

## Paramagnetic Resonance of CdTe : Mn and CdS : Mn\*

JOHN LAMBE

*Scientific Laboratory, Ford Motor Company, Dearborn, Michigan*

AND

CHIHIRO KIKUCHI

*Department of Nuclear Engineering, University of Michigan, Ann Arbor, Michigan*

(Received February 15, 1960)

Paramagnetic resonance absorption experiments have been carried out on CdTe and CdS crystals containing manganese. In CdTe, the lines are found to be very broad at 300°K. At 4.2°K lines narrow sufficiently to measure parameters with the result  $g=2.010$ ,  $A=0.0055\text{ cm}^{-1}$ , and  $3a=0.0084\text{ cm}^{-1}$ , where  $3a$  is the zero-field splitting. The superhyperfine splitting is the same as for CdS with components spaced at 1.4 gauss giving  $A_{\text{Cd}}=2.6\times 10^{-4}\text{ cm}^{-1}$ . In CdS an interaction with conduction electrons is found which can broaden lines at 300°K. At low temperatures an anomalous spectrum is found in CdS with  $D=0.0295\text{ cm}^{-1}$ .

## I. INTRODUCTION

TO date, extensive studies have been made on the paramagnetic resonance of manganese in a variety of  $A_{\text{II}}B_{\text{VI}}$  compounds. Van Wieringen<sup>1</sup> and Matsumura<sup>2</sup> have surveyed the properties of a number of polycrystalline samples of such compounds. A start in the detailed study of these materials was made by Matarrese and Kikuchi,<sup>3</sup> who investigated the spin-resonance properties of a single crystal of cubic ZnS:Mn. Later Keller, Gelles, and Smith<sup>4</sup> reported the results of their measurements on  $\text{Mn}^{++}$  in hexagonal ZnS, and recently Walsh<sup>5</sup> has investigated the effect of pressure on the cubic field splitting of  $\text{Mn}^{++}$  in cubic ZnS. Other materials that have been investigated in some detail are MgO, by Low<sup>6</sup> and CdS by Dorain.<sup>7</sup> The purpose of this paper is to present some of the results for  $\text{Mn}^{++}$  in cubic CdTe and some further observations on CdS:Mn.

## II. EXPERIMENTAL METHOD

The measurements at 300, 78, and 4.2°K were carried out in an X-band (9400 Mc/sec) magnetic resonance spectrometer using a lavite cavity with 5-kc/sec magnetic field modulation, as described elsewhere.<sup>8</sup> The CdS single crystals grown from the vapor phase were presented to us by Professor S. Cyzak of The University of Detroit. The CdTe single crystals containing about 0.01%  $\text{Mn}^{++}$  were grown for us by Professor D. Mason of the Chemical and Metallurgical Engineering Department of the University of Michigan. The CdTe crystals were oriented by means of the cleavage planes, which are

known to be  $[110]$  planes. This was also confirmed by the angular dependence of the spin-resonance spectrum. The  $c$  axis of the CdS crystals was located by polarized light; the final adjustments, however, were made by orienting the sample in the cavity or by rotating the magnetic field until the maximum spread in the spin-resonance spectrum was obtained. The resistivity of the CdTe crystals was high enough so as not to load the cavity. For CdS, the resistivity varied over a wide range, and some crystals having resistivity as low as 5 ohm cm were used.

## III. EXPERIMENTAL RESULTS

## A. CdTe:Mn

The striking characteristics of this material are (1) the temperature-dependent linewidth, (2) the unusually large cubic field splitting with positive  $g$ -value shift, and (3) superhyperfine structure comparable to that of CdS:Mn. Figure 1 shows the spectra at room and liquid nitrogen temperatures. At 300°K the linewidth is so wide as to obliterate any fine structure. At 78°K the lines narrow and structure such as shown in Fig. 1 is produced. The sharp line between the third and the fourth hfs is due to hydrazyl. Its position indicates that  $\Delta g(\text{CdTe:Mn})=0.0065$ . The details of the spectrum at an angle of 0° between cubic axis and magnetic field at liquid helium temperature is shown in Fig. 2. At

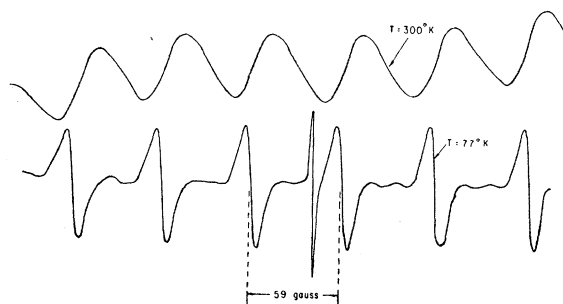


FIG. 1. Absorption observed in CdTe at 300°K and 77°K. The narrow line at 77°K is a hydrazyl marker.

