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Exciton and Magneto-Optical Effect in Strained and Unstrained Germanium*

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Measurements have been made of the direct transition magneto-optical effect in strained and unstrained germanium at 77°K. The results indicate that the absorption peaks correspond to transitions to exciton levels associated with each Landau level in qualitative agreement with the calculations of Loudon, and Howard and Hasegawa. A definitive experiment is suggested to test this theory.

I. INTRODUCTION

Recent experiments[1,2] on the direct transition exciton and magneto-optical effect in germanium have been made for samples glued to a backing, usually glass. It has been pointed out by Macfarlane, MacLean, Quarrington, and Roberts[3] that samples mounted in this way become strained when cooled because of the difference in contraction of the sample and backing. This group made transmission measurements at 77°K on the same germanium sample, first mounted free of any backing, and then glued to a glass substrate. They observed for the backed sample that the exciton absorption, E_x, shifted to higher energies and a second absorption appeared at an energy greater than E_x. The conclusion was that backing the samples on glass produced a compressional strain that distorts the energy band structure. As a further check of this theory, fused silica was used as the backing material to produce a tension on the sample when cooled. The results were a shift of E_x towards lower energy as expected. Edwards and Lazazzera[4] have also reported transmission measurements for free-mounted germanium at 77°K with approximately the same results as found by MMQR. The effect of the strain on the energy band structure has been examined by Kleiner and Roth[5] to obtain information about the deformation potential for the band edges. They concluded that the backing produces a shear strain that splits the valence band into two edges and also increases the energy gap. For the backed samples they associate an exciton level with each valence band edge and thus explain the second absorption. The shift in E_x is associated with the increased energy gap.

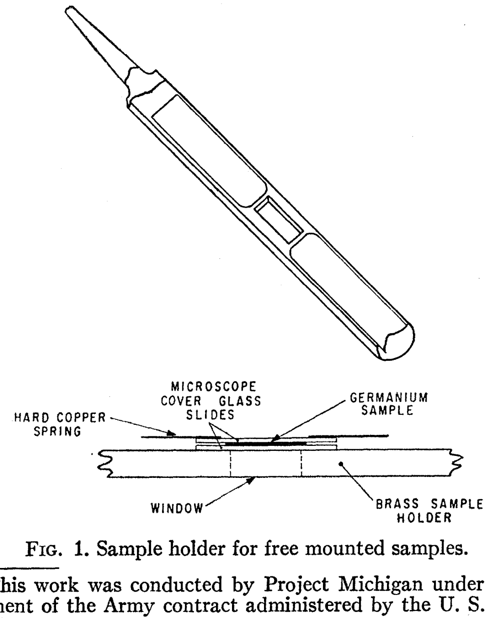

Fig. 1. Sample holder for free mounted samples.

From these investigations, it is therefore obvious that in order for an experiment to accurately represent the intrinsic characteristics of the specimen and not some property of the environment the sample must be mounted strain-free. This problem of a strain-free sample arises only for the case of the direct transition magneto-optical effect. Here the samples must be thin (about 5 microns) to observe the effect. For the indirect transition, the samples are several millimeters thick and self supporting. Thus, the question of strain does not arise.

The purpose of this paper is to report the results of direct transition magneto-optical effect measurements on strained and unstrained germanium samples at 77°K. An interpretation of these data is made in terms of transitions to exciton levels associated with each Landau level. The instrumentation and experimental technique are briefly described in Sec. II. In Secs. III and IV are given the experimental results and analysis for the unstrained and strained specimen, respectively.

II. EXPERIMENTAL TECHNIQUE

The germanium samples were made from either [100] or [110] wafers cut from intrinsic single crystals. The thin specimens were made by careful grinding and polishing techniques, and a special attempt was made to minimize the adverse surface effects of the grinding. Each wafer was cut to a square about 2 cm on a side and

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* This work was conducted by Project Michigan under a Department of the Army contract administered by the U. S. Army Signal Corps.

[1] S. Zwerdling, B. Lax, L. Roth, and K. Button, Phys. Rev. **114**, 80 (1959); hereafter referred to as ZLRB.

[2] D. F. Edwards, R. W. Terhune, M. Bruemmer, and C. W. Peters, Bull. Am. Phys. Soc. 4, 154 (1959).

