concerned, it is more reasonable to attribute these peaks to the electronic transition occurring at the donor energy levels than to the excitons. On the other hand, there are some reasons which make it difficult to consider that these peaks are a structure-sensitive property as was indicated by Sproull and Tyler; that is, large absorption constant and small temperature shift.

The author intends to continue this work. He wishes to express his gratitude to Dr. Y. Ishikawa, Research Laboratory of Nippon Electric Company, under whom this work was undertaken.

---

[*] Now in the Department of Physics, University of Missouri, Columbia, Missouri.

[1] W. W. Tyler and R. L. Sproull, Phys. Rev. **83**, 548 (1951); W. W. Tyler, Phys. Rev. **76**, 1887 (1949).

[2] R. L. Sproull and W. W. Tyler, in *Semiconducting Materials* (Butterworths Scientific Publications, London, 1951), p. 122.

[3] After this work was performed, the author received a communication from Dr. Sproull that R. J. Zollweg of Cornell University has found similar peaks in this region.

[4] Ishikawa, Sato, Okumura, and Sasaki, Phys. Rev. **84**, 371 (1951).

Mechanism for Photovoltaic and Photoconductivity Effects in Activated CdS Crystals

D. C. REYNOLDS, *Aeronautical Research Laboratory, Wright Air Development Center, Air Research and Development Command, United States Air Force, Wright-Patterson Air Force Base, Ohio*

AND

S. J. CZYZAK, *Physics Department, University of Detroit, Detroit, Michigan*

(Received September 17, 1954)

In previous papers,[1,2] experimental results with activated CdS crystals were reported that could be explained by the Brosser-Kallmann-Warminsky theory of conduction.

Brosser, Kallmann, and Warminsky[3] suggest two possible mechanisms which can explain conduction in activated crystals: (a) They propose that the holes formed by excitation are localized in the filled band and cannot migrate to the electrodes; as long as this is the case, electrons in the conduction band can be in thermal potential equilibrium with the electrodes. This permits a re-supply of electrons from the cathode. The conductivity then depends on the number of bound holes and on the length of time the holes are localized. (b) They apply the Riehl-Schön model. Here it is assumed that part of the excited electrons pass into a band which is somewhere between the conduction band and the filled band and in which the electrons can move freely. The electron density in this band is in thermal potential equilibrium with the electrodes and electrons remain in this band for a relatively long time. As long as there are sufficient electrons in this band, additional electrons can pass from the electrodes. During this period, metallic conduction is possible.

Recent investigation of the spectral response of the photovoltaic effect in activated CdS single crystals[2] shows a response in the red portion of the spectrum. Photoconductivity measurements as a function of wavelength show two peaks: one at the absorption cutoff and the other in the longer-wavelength region. When the photoconductivity is measured from short wavelengths toward long wavelengths and *vice versa*,[1] a shift in the position of the peaks is observed. When the photoconductivity is measured from short to long wavelengths, the peaks are shifted toward long wavelengths because of long-lived electrons in the impurity band; this also causes a tailing out in the long-wavelength region. When the experiment is reversed, photocurrent is not observed until sufficient energy is available to excite electrons to the impurity band; this diminishes the long-wavelength tail.

The energy separation of the bands in CdS would not give rise to the photovoltaic response in the red region mentioned above. The excitation of electrons in impurity levels below the conduction band by light of wavelengths in the red and near infrared could explain the spectral response by allowing a two-step process to the conduction band; however, this would not explain the photoconductivity.

These long lifetimes cannot be explained by the above-mentioned two-step excitation process unless we assume that the holes are fixed. If this were the case, the photovoltaic effect would not be observed. Therefore, to be consistent with both photovoltaic and photoconductivity effects, it appears that the intermediate energy level must be a band. This conforms to the Riehl-Schön model.

---

[1] Reynolds, Czyzak, Allen, and Reynolds (to be published).

[2] Reynolds, Leies, Antes, and Marburger, Phys. Rev. **96**, 533 (1954).