\* This work was supported in part by Air Force Office of Scientific Research.

<sup>1</sup> J. S. Van Wieringen, *Discussions Faraday Soc.* **19**, 148 (1955).

<sup>2</sup> O. Matsumura, *J. Phys. Soc. Japan* **14**, 108 (1959).

<sup>3</sup> L. M. Matarrese and C. Kikuchi, *J. Phys. Chem. Solids* **1**, 117 (1956).

<sup>4</sup> S. P. Keller, F. L. Gelles, and W. V. Smith, *Phys. Rev.* **110**, 850 (1958).

<sup>5</sup> W. M. Walsh, *Bull. Am. Phys. Soc.* **3**, 178 (1958); see also *Phys. Rev.* **114**, 1473, 1485 (1959).

<sup>6</sup> W. Low, *Phys. Rev.* **105**, 793 (1957).

<sup>7</sup> P. B. Dorain, *Phys. Rev.* **112**, 1058 (1958).

<sup>8</sup> J. Lambe and R. Ager, *Rev. Sci. Instr.* **30**, 599 (1959).

4.2°K, the principal lines ( $M = \frac{1}{2}$ ) exhibit the superhyperfine structure, as indicated in Fig. 3. This structure was not found in other fine structure components. The separation between superhyperfine components is 1.4 gauss.

### B. CdS:Mn

Room-temperature measurements on insulating CdS had been made by Dorain.<sup>7</sup> We made measurements on insulating crystals and obtained similar results. Our value of superhyperfine spacing is 1.4 gauss, however. Especially it was seen that the superhyperfine structure was easily resolved at 300°K. When crystals with low resistivity were used, it was seen that one could not resolve the superhyperfine structure. It was necessary to cool such crystals before the superhyperfine structure was resolvable.

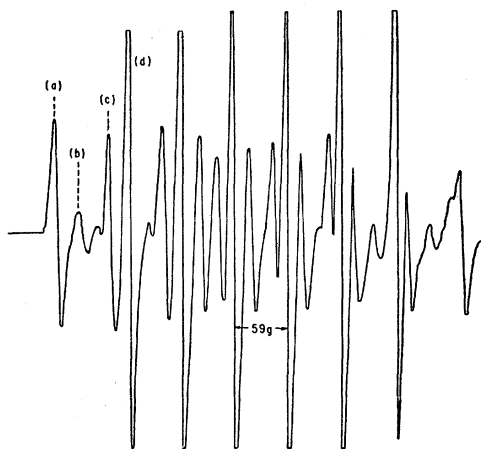


FIG. 2. Absorption observed in CdTe at 4.2°K. The lines noted are assigned as follows (a)  $m = -\frac{5}{2}$ ,  $M = -\frac{3}{2} \rightarrow -\frac{3}{2}$ ; (b)  $m = -\frac{5}{2}$ ,  $M = \frac{3}{2} \rightarrow \frac{3}{2}$ ; (c)  $m = -\frac{3}{2}$ ,  $M = -\frac{3}{2} \rightarrow -\frac{1}{2}$ ; (d)  $m = -\frac{5}{2}$ ,  $M = -\frac{1}{2} \rightarrow \frac{1}{2}$ . The line (c) thus belongs to a different hyperfine group.

This situation is illustrated in Fig. 4, which shows the increasing resolution of superhyperfine structure of a low resistivity crystal as the temperature is lowered. One finally sees well-resolved lines at 4.2°K, comparable to the resolution obtained at 300°K for insulating crystals.

