considerably.

### 5. DISCUSSION

Perhaps the most interesting feature of the experimental results is the occurrence of regions of rapid decrease with field of the absorption of transverse waves,

which can be identified with the Kieldaas absorption edges. Kieldaas<sup>10</sup> calculated the field dependence of the absorption of circularly polarized waves, and he emphasized that difficulties may be encountered in measurements with linearly polarized shear waves, as used in these experiments, since the two circularly polarized components may have different velocities, resulting in a rotation of the plane of polarization. He showed that the polarization rotation is greatest at the field corresponding to the absorption edge, where, for the free electron model, it is given by

$$\delta\phi = \pi m v_F \nu d / 6M s^2, \qquad (11)$$

where d is the path length and v the frequency of the sound wave. Taking Fawcett's<sup>11</sup> value of  $5.4 \times 10^7$ cm/sec for  $v_F$  in tin we find that  $\delta \phi$  is approximately  $\pi/10$  under the conditions of these experiments. Such a polarization rotation should reduce the amplitude of the observed signal by about  $\cos \pi/10$ , or increase the apparent attenuation by about 5%. Tin is not a freeelectron metal so this estimate is only approximate and may be too low. However, the fact that tin is known to have a number of sheets of Fermi surface12 should reduce the polarization rotation since, at each absorption edge, only a fraction of the electrons are contributing to it.

Polarization rotation cannot normally create absorption edges, since it is only large near them, but it can alter their shape. Since rotation of the plane of polarization always increases the apparent attenuation, it tends to blur out the absorption edges. Experimentally there seems to be little tendency for this to occur in tin, and the experimental results of Fig. 1 have the general form expected for the field dependence of the attenuation in a metal with a number of pieces of Fermi surface of different sizes and shapes. This supports the view that the polarization rotation in tin is small. Morse and Gavenda<sup>18</sup> have reported observations of polarization rotation of shear waves in copper in a longitudinal field, but copper has a considerably smaller ionic mass than tin and, since copper has only one sheet of Fermi surface, the polarization rotation near the absorption edge is likely to be comparatively large. In addition, the ultrasonic path lengths were considerably greater than those used in these experiments. It would be of interest to study the variation of apparent attenuation with specimen thickness in a number of metals and, in addition, to attempt measurements with circularly polarized waves.

The most clearly defined absorption edges have been marked in Fig. 1. A number of these are quite distinct, while others are smaller and further reduced at 4.2°K. Table I gives the fields at which the absorption edges

| q                                | H <sub>A</sub><br>(kG)  | \$<br>(10⁵ cm/sec)           | $K^{1/2}$<br>(10 <sup>-7</sup> cm)                                     | $(10^{-15} \text{ cm}^2)$      |
|----------------------------------|---|------------------------------|--|--------------------------------|
| [001]<br>[100]<br>[110]<br>[101] | $\begin{array}{cccc} A & 1.6 \\ B & 2.2 \\ C & 3.7 \\ D & 6.3 \\ E & 8.5 \\ F & 2.2 \\ G & 3.1 \\ H & 2.5 \\ I & 2.7 \end{array}$ | 1.85<br>1.88<br>1.90<br>1.89 | $1.07 \\ 0.78 \\ 0.47 \\ 0.27 \\ 0.21 \\ 0.77 \\ 0.55 \\ 0.67 \\ 0.62$ | 11.46.02.20.730.445.93.04.53.8 |

TABLE I. Fermi surface curvatures deduced from the absorption edges of Fig. 1.

are observed and the Fermi surface curvatures to which they correspond, calculated from Eq. (10).

A detailed discussion of these results must await a more thorough knowledge of the Fermi surface of tin than we possess at present, but two prominent features deserve comment. In each set of results there appears to be a well-defined absorption edge at about 2.5 kG and these could all be accounted for by a roughly spherical piece of Fermi surface with a radius of approximately  $1.5 \times 10^7$  cm<sup>-1</sup>, or about one-third of the separation between the center of the Brillouin zone and its nearest boundary.<sup>12</sup> The very large absorption edge A, when the field is along [001], implies a large sheet of Fermi surface with a large curvature along the *c* direction, and it is interesting that the nearly free electron Fermi surface of tin<sup>12</sup> has such a piece, in the fourth zone hole surface.

The low-field oscillations are probably due to electrons which execute periodic motion in the direction of the field. The approximate periodicity of these oscillations indicates that the maximum velocity of the electrons along the field is a substantial proportion of the Fermi velocity. Such orbits have also been postulated by Koch and Kip<sup>14</sup> to explain their observations of cyclotron resonance with tilted magnetic fields in tin, and detailed studies of the Fermi surface of lead<sup>2,15</sup> have revealed a surface in the third Brillouin zone which is essentially a series of distorted cylinders running along the zone edges. The fact that the oscillations are not exactly periodic in 1/H is presumably due to interference between orbits from different regions of Fermi surface.

Longitudinal magnetoacoustic oscillations have also been observed by Rayne and Chandrasekhar<sup>16</sup> in indium and by Mackinnon, Taylor, and Daniel<sup>17</sup> in cadmium. The latter authors interpret these oscillations in terms of periodic orbits in the direction of the field. In addition, Mackinnon and Daniel<sup>18</sup> have observed

<sup>&</sup>lt;sup>11</sup> E. Fawcett, in *The Fermi Surface*, edited by W. A. Harrison and M. B. Webb (John Wiley & Sons, Inc., New York, 1960), p. 197.

 <sup>&</sup>lt;sup>12</sup> A. V. Gold and M. G. Priestley, Phil. Mag. 5, 1089 (1960).
 <sup>13</sup> R. W. Morse and J. D. Gavenda, Phys. Rev. Letters 2, 250 (1975). (1959).