[3] Brosser, Kallmann, and Warminsky, Z. Naturforsch. **4A**, 631 (1949).

Electronic Susceptibility in Certain Alloys[*]

E. N. ADAMS, II, AND R. ZITTER

Chicago Midway Laboratories, Chicago, Illinois

(Received October 18, 1954)

In recent measurements of magnetic susceptibility *vs* composition in the $MgCu_2-MgZn_2$ system (Fig. 1), Klee and Witte[1] have discovered some interesting features in the dependence of susceptibility on electron concentration, and have analyzed the experimental results using the model of nearly free electrons moving in a weak cosine potential. In particular they attribute the two peaks on the left part of the experimental cuve of Fig. 1 to anomalies in the orbital magnetism of the valence electrons associated with the successive touching of the Fermi surface to the two kinds of faces of the

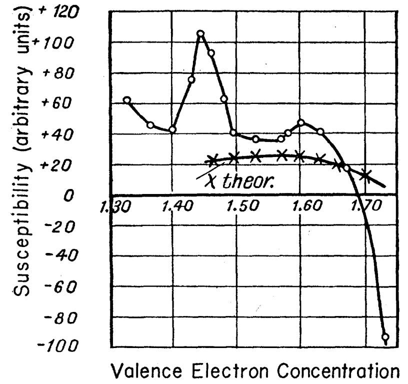

FIG. 1. Valence electron contribution to room-temperature magnetic susceptibility of $MgCu_2$–$MgZn_2$ system (after Fig. 5 of Klee and Witte). χ_{theor} represents the susceptibility of a free electron gas.

higher Brillouin zone of Fig. 2. The purpose of this note is to point out that if one takes such a treatment seriously, the experimental curve actually provides direct evidence of the strong effect of band-band interaction on the electron susceptibility.

For the simple model used by Klee and Witte, all contributions to the orbital susceptibility can be calculated to good accuracy.[2] It is not difficult to show that when the Fermi surface is near a single kind of zone face the nearly free electron model yields (for cubic symmetry):

$$\chi=\chi_0+\chi_1+\chi_3, \tag{1}$$

$$\chi_1=\tfrac{2}{3}N\chi_0\{1-[1-(1/s^2)]^{\frac{1}{2}}\} \qquad (s\leqslant -1) \tag{2a}$$

$$=\tfrac{2}{3}N\chi_0 \qquad (-1\leqslant s\leqslant 1), \tag{2b}$$

$$\chi_3=\tfrac{1}{2}N\chi_0\{s\sin^{-1}(1/s)-3+(5/3)[1-(1/s^2)]^{\frac{1}{2}} +\tfrac{2}{3}s^2(1-[1-(1/s^2)]^{\frac{1}{2}})\} \qquad (s\leqslant -1) \tag{3a}$$

$$=\tfrac{1}{2}N\chi_0\{-\tfrac{1}{2}\pi s-3+\tfrac{2}{3}s^2\} \qquad (-1\leqslant s\leqslant 1). \tag{3b}$$

Here χ_0 is the susceptibility of a free electron gas of the given electron concentration, N is the number of equivalent pairs of zone faces, χ_1 and χ_3 are defined in reference 2, $\chi_0+\chi_1$ gives the total electronic susceptibility in the Peierls[3] approximation, χ_3 is the contribution to χ from the band-band interaction, and s is a dimensionless parameter which measures the difference between the Fermi energy and the energy at the zone faces in units of half the minimum energy gap between bands. The Fermi surface touches the zone face for $s=-1$ and overlaps it for $s=+1$.

Figure 3 shows the behavior of the theoretical susceptibility as the Fermi surface is brought up to a zone face. Curve (1) shows the susceptibility $\chi_0+\chi_1$, curve (2) χ_3, and curve (3) the total susceptibility. It is evident from Fig. 1 that the experimental behavior is like that of curve (3) and not at all like that of curve (1), so the susceptibility contribution χ_3 is qualitatively very important.