At 300°K, the low resistivity crystal has a resistivity of 5 ohm cm. This indicates a conduction electron concentration of  $10^{17}/\text{cm}^3$  using a mobility of 200  $\text{cm}^2/\text{sec}/\text{volt}$ . At 4.2°K the resistivity increased by a factor of about 10. Assuming a tenfold increase in mobility, this indicates the conduction electron concentration dropped to  $10^{15}/\text{cm}^3$ . The source of electrons is not known. The donor concentration is high enough so that the CdS is almost degenerate. Normally,  $n$ -type CdS is highly resistive at 4.2°K for donors which have been studied.

An interesting aspect of these low resistivity CdS crystals was noted at 4.2°K. It appears that an entirely new  $\text{Mn}^{++}$  spectra is also present, as seen in Fig. 5.

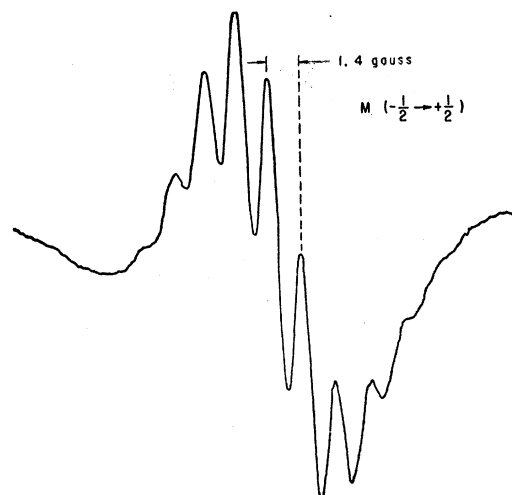


FIG. 3. Superhyperfine structure in CdTe at 4.2°K. Only on  $M = -\frac{1}{2} \rightarrow \frac{1}{2}$  transitions was this structure observable.

This new spectra is weaker than the main spectra by a factor of 50. It consists of 5 groups of lines. These groups have a maximum separation when the  $c$  axis is parallel to the magnetic field. The angular variation is such that it appears that the main feature is the term described by  $DS_z^2$  in the Hamiltonian where the  $D$  here is much larger than the  $D$  term in the spectra described by Dorain. In the normal spectra  $D$  is  $0.00082 \text{ cm}^{-1}$ . Here we have a  $D$  of  $0.0295 \text{ cm}^{-1}$ .

## IV. DISCUSSION

### A. CdTe:Mn

The theoretical expressions needed for the evaluation of the cubic field coefficient,  $a$ , can be readily deduced

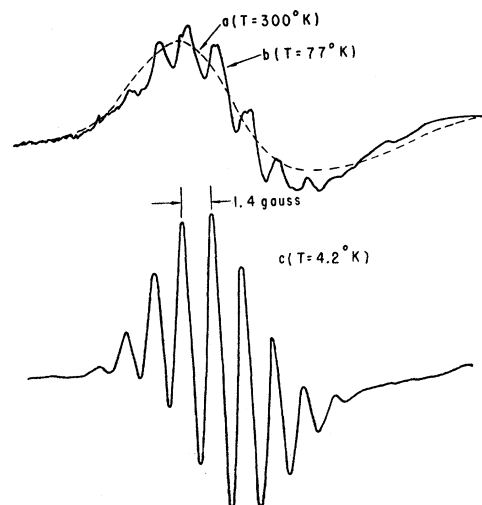


FIG. 4. Absorption at various temperatures in a low resistivity CdS crystal for an  $M = -\frac{1}{2} \rightarrow \frac{1}{2}$  transition. The structure is not observable at all at 300°K (curve a). In insulating crystals the structure is completely resolved at 300°K.

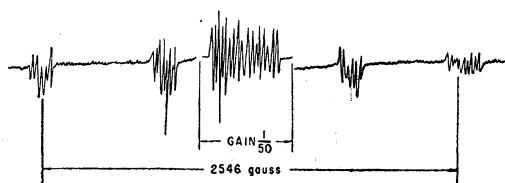


FIG. 5. Anomalous spectra observed in conducting CdS Mn crystals at 4.2°K. The central strong group is the usual spectra associated with CdS:Mn and is 50 times as strong as the anomalous spectra.