[3] G. G. Macfarlane, T. P. McLean, J. E. Quarrington, and V. Roberts, Phys. Rev. Letters 2, 252 (1959): hereafter referred to as MMQR.

[4] D. Edwards and V. Lazazzera, Bull. Am. Phys. Soc. **5**, 177 (1960).

[5] W. H. Kleiner and L. M. Roth, Phys. Rev. Letters 2, 334 (1959).

a thickness of about 1 mm. The trimmings are then used as material to help maintain parallel surfaces and are called blocking material. The 2-cm square is glued at the center of a 3-inch diameter optical flat with an acetone soluble thermosetting glue.[6] The trimmings are glued adjacent to this piece in approximately the same position as before they were cut off. In addition, three or four blocks of the same thickness are glued equally spaced at the edge of the flat. To help insure parallel surfaces these eight or nine pieces are glued at the same time using a thin layer of glue and are held under pressure until the glue hardens. The first surface is then ground lightly using 3200 grit carborundum on an optical flat to remove any saw marks. A scratch-free, highly reflecting surface is now obtained by polishing with Linde A[7] on a moist Metcloth[8] stretched over an optical flat. About 25 microns of material is removed by the polishing to reduce any layer damaged by the grinding. The resulting surface is optically flat to less than a fringe over approximately the center 90% of the sample. For this first surface, no attempt is made to reduce the thickness of the germanium wafer. The wafer and blocks are now removed, either by gently heating or dissolving the glue in a solvent, and each piece is turned over and glued with the polished surface towards the optical flat. Sometimes a section of microscope slide is used between the germanium pieces and the flat. The thickness of the wafer is now reduced to about 100 microns using 400 or 600 grit corborundum. Periodic checks are made to insure that the wafer surfaces remain parallel. The wafer thickness is next reduced to about 25–30 microns using 3200 grit. The last 20–25 microns are removed using the Linde A polishing compound on Metcloth as before. Once the second surface has been polished, the sample thickness can be checked from the interference fringes produced by multiple internal reflections in the transparent spectral region of the germanium. By carefully polishing and frequent checking for parallel surfaces, fringes usually can be obtained for samples about 15 to 20 microns thick. The polishing is continued until the samples are about 5 microns thick. The wafer is now masked and cut, using a dental dust blast, into samples about 4 mm×12 mm along definite crystallographic directions. The samples are floated from the microscope slides by dissolving the glue in warm dichlorethylene.

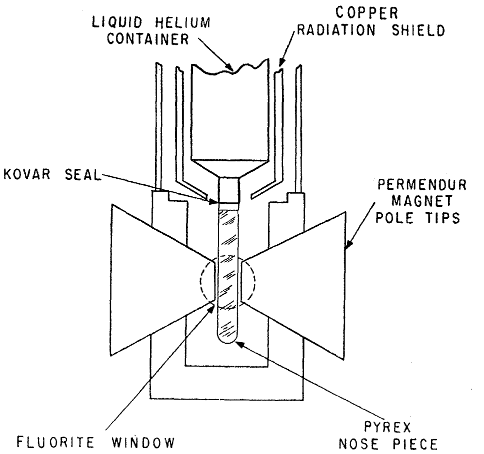

FIG. 2. Sample end of metal liquid helium dewar showing glass nose piece and magnet pole tips.

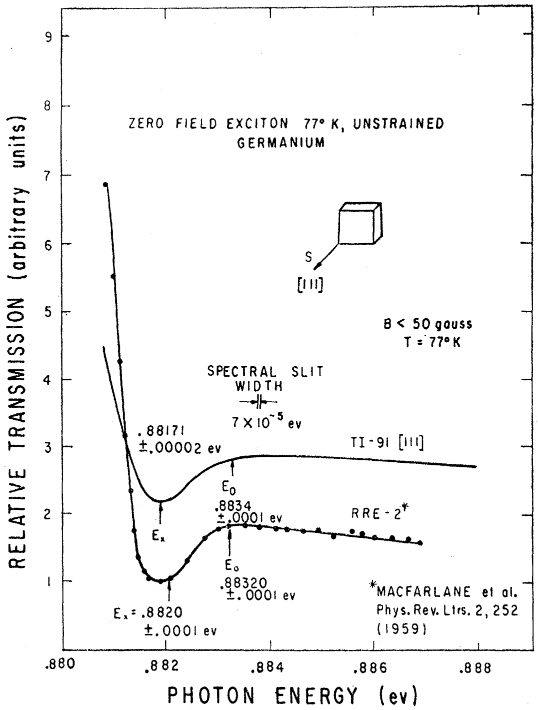

FIG. 3. Zero field exciton transmission for strain-free germanium at 77°K.