Our formulas (2–4) indicate that in the very nearly free electron model the ratio of the peak susceptibility to the free electron susceptibility is independent of the width of the energy gap. Putting $N=12$ (for the large zone faces), we get for this ratio a value of 4.5, in excellent agreement with the height of the first observed peak. Similarly, with $N=4$ (for the small faces), we get a value 2.2 which agrees well with the height of the second peak, although actually our formulas would not be expected to apply to parts of the curve very much to the right of the first peak.

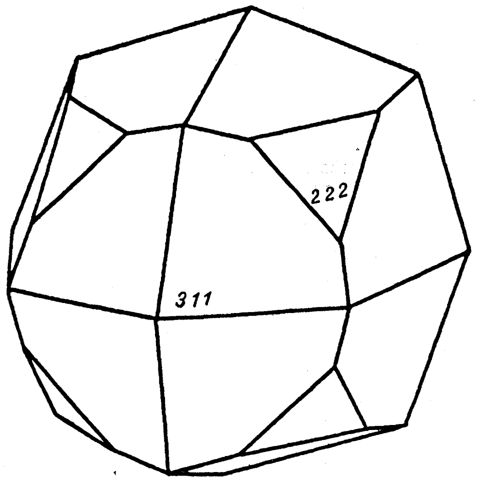

FIG. 2. Higher Brillouin zone formed from planes (3,1,1) and (2,2,2) (after Klee and Witte).

In view of the basic complexity of the susceptibility problem the quantitative success of our theory should

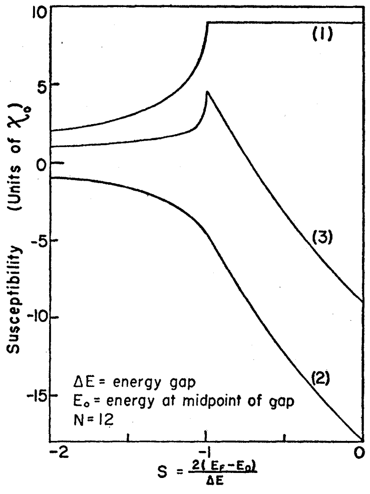

FIG. 3. Theoretical valence electron susceptibility calculated on nearly free electron model. The susceptibility is shown over a range of concentrations about that for which the Fermi surface touches a single zone face. s measures the deviation of the Fermi energy from the midpoint of the energy gap.

not be stressed unduly. Nevertheless, while maintaining strong reservations of judgement because of our very literal application of the nearly free electron model, we are inclined to view the results of Klee and Witte as providing an experimental demonstration of the great strength of band-band interaction in influencing the magnetic properties of electrons in metals.

---

* This research was supported in part by the United States Air Force.

[1] H. Klee and H. Witte, Z. Phys. Chem. **202**, 352 (1954).

[2] E. N. Adams, II, Phys. Rev. **89**, 633 (1953).

[3] R. Peierls, Z. Physik. **80**, 763 (1933).

Quantum Statistics of Closed and Open Systems

F. Ansbacher and P. T. Landsberg

Department of Natural Philosophy, University of Aberdeen, Scotland

(Received November 1, 1954)

The exact mean occupation numbers for an ideal Fermi-Dirac or Bose-Einstein gas on the basis of a canonical ensemble are respectively given by[1,2]

$$n(N,j)=1\bigg/\left\{\frac{Z_{N+1}}{Z_N}\frac{n(N+1,j)}{n(N,j)}\exp\eta(j)\pm 1\right\}\qquad(\text{all } j,\text{ all } N,\ T>0).\quad(1)$$

$\eta(j)$ is the energy divided by κT of the jth quantum state and Z_N is the partition function if N particles are in the volume V. It has been shown[3,4] that these expressions go over into those which are obtained on the basis of a grand canonical ensemble under those limiting conditions for which

$$n(N+1,j)/n(N,j)\sim 1\ (\text{all } j,\ T>0),\qquad(2)$$

where $\sim$ denotes an equality for the limiting case. It has been pointed out[3,4] that condition (2) should hold if the system is infinitely large, but has a finite and nonzero volume density of particles (the "limit L"). The proof of this statement was made to depend on the inequalities

$$n(N+1,j)/n(N,j)>1\ (\text{all } j,\text{ finite } N,\ T>0),\quad(3)$$

which hold for Fermi-Dirac[3] and Bose-Einstein[5] systems. But the argument employed was not rigorous.[6]