from the spin Hamiltonian

$$H = g\beta\mathbf{S} \cdot \mathbf{H} + A\mathbf{I} \cdot \mathbf{S} + (a/15)[T_{40} + (5/14)^{1/2}(T_{44} + T_{4-4})],$$

in which the  $T_{lm}$ 's are functions of the spin operator transforming like the spherical harmonics  $Y_{lm}$ . Specifically,

$$T_{40} = \frac{1}{8}[35S_z^4 - 30S(S+1)S_z^2 + 25S_z^2 - 6S(S+1) + 6S^2(S+1)^2],$$

and

$$T_{4\pm 4} = [(70)^{1/2}/16]S_{\pm}^4.$$

The cubic field coefficient  $a$  is defined so that  $3a$  is the separation of the doublet and the quartet states, into which a cubic crystalline electric field will split the ground state of  $^6S_{5/2}$ . Perturbation calculations give for the separation,  $\Delta H$ , of the fine structure satellites from the principal component ( $M = \frac{1}{2}$ ):<sup>9</sup>

$$M = -\frac{1}{2}; \quad g\beta\Delta H = -\frac{5}{2}a - \frac{5}{16}\frac{a^2}{g\beta H} + \frac{A^2 m}{g\beta H},$$

$$M = \frac{5}{2}; \quad g\beta\Delta H = -2a - \frac{2A^2 m}{g\beta H},$$

$$M = -\frac{3}{2}; \quad g\beta\Delta H = 2a + \frac{2A^2 m}{g\beta H},$$

$$M = \frac{3}{2}; \quad g\beta\Delta H = \frac{5}{2}a - \frac{5}{16}\frac{a^2}{g\beta H} - \frac{A^2 m}{g\beta H}.$$

The above results apply when the magnetic field is along the crystal 4-fold axis. As in ZnS:Mn, the two fine structure components tend to merge on the high field side, indicating that  $A$  and  $a$  have opposite signs.

TABLE I. The properties of  $Mn^{++}$  in  $CaF_2$ ,  $MgO$ ,  $ZnS$  and  $CdTe$ .

Material	$A$ (cm <sup>-1</sup> )	$g$	$3a$ (cm <sup>-1</sup> )	Coordi- nation	Reference
$CaF_2$	0.00978	1.998	0.00019	8	10
$MgO$	0.00810	2.0014	0.00558	6	6
$ZnS$	0.00638	2.0025	0.00233	4	3
$CdTe$	0.0055	2.010	0.0084	4	This paper

<sup>9</sup> Adopting the notation by Matarrese and Kikuchi (reference 3), the fine structure components will be indicated by their upper electron spin magnetic quantum number.

According to Watanabe,<sup>10</sup>  $a$  should be positive. Assigning then,  $m = -\frac{5}{2}$  and  $\frac{5}{2}$  to the low and high field hfs components, respectively, a pattern, as shown in Fig. 6 is obtained. The terms in  $a^2$  have been neglected because their contributions to the separations are of the order of a few tenths of a gauss. Comparison of the calculated and the experimental results gives  $a/A = -0.51$ . Since  $A/g\beta = 59$  gauss,  $a/g\beta = 30$  gauss.

This large value of  $a$  is surprising. Table I gives a summary of the properties of  $Mn^{++}$  in  $CaF_2$ ,  $MgO$ ,  $ZnS$ , and  $CdTe$ , which are all cubic. If it is assumed that the crystalline electric potential arise from point charges of magnitude  $Z$  on the nearest neighbors, the quantity  $R^5(Dq)/Z$  for structures having coordination 4, 6, and 8, respectively, are in the ratio  $(-1):(9/4):(-2)$ .  $R$  is the nearest neighbor distance. The crystal parameters  $a_0$  and the  $R$ - $X$  distances are as indicated in Table II. As pointed out by Baker, Bleaney, and Hayes,<sup>11</sup> the ionic assumption and the known anion-cation distances in  $CaF_2$  and  $MgO$  lead to a ratio of the cubic field