The crucial part of the direct transition measurements is obtaining a sample that is strain-free at all temperatures. To help insure this, the samples were mounted free from any backing in the holders of the type shown in Fig. 1. The samples were placed between two microscope cover glass slides and this sandwich is then slipped under the spring clips of the sample holder as shown at the bottom of Fig. 1. This arrangement permits easy handling of the delicate samples and also the free movement of the sample with respect to the cover glass when the holder is cooled. To insure that the sample is at the temperature of the coolant, the entire holder, with sample in place, is immersed in the coolant. The sample end of the metal Dewar[9] used for these measurements is shown in Fig. 2. The nose piece is a Kovar metal-to-glass seal with the infrared beam passing through the

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[6] NU-C-70, Hugh Courtright & Company, 7600 Greenwood Avenue, Chicago 19, Illinois.

[7] Linde A, Linde Company, Division of Union Carbide Corporation, New York, New York.

[8] Metcloth, Buehler, Ltd., Evanston, Illinois.

[9] D. F. Edwards, R. W. Terhune, and V. J. Lazazzera, Rev. Sci. Instr. 29, 1049 (1958).

glass. The tips of the pole pieces are part of the Dewar wall and magnetic fields up to 25 kilogauss are possible.

A high resolution Fastie-Ebert grating spectrometer[10] with 3-meter focal length optics, single pass, and a 127×203 mm (300 lines/mm) Bausch and Lomb grating operated in second order was used for these measurements. The detector was an Eastman lead sulfide detector cooled to 77°K. The entire optical path was evacuated to less than 50 microns pressure with the exception of a short distance between the source and entrance to the evacuated spectrometer tank. This path was filled with dry nitrogen. The purpose of the evacuation and dry nitrogen is to remove all water vapor and CO_2 from the optical path. A combination of an *ADP* crystal and a coated silicon crystal were used in the fore optics to remove the unwanted orders of radiation from the incoming beam. A polaroid-type *HR* polarizer was used in the fore optics for the polarized light experiments. The sample was placed in the aft optics to avoid possible heating by the source. The resolving power of the instrument was not used to its fullest because of the broad nature of the absorption lines. For a resolving power of about 13 000 the spectral slit width was about 1/15 the width of the narrowest line and gave a signal-to-noise ratio of about 100 with the sample in the beam.

III. UNSTRAINED SAMPLE

In our laboratory we have repeated the zero-field exciton transmission measurements of MMQR at 77°K and the results for an unstrained sample are shown as curve *TI*-91, Fig. 3. The exciton absorption line, $E_x = 0.88171 \pm 0.00002$ ev, represents the excitation of an electron from the valence band to the ground state of the direct transition exciton. The spectral slit width for this measurement was 7×10^{-5} ev. For comparison, curve *RRE*-2 is the data of MMQR for a free mounted sample at 77°K. They give the position of the exciton as $E_x = 0.8820 \pm 0.0001$ ev. It should be noted for both curves that there is just the single absorption, E_x, followed by the monotonically decreasing transmission; no other absorptions are present.[11] Elliott[12] has investigated theoretically the direct transition between spherical energy bands including the Coulombic effect between the hole and electron. He showed that one should expect a sharp absorption peak for the exciton followed by a region of continuous absorption beginning at the energy gap, E_0, of the form

$$e^x/\sinh x, \quad \text{where } x = \pi[(E_0 - E_x)(h\nu - E_0)]^{\frac{1}{2}}. \tag{1}$$

By fitting the experimental data of Fig. 3 with the theoretical curve, Eq. (1) the direct transition energy gap, E_0, can be evaluated. MMQR have done this and find $E_0 = 0.8832 \pm 0.0001$ ev. For sample *TI*-91 the direct transition energy gap was estimated to be $E_0 = 0.8834 \pm 0.0001$ ev.