In fact, let

$$n(N+1,j)/n(N,j)=1+\alpha(N,j),\qquad \alpha(N,j)>0\ (\text{all } j,\text{ all } N);\quad(4)$$

then

$$\textstyle\sum_j\alpha(N,j)n(N,j)=1.\qquad(5)$$

It is easy to see from (5) that $\alpha\leqslant 1/N$ for *some* (or possibly all) quantum states, so that (2) may hold as $N\rightarrow\infty$, whatever the volume V of the system, However, (5) does not ensure that (2) holds for *all* quantum states, though this now becomes a reasonable conjecture. The argument which was previously used fails now because the inequality $n(N+1,j)/n(N,j)$ $\sum_k n(N+1,k)/\sum_k n(N,k)$ does not necessarily hold for all states j.

We therefore consider it worth while to give an independent and rigorous argument which leads to (2) in the limit L. In the Fermi-Dirac case we use (3) and the result[2]

$$n(N+1,j)=(Z_N/Z_{N+1})[1-n(N,j)]\exp[-\eta(j)].\quad(6)$$

Replacing first $n(N+1,j)$ by $n(N,j)$ on the left, and then $n(N,j)$ by $n(N+1,j)$ on the right, we find

$$\cdots>n(N+1,j)>\mu(N,j)>n(N,j)>\mu(N-1,j)>\cdots,\quad(7)$$

where

$$\mu(N,j)\equiv 1/[1+(Z_{N+1}/Z_N)\exp\eta(j)].\quad(8)$$

For all limiting processes for which $Z_{N+1}/Z_N\sim Z_N/Z_{N-1}$ we must have $n(N,j)\sim\mu(N,j)$. Comparison of (8) and (1) shows then that (2) holds.

In the Bose-Einstein case no relation of type (7) can be found which has equal generality, and one must proceed in a different way. The basic recurrence relation is in this case[5]

$$x_{N+1}a_{N+1}=a_N+1-(1/x_N),\quad(9)$$

where $x_N\equiv n(N,j)/n(N-1,j)$, $a_N\equiv(Z_N/Z_{N-1})\exp\eta(j)$. For all limiting processes for which $a_{N+1}\sim a_N$ ($\sim a$ say) and $x_{N+1}\sim x_N$ ($\sim x$ say), one finds that x must be a solution of $ax^2-(a+1)x+1\sim 0$, whence $x\sim 1$ or $1/a$. The last possibility is ruled out since $x_N>1$, $a_N>1$ for all j and finite N. Hence (2) must hold again in these cases. It remains to discuss the various limiting relations whose existence has been assumed in the above argument.

For Fermi-Dirac systems the relation $Z_{N+1}/Z_N\sim Z_N/Z_{N-1}$ is valid in the limit L (and possibly for other limiting processes). Let

$$P\equiv V^{-1}\textstyle\sum_j\mu(N,j),\quad Q\equiv V^{-1}\sum_j\mu(N-1,j),$$

$$\epsilon\equiv 1-\frac{Z_{N+1}/Z_N}{Z_N/Z_{N-1}},\quad 0\leqslant\epsilon\leqslant 1,$$

$$c_j\equiv\frac{\epsilon(Z_N/Z_{N-1})\exp\eta(j)}{1+(Z_N/Z_{N-1})\exp\eta(j)}.$$

Then

$$VP=\textstyle\sum_j[1+(Z_N/Z_{N-1})\exp\eta(j)]^{-1}[1-c_j]^{-1},$$

and

$$\frac{1}{1-c_j}\geqslant 1+\frac{\epsilon Z_N/Z_{N-1}}{1+(1-\epsilon)Z_N/Z_{N-1}}.$$