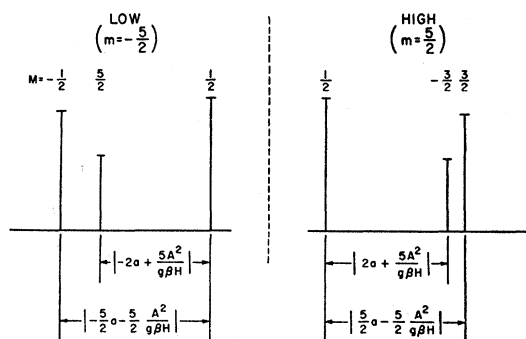


FIG. 6. Plot of predicted spectra and assignments for the case of  $A$  negative and  $a$  positive. The spacing are given by the equivalent values of  $A$  and  $a$  in gauss. For  $CdTe$ ,  $A \rightarrow 59$  gauss and  $a \rightarrow 30$  gauss.

splittings in reasonable agreement. However, they also note that there is a sharp disagreement between  $CaF_2$  and  $ZnS$ , for which the  $a$ 's should be equal according to the ionic model. The discrepancy is even more pronounced for  $CdTe$ ; the calculated ratio of a ( $ZnS$ ): $a$ ( $CdTe$ ) is 2.3. The measured ratio is 0.28. In addition, as first pointed out by Watkins,<sup>12</sup>  $\Delta g$  is positive in contradiction to Watanabe's theory.

It should perhaps be noted that in Watanabe's theory the energy band structure of the diluent matrix is not taken into account. The atomic excited levels of  $Mn^{++}$  that lead to the cubic field splitting and the  $g$  shift are about 3.3 to 5.4 eV above the  $^6S_{5/2}$  ground state. If the band gap is large, such as is the case for  $MgO$  and  $CaF_2$  (about 7 and 10 eV, respectively), it is possible that the ionic theory is applicable. On the other hand, if the

<sup>10</sup> H. Watanabe, Progr. Theoret. Phys. (Kyoto) **18**, 405 (1957).

<sup>11</sup> J. M. Baker, B. Bleaney, and W. Hayes, Proc. Roy. Soc. (London) **A247**, 141 (1958).

<sup>12</sup> G. D. Watkins, Phys. Rev. **110**, 986 (1958).

gap is small, such as with ZnS and CdTe having about 4 and 1 eV, respectively, the applicability of the ionic theory becomes somewhat doubtful. However, a careful theoretical analysis is necessary before any definite comments can be made. On the experimental side, a systematic study of materials such as ZnTe is needed.

It is of interest to note the very short spin-lattice relaxation time at 300°K for CdTe:Mn compared to ZnS or insulating CdS. It should be noted that the CdTe used here was highly resistive so that this effect was not due to a temperature dependent, conduction electron scattering effect. It appears that the strong crystal coupling manifests itself in the spin lattice relaxation time. One can estimate the values of  $T_1$  at 300°K and 77°K from linewidth. The value of  $T_1$  at 4.2°K was estimated to be of the order of 10 milliseconds from saturation behavior. These values are summarized in Table III.

Another significant result is the large superhyperfine structure comparable to that of CdS:Mn. If the superhyperfine structure interaction is assumed isotropic, as indicated by the experimental results, the twelve second nearest cadmiums are all equivalent, in contrast to those of CdS. The terms in the Hamiltonian con-

TABLE II. Crystal parameters  $a_0$  and the  $R$ - $X$  distances for the crystals used.

Crystal	$a_0$ (Å)	$R$ - $X$ (Å)
CaF <sub>2</sub>	5.451	2.36
MgO	4.203	2.10
ZnS	5.412	2.36
CdTe	6.41	2.78

tributing to the superhyperfine structure are given by

$$H_{\text{hfs}} = \sum_{i=1}^{12} A S \cdot I_i.$$

However, all sites are not equivalent in nuclear surroundings because the odd isotopes Cd<sup>111</sup> and Cd<sup>113</sup> constitute only 25% of cadmium, the other isotopes having zero spin. Since  $g(\text{Cd}^{111}) \cong g(\text{Cd}^{113})$ , the probability of occupation of a cadmium site by an odd isotope is  $\frac{1}{4}$  and the absorption lines occur at

$$E = A_{\text{Cd}} m; \quad m = 0, \pm \frac{1}{2}, \pm 1, \dots, \pm 11/2, \pm 6,$$

with relative intensities

$$I(m) = \sum_{m'=m}^{11 \text{ or } 12} \frac{w(2m')}{2^{2m'}} \frac{(2m')!}{(m'+m)!(m'-m)!}.$$

Here

$$w(n) = \frac{12!}{n!(12-n)!} p_0^n p_E^{12-n}$$

with

$$p_0 = \frac{1}{4} \quad p_E = \frac{3}{4}.$$

TABLE III. Estimated value of  $T_1$  for CdTe:Mn at various temperatures.

