must have $ql \ll 1$, where l is the electron mean free path, and $q \ll \omega_c v_F^{-1}$, where v_F is the Fermi velocity.

[3] It can easily be seen that if $\vec{B}_0$ is not parallel to the x axis, $\lim q_z^2/q_y^2 \neq -1$ as $|q_y| \to \infty$. Therefore all the terms involving q will be much larger than those in which q does not appear. If $\vec{B}_0$ is parallel to the x axis, ϵ_{xy}, ϵ_{xz}, ϵ_{yx}, and ϵ_{zx} vanish, so that our approximation is valid in any case.

[4] A number of special cases, including all retardation effects, have been investigated in detail. This more detailed work will be published elsewhere.

[5] Because we have taken $\underline{\epsilon}(\omega)$ to be independent of q, the magnetic permeability is equal to unity and $\vec{B}$ is equal to $\vec{H}$.

[6] Throughout this paper we have treated ϵ_L as a constant. In fact, Eq. (12) holds without change if $\epsilon_L = \epsilon_\infty(\omega^2 - \omega_L^2) \times (\omega^2 - \omega_T^2)^{-1}$, where ϵ_∞, ω_L, and ω_T are the high-frequency dielectric constant, longitudinal-optical-, and transverse-optical-phonon frequencies of a polar semiconductor, respectively. The solution of Eq. (12) in that case is slightly more complicated, but it gives the coupled magnetoplasma-optical-phonon surface waves. Further details on this magnetoplasmon–optical-phonon coupling will be presented elsewhere.

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High-Resolution X-Ray Photoemission Spectrum of the Valence Bands of Gold[†]

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(Received 16 December 1971)

High-resolution gold-valence-band photoemission spectra were obtained by the use of monochromatized Al $K\alpha$ radiation and a single-crystal specimen. After background and scattering corrections were made, the results were compared directly with broadened theoretical density-of-states functions. The following conclusions were drawn: (i) ***Relativistic*** band-structure calculations are required to fit the spectrum. (ii) Both the Korringa-Kohn-Rostoker calculation of Connolly and Johnson and the relativistic-augmented-plane-wave calculation by Christensen and Seraphin give density-of-states results that (after broadening) follow the experimental curve closely. (iii) Of the theoretical functions available to date, those with full Slater exchange agree best with experiment (perhaps because of a cancellation of errors). Fractional ($\frac{2}{3}$ or $\frac{5}{6}$) exchange gives d bands that are too wide. (iv) Eastman's 40.8-eV ultraviolet photoemission spectrum is similar to the x-ray spectrum, suggesting little dependence on photon energy above 40 eV. (v) Both (ii) and (iv) imply an absence of strong matrix-element modulation in the photoemission spectrum of gold.

I. INTRODUCTION

Electronic band structures are of fundamental importance in understanding properties of metals. A knowledge of the valence-band density of states of a metal can, in principle, yield considerable information about that metal's band structure. X-ray photoemission experiments, in which valence electrons are ejected from the specimen by photons from a monochromatic source and energy analyzed in an electron spectrometer, yield spectra that are closely related to the valence-band density of states. However, the extent to which these photoemission spectra and the density of states can be directly compared is still somewhat uncertain.

In this paper the high-resolution x-ray photoemission spectrum of the valence band in a gold single crystal is reported.[1] The spectrum is compared with lower-energy photoemission spectra and with band-structure results. The following questions are at least partially answered in the affirmative: (a) Do ultraviolet photoelectron spectroscopy (UPS) results approach x-ray photoelectron spectroscopy (XPS) data as the uv photon energy increases toward the upper end of the readily available energy range (~40 eV)? (b) Is it meaningful to compare XPS spectra directly with valence-band densities of states, or are matrix-element-modulation effects so large as to obviate such comparisons? (c) Can XPS spectra establish the necessity for relativistic band-structure calculations in heavy elements