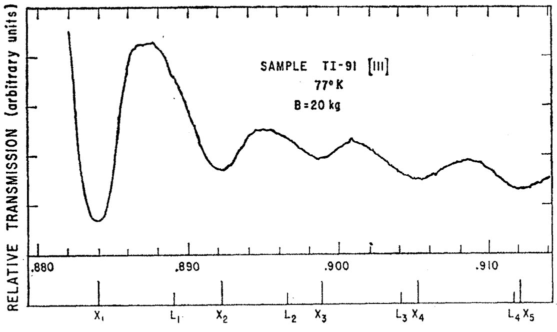

FIG. 4. Portion of magneto-absorption spectrum for strain-free germanium at 77°K and magnetic field of 20 kilogauss. Levels X_i correspond to exciton transitions and L_i correspond to Landau transitions determined from Eq. (2).

With the application of a magnetic field the continuous absorption for $h\nu > E_0$ becomes a series of lines or oscillations, and is called the magneto-absorption effect. A portion of the magneto-absorption spectrum is shown in Fig. 4 for the unstrained sample, *TI*-91, and a magnetic field of 20 kilogauss. On this transmission plot each minimum represents an absorption peak and are represented in the lower figure by the energies X_i ($i = 1, 2, 3, \ldots$). The energy of each of the absorption peaks for various values of applied magnetic field is shown in Fig. 5. From this figure several points should be noted. First, for zero field only the single absorption, E_x, is observed as was shown in Fig. 3. Second, the lowest absorption behaves quadratically with magnetic field and can be traced to zero field. The second level is also quadratic in B and appears to originate from the region of E_x, but the absorption peaks are well defined for fields less than 8 kilogauss. The third point to note is that the higher levels appear to be linear with B. However, if the same change of curvature in going from the lowest to the second level is extended to the higher levels, it is reasonable to believe that any curvature above the second level would not be discernible. If we assume that these higher levels depend linearly on magnetic field, i.e., assume the absorption lines correspond to transitions between Landau levels, then the energy separation between two levels, n and n', will be of the form[13]

$$E_{nn'} = E_0 + (n + \tfrac{1}{2})\hbar\omega_{c1} + (n' + \tfrac{1}{2})\hbar\omega_{c2}, \tag{2}$$

with the condition

$$\Delta n = n' - n = 0, -2,$$

where n and n' refer to the Landau quantum numbers, and $\omega_{c1} = eB/m_1{}^*c$ is the cyclotron frequency for band 1, and similarly for band 2. For zero magnetic field,

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[10] W. G. Fastie, J. Opt. Soc. Am. **42**, 641 (1954); **43**, 1174 (1953).

[11] For sample *RRE*-2 the deviation in the region of 0.8855 ev might be due to a slightly strained sample (see Fig. 7), and would thus account for the difference in the E_x value.

[12] R. Elliott, Phys. Rev. **108**, 1384 (1957).

[13] See for example, E. Burstein, G. S. Picus, R. F. Wallis, and F. Blatt, Phys. Rev. **113**, 15 (1959); L. Roth, B. Lax, and S. Zwerdling, Phys. Rev. **114**, 90 (1959).