$T$	$T_1$ (sec)
300 °K	$10^{-8}$
77 °K	$10^{-6}$
4.2°K	$10^{-2}$

The intensities of the 5 strongest components are in the ratio 1.00:0.835:0.499:0.215:0.069. The observed spectrum is in reasonable agreement with the above result. The separation between successive superhyperfine components is 1.4 gauss, so that  $A_{\text{Cd}} = 2.8$  gauss or  $2.6 \times 10^{-4} \text{ cm}^{-1}$ .

### B. CdS:Mn

It has been noted that the superhyperfine coupling obtained for CdS is essentially the same as that for CdTe (our value for  $A_{\text{Cd}}$  in CdS is in agreement with more recent, unpublished measurements by Dorain). This means that in spite of the differences in  $A_{\text{Mn}}$  between these two materials, the measure of the overlap onto the Cd ions is the same. This is important in any theory of the nature of the bonding in these materials. No detailed calculations have been made to date on this point.

Superhyperfine structure in the photosensitive CdS center, tentatively assigned to  $\text{Fe}^{++}$ , was looked for, but was not found.<sup>13</sup> The reason for the absence of structure may be the same as that of  $\text{Cr}^{+++}$  in  $\text{ZnF}_2$ .<sup>14</sup>

The broadening of the lines in conducting CdS is an interesting manifestation of an effect which has been observed in silicon<sup>15</sup> at low temperatures. It was observed that conduction electrons shortened  $T_1$  substantially. In our case a sufficient number of electrons are present in conducting crystals to show this effect at room temperature.

This effect has been treated theoretically<sup>16</sup> and one can estimate the expected magnitude. If we assume a scattering cross section,  $\sigma$ , of  $10^{-16} \text{ cm}^2$  between  $\text{Mn}^{++}$  and conduction electrons, then for  $10^{17} \text{ electrons/cm}^3$  we have

$$T_1 \cong (n\sigma N)^{-1} \cong 10^{-7} \text{ sec.}$$

Thus, it is seen that such an effect could easily broaden lines sufficiently to obscure the superhyperfine structure. The cooling process reduces  $n$  and permits resolution of the structure.

<sup>13</sup> J. Lambe, J. Baker, and C. Kikuchi, Phys. Rev. Letters **3**, 270 (1959).

<sup>14</sup> M. Tinkham, Proc. Roy. Soc. (London) **A236**, 536 (1958).

<sup>15</sup> G. Feher and R. C. Fletcher, Bull. Am. Phys. Soc. **1**, 125 (1956).

<sup>16</sup> D. Pines, J. Bardeen, and C. P. Slichter, Phys. Rev. **106**, 489 (1957).

The anomalous spectra observed in conducting crystals which is characterized by a large  $D$  value as shown in Fig. 5 has not been satisfactorily explained. It may be due to  $Mn^{++}$  which is lodged near some defect in the lattice which produces a strong axial field.

After this work was completed, we learned from Professor W. Hayes that parallel and independent work has been carried out at the Clarendon laboratory, Oxford, and is being readied for publication. Results obtained for CdTe are similar to the data reported here.

## Magneto-Attenuation of Sound in Semimetals: Longitudinal Waves\*

MICHAEL J. HARRISON†

*Department of Physics and Institute for the Study of Metals, University of Chicago, Chicago, Illinois*

(Received April 15, 1960)

The calculation of the magnetic field dependence of ultrasonic attenuation in a semimetal is discussed on a simple model of its band structure. The results are applied to the case where the electron and hole mean free paths are large compared to the wavelength of sound. A series of oscillations and a large peak in the attenuation as a function of magnetic field are derived. The oscillations are geometric resonances of the type previously derived for metals, and the large peak is associated with the presence of density waves in the electron-hole carrier gas. The theoretical results are discussed, compared with experimental data, and found to agree semiquantitatively with the latter.