 <sup>&</sup>lt;sup>14</sup> J. F. Koch and A. F. Kip, Phys. Rev. Letters 8, 473 (1962).
 <sup>15</sup> A. V. Gold, Phil. Trans. Roy. Soc. (London) A251, 85 (1958).
 <sup>16</sup> J. A. Rayne and B. S. Chandrasekhar, Phys. Rev. 125, 1952 (1962).

<sup>&</sup>lt;sup>17</sup> L. Mackinnon, M. T. Taylor, and M. R. Daniel, Phil. Mag. 7, 523 (1962).

<sup>&</sup>lt;sup>18</sup> L. Mackinnon and M. R. Daniel, Phys. Letters 1, 157 (1962).

resonant oscillations in cadmium in a longitudinal field, which they ascribe to orbits which have a net velocity in the direction of the field, and which are sufficiently convoluted to allow a resonant absorption when the displacement during one period is a multiple of the acoustic wavelength. Such orbits can arise from pieces of Fermi surface having the form of a distorted cone, and the period of the resonant oscillations allows the determination of the rate of change of Fermi surface area with wave vector in the field direction, for those orbits which are responsible for the resonance.

The attenuation of longitudinal waves in lead appears to approach a constant value at high magnetic fields. This is in accord with the theory since there are no open orbits present when the magnetic field is along the axes of the specimens used in these experiments.<sup>19</sup> The attenuation of transverse waves in tin is decreasing with field at the highest fields in all the specimens measured, but it is not clear whether it is tending towards a finite or zero limiting value. According to Alekseevskii,

<sup>19</sup> N. E. Alekseevskii and Yu. P. Gaĭdukov, Zh. Eksperim. i Teor. Fiz. 41, 354 (1961) [translation: Soviet Phys.—JETP 14, 256 (1962) 7.

Gaĭdukov, Lifshits, and Peschanskii<sup>20</sup> open orbits exist when the field is in the [100], [110], and [101] directions, but not in the [001] direction. It may be significant that the attenuation at high fields has fallen to a considerably lower value in the crystal with no open orbits than in the others. Experiments in higher fields and further consideration of the theory are required for a complete understanding of the limiting behavior of ultrasonic attenuation in high longitudinal magnetic fields.

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I have profited greatly from discussions with Professor A. B. Pippard during the course of this work, which was carried out with financial assistance from the Department of Scientific and Industrial Research.

Valuable discussions with Professor R. H. Good, Jr., and Professor J. M. Keller are also gratefully acknowledged.

<sup>20</sup> N. E. Alekseevskii, Yu. P. Gaĭdukov, I. M. Lifshits, and V. G. Peschanskii, Zh. Eksperim. i Teor. Fiz. **39**, 1201 (1960) [translation: Soviet Phys.—JETP **12**, 837 (1961)].

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# Specific Heats of Zirconium Alloys at Low Temperatures

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The specific heats of dilute alloys of silver, cadmium, indium, tin, and antimony in hexagonal zirconium have been measured from 1.2 to 4.5°K. For each alloy the specific heat obeys the relation  $c = \gamma T + \beta T^3$ within the experimental error. All of these solutes increase  $\gamma$  linearly with concentration and  $d\gamma/dx$  is linearly related to the chemical valence of the solute. The increase in  $\gamma$  in the tin-zirconium alloys shows that all electrons outside closed shells cannot be treated as equivalent in the rigid band model of alloying. All of these solutes increase the density of states of zirconium, providing evidence for a zone overlap in the zirconium d band and for a small number of electrons in a new band. All of the solutes increase the lattice specific heat and the Debye temperature is a linear function of solute concentration for each of these alloy systems.  $d\theta/dx$  is not simply related to the solute valence but shows a close correlation with the magnitude of the rate of change of the distance between atoms at (0,0,0) and  $(\frac{1}{3},\frac{2}{3},\frac{1}{2})$  of the hexagonal cell. Additions of tin to zirconium do not change the average interaction potential of the BCS theory appreciably.

### I. INTRODUCTION

'HE electronic specific heat provides one of the best methods for experimentally determining the changes in the density of electronic states which take place during alloying and, thus, indirectly the band structure of the solvent metal.<sup>1-3</sup> Although the

Strickland (The Physical Society, London, 1952), Vol. 15, p. 76.

original conception of the rigid band model<sup>4</sup> of alloying did not allow for the screening by the conduction electrons of the additional charge of the solute ions, Friedel<sup>5</sup> has shown that this model does correctly predict the affect of alloying on the density of states using the Thomas-Fermi approximation and assuming that exchange and correlation effects do not change during alloying. For alloys of metals containing closed dshells, the rigid band model describes the situation fairly well. Rayne<sup>6</sup> has shown that for germanium and zinc in

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<sup>†</sup> Operated by the Union Carbide Corporation for the U.S. Atomic Energy Commission.

<sup>&</sup>lt;sup>1</sup>N. F. Mott and H. Jones, *The Theory and Properties of Metals and Alloys* (Clarendon Press, Oxford, 1936), p. 179. <sup>2</sup> F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), p. 149. <sup>3</sup> G. V. Raynor, in *Reports of Progress in Physics*, edited by A. C. Strichlerd (The Discrete Content) and (The Discrete Content).

<sup>&</sup>lt;sup>4</sup> H. Jones, Proc. Phys. Soc. (London) **49**, **243** (1937). <sup>5</sup> J. Friedel, in *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, **1954**), Vol. 3, p. **465**. <sup>6</sup> J. A. Rayne, Phys. Rev. **110**, 606 (1958).