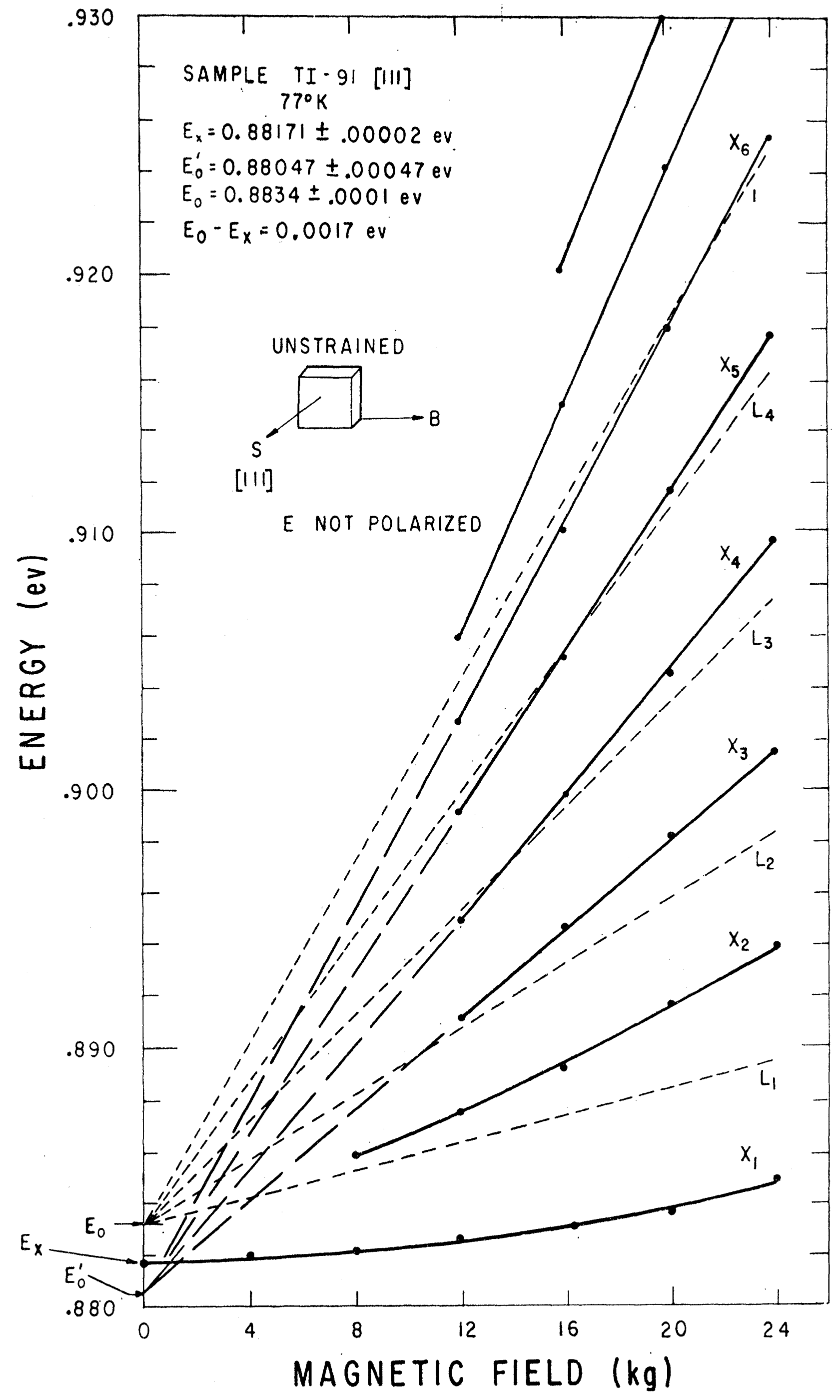

FIG. 5. Magneto-absorption spectrum for strain-free germanium at 77°K. Levels X_i correspond to exciton transition and L_i correspond to Landau transitions determined from Eq. (2).

$E_{nn'}=E_0$, and thus the extension of the higher levels in Fig. 5 to zero field would give the direct transition energy gap $E_0'=0.88047\pm0.00047$ ev, a value less than the exciton energy, E_x. But it is not possible for the energy of the bound electron-hole of the exciton to have a higher energy than the free carriers in the conduction bands. In other words, if the higher levels corresponded to Landau transitions, the exciton would have a negative binding energy which is contradictory to the usual definition of an exciton.

Loudon[14] has extended the calculations of Elliott[12] to the case of optical absorption in the presence of a

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[14] R. Loudon, Doctoral dissertation, University of Oxford, 1959 (to be published).

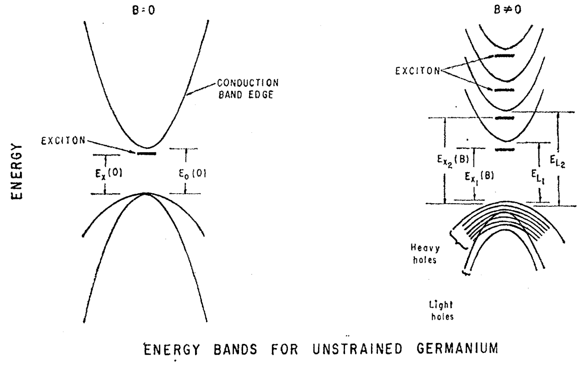

FIG. 6. Energy band structure for strain-free germanium with and without a magnetic field.