### I. INTRODUCTION

RECENT experiments<sup>1,2</sup> on the attenuation of ultrasonic waves in semimetallic crystals maintained at liquid helium temperatures have revealed a marked magnetic field dependence over a wide range of field strengths. Some features of the field dependence, in particular the occurrence of geometric resonances,<sup>3,4</sup> are shared by metals<sup>5-9</sup> studied under similar circumstances. The amplitude of the geometric resonances as well as the mean level of attenuation in the region of geometric resonances is significantly less in semimetals than in metals. However there exists for semimetals an extremely large increase in the attenuation as the field is increased past the point where the geometric resonances are no longer observed.<sup>1</sup> In some cases a subsequent decrease in the attenuation has also been observed. In

metals, on the other hand, the attenuation appears to saturate<sup>4-9</sup> under these conditions. This effect constitutes perhaps the chief difference between the behavior of metals and semimetals.

Blount<sup>10</sup> has given a detailed theory of the attenuation applicable to semimetals in the absence of a magnetic field. However, theoretical studies<sup>4,11-14</sup> of the magnetic field dependence of the attenuation have confined themselves to a discussion of a free electron model of a metal. It is the purpose of the present paper to study the magnetic field dependence of the attenuation in a simple model of a semimetal. The methods used are based on those developed in CHH rather than those of Blount. The model consists of the following. We work in the effective mass approximation, and take both electrons and holes to have isotropic effective masses. We describe the modulation of the energies of these particles by the passing sound wave in terms of deformation potential energies proportional to the local dilation in the lattice. The electron and hole energies are then respectively

$$\begin{aligned} E_e &= E_e^0 + V_{De} \nabla \cdot \mathbf{d}, \\ E_h &= E_h^0 + V_{Dh} \nabla \cdot \mathbf{d}, \end{aligned} \quad (1.1)$$

where  $E_e^0$  and  $E_h^0$  are the corresponding particle energies in the unstrained crystal and  $\mathbf{d} \propto \exp[i(\mathbf{q} \cdot \mathbf{r} - \omega t)]$  is the displacement field associated with a sound wave of wave vector  $\mathbf{q}$  and frequency  $\omega$ . (1.1) then defines

\* A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the University of Chicago.

† National Science Foundation Predoctoral Fellow, 1957-1959. Now at the Department of Mathematical Physics, University of Birmingham, Birmingham, England.

<sup>1</sup> D. H. Reneker, Phys. Rev. Letters **1**, 440 (1958); Phys. Rev. **115**, 303 (1959).

<sup>2</sup> Y. Eckstein (private communication).

<sup>3</sup> A. B. Pippard, Phil. Mag. **2**, 1147 (1957).

<sup>4</sup> M. H. Cohen, M. J. Harrison, and W. A. Harrison, Phys. Rev. **117**, 937 (1960), hereafter referred to as CHH.

<sup>5</sup> H. E. Bömmel, Phys. Rev. **100**, 758 (1955); W. P. Mason and H. E. Bömmel, J. Acoust. Soc. Am. **28**, 930 (1956).

<sup>6</sup> R. W. Morse, H. V. Bohm, and J. D. Gavenda, Phys. Rev. **109**, 1394 (1958).

<sup>7</sup> R. W. Morse and J. D. Gavenda, Phys. Rev. Letters **2**, 250 (1959); J. D. Gavenda and R. W. Morse, Bull. Am. Phys. Soc. **3**, 167 (1959).

<sup>8</sup> R. W. Morse, H. V. Bohm, and J. D. Gavenda, Bull. Am. Phys. Soc. **3**, 44 (1958); T. Olson and R. W. Morse, Bull. Am. Phys. Soc. **3**, 167 (1959).

<sup>9</sup> J. R. Neighbours and G. A. Alers, Phys. Rev. Letters **3**, 265 (1959).

<sup>10</sup> E. I. Blount, Phys. Rev. **114**, 418 (1959).

<sup>11</sup> T. Kjeldaas, Phys. Rev. **113**, 1473 (1959).

<sup>12</sup> S. Rodriguez, Phys. Rev. **112**, 80 (1958).

<sup>13</sup> T. Kjeldaas and T. Holstein, Phys. Rev. Letters **2**, 340 (1959).

<sup>14</sup> M. S. Steinberg, Phys. Rev. **109**, 1486 (1958); **110**, 772 (1958).