magnetic field taking into account the effect of the exciton. His conclusions are that associated with each Landau level in the conduction band there is an exciton level and the most important absorption peaks in the magneto-absorption spectrum correspond to the transitions to these exciton levels with the Landau absorption an insignificant shoulder. This same conclusion was arrived at independently by Howard and Hasegawa,[15] who examined the magneto-absorption spectrum of impurity states. Thus, the conclusion of Fig. 5 is that the higher levels, as well as the two lowest levels, correspond to exciton transitions with a nonlinear field dependence and originate from the region of E_x. The model of this energy band structure is illustrated in Fig. 6. For zero field the exciton absorption $E_x(0)$ is the strong absorption peak followed by the smooth direct transition absorptions for $h\nu \geq E_0$. For $B \neq 0$ the strong absorptions of the magneto-absorption spectrum are for transitions to the exciton levels, $E_{xi}(B)$, $(i=1, 2, \ldots)$ associated with each Landau level $E_{Li}(B)$. The position of the Landau levels can be estimated using Eq. (2) and the cyclotron resonance effective masses, $m_v^* = 0.22m_0$ (heavy hole) and $m_c^* = 0.034m_0$. They are shown in Fig. 4 by the energies $L_i (i=1, 2, \ldots)$ for an applied magnetic field of 20 kilogauss. From this figure the most important absorption is the exciton absorption, x_i, with the Landau absorption an insignificant shoulder. For Landau levels L_1 and L_2 there is some indication of an absorption peak but are insignificant compared to the exciton absorptions. The Landau levels are shown in Fig. 5 by the dashed lines and are labeled L_i $(i=1, 2, \ldots)$. We have arbitrarily considered only transitions between the heavy holes and the conduction band with $\Delta n = -2$. The difference between the Landau level and the corresponding exciton level represents the exciton binding energy. At zero field the exciton binding energy, $E_{exi} = E_{Li} - E_{xi}$, is 0.0017 ev and increases quadratically with magnetic field in qualitative agreement with the calculations of Yafet, Keyes, and Adams.[16] For a given magnetic field, the E_{exi} values increase with the index i. This may just be fortuitous because of the manner used in selecting the Landau levels.

IV. STRAINED SAMPLES

The zero-field exciton transmission is shown in Fig. 7 for a few strained samples at 77°K. The curve *TI*-91 is for the unstrained sample of Fig. 3 and is included for comparison. Curve *BTL*-61 is the transmission of the sample displaying the greatest shift of E_x and presumably greatest strain that we measured. The strain in

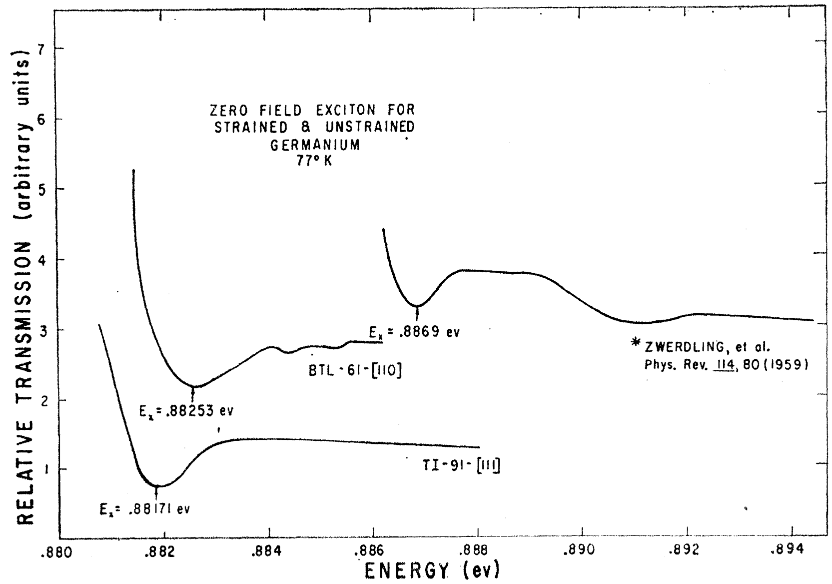

FIG. 7. Zero field exciton transmission for strained germanium samples at 77°K.

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[15] R. E. Howard and H. Hasegawa, Bull. Am. Phys. Soc. 5, 178 (1960).

[16] Y. Yafet, R. W. Keyes, and E. N. Adams, J. Phys. Chem. Solids 1, 137 (1956).

sample *BTL*-61 was accidental and was probably produced by localized binding between the sample and the cover glass slides. Unfortunately, the strain in the sample could not be measured. The curve at the extreme right is that of ZLRB, and is for a sample glued to a glass substrate. The strain in each of these samples is compressional and is produced by the difference in the contraction of the substrate and the sample when cooled. The general properties of the strained samples as compared to the unstrained samples are the following: (1) the position of the absorption E_x is shifted towards higher energies, and (2) additional absorptions are evident at energies greater than E_x. These effects have been attributed[5] to the shear strain which splits the valence band edge into two edges and also increases the energy gap.

The magneto-absorption effect has been measured for a few strained samples and the results are shown in Figs. 8 and 9. Both samples have the same general characteristics as for the unstrained sample, Fig. 5, with the exception of the shift in energies produced by the strains. The two lowest levels of Figs. 8 and 9 behave quadratically with magnetic field, with the lowest level being traced to zero field. The higher levels appear to be linear and extrapolate to a point, the energy of which is less than E_x. It should be noted that sample *TI*-91*A* is under a slight tension as demonstrated by the fact that E_x has shifted towards energy lower than for the unstrained sample, Fig. 3. Thus it is evident from Figs. 8 and 9 that for samples accidentally strained, at least up to a certain amount, the intense transitions are to exciton levels associated with each Landau level the same as for the unstrained sample. For sample *BTL*-61 the magneto-absorption measurements were made using polarized radiation. Within the limits of the experiment no difference could be detected in the positions of the absorptions for $E \perp B$ and $E \| B$, where E is the electric vector for the polarized beam. The strain was compressional and presumably along a [100] crystallographic direction.

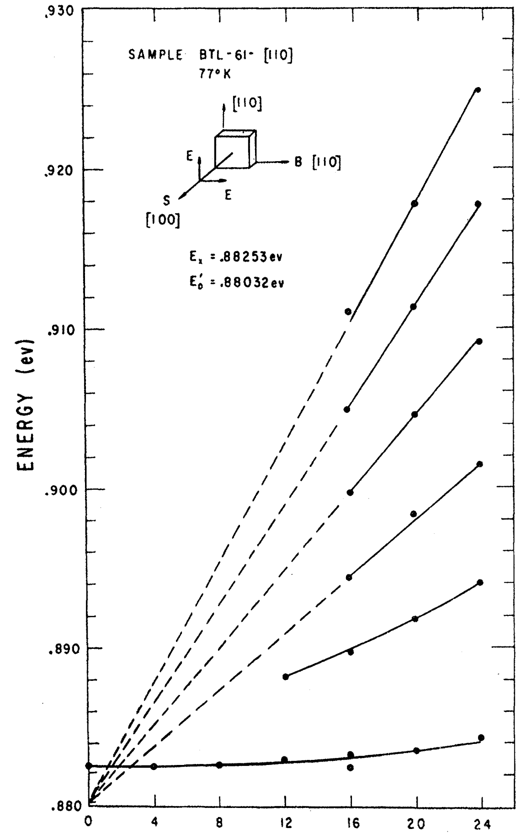

FIG. 8. Magneto-absorption spectrum for a sample under a "slight" compressional strain.

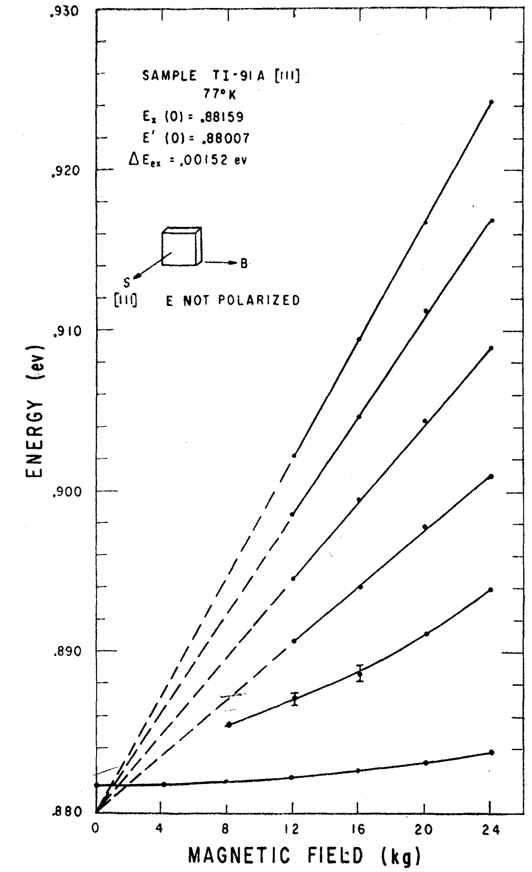

FIG. 9. Magneto-absorption spectrum for a sample under a "slight" tensional strain.

V. CONCLUSIONS

Results of the measurements of the direct transition magneto-optical effect in unstrained and "slightly" strained samples, indicate that the absorption peaks correspond to transitions to the exciton level associated with each Landau level and the Landau absorption is an insignificant shoulder. These experimental results are in qualitative agreement with the calculations of Loudon, and Howard and Hasegawa. For a sample glued to a glass substrate the strain is relatively large and the magneto-absorption spectrum becomes rather complicated. An example of this can be seen from the measurements of ZLRB where at 77°K at least three zero field absorptions are observed.

A definitive experiment that would verify that the intense absorptions were due to excitons would be to measure the photoconductivity at $h\nu = E_{xi}(B\neq 0)$. For a true exciton no photoconductive effect should appear. While this should in principle verify that the absorption is due to an exciton, it may be a difficult measurement to make because of effects such as impact ionization.

ACKNOWLEDGMENTS

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Low-Temperature Specific Heat of Body-Centered Cubic Alloys of 3*d* Transition Elements*

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The electronic specific heat coefficient was measured in the temperature range 1.4° to 4.2°K for 48 solid solution alloys in the following binary systems: Ti-V, V-Cr, V-Fe, Cr-Mn, Cr-Fe, and Fe-Co. The electronic specific heat vs electron concentration curves show three quite well separated regions of high density of states. The first of these occurs in alloys with atomic magnetic moments near zero. The second one is found in alloys which have increasing magnetic moments with increasing electron concentration, up to Fe+35% Co along the Pauling-Slater curve. The third region of high density of states extends from Fe+35% Co to the limit of the bcc solid solutions at Fe+75% Co, a range where the magnetic moment decreases with increasing electron concentration.

INTRODUCTION

THE details of the structure of the *d* band for 3*d* transition elements in the solid state are not definitely known as yet. Various points of view were recently discussed by Mott and Stevens,[1] Lomer and Marshall,[2] and Marshall and Weiss.[3] Experimentally, measurement of the electronic specific heat at low temperatures gives information on the density of states at the Fermi energy level. In the 3*d* transition elements and their alloys the major contribution to the density of states comes from the *d* band. By measuring the electronic specific heat for a series of isostructural solid solution alloys, the density of states in the *d* band can be determined as a function of the electron concentration (the average number of electrons per atom outside the closed argon shell). Low-temperature specific heat results for body-centered cubic Cr-Fe and Cr-Mn alloys have been already published in a brief note.[4] The coefficient of the term of the low-temperature specific heat linear in temperature was found to reach very high values in alloys near Cr+19 at. % Fe, and in the corresponding Cr-Mn alloys. At the time this note was published, it was uncertain whether or not these very high values might be interpreted as electronic specific heat coefficients. The present paper reviews recent information bearing on this question, and it provides additional data extending the electron concentration range of the bcc alloys studied. Measurements were made with 48 alloys in the binary systems Ti-V, V-Cr, Cr-Fe, Fe-Co, V-Fe, and Cr-Mn.

EXPERIMENTAL PROCEDURES

Most of the alloys were prepared by induction melting in recrystallized alumina crucibles in He of one atmosphere. Alloys containing vanadium were arc melted in a water-cooled copper crucible under He atmosphere. All alloy specimens were homogenized for three days at 1170°C in a purified mixture of 92% He+8% H_2 gas, wrapped in Mo or Nb sheets. At the end of the homogenizing anneal the specimens were quenched in cold water. After this treatment, some alloy specimens were cold worked and reannealed at the following temperatures: The $Cr_{0.06}Fe_{0.94}$ specimen

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[1] N. F. Mott and K. W. H. Stevens, Phil. Mag. 2, 1364 (1957).

[2] W. M. Lomer and W. Marshall, Phil. Mag. 3, 185 (1958).

[3] W. Marshall and R. J. Weiss, Suppl. J. Appl. Phys. 30, 220S (1959).

[4] C. T. Wei, C. H. Cheng, and P. A. Beck, Phys. Rev. Letters 2, 95 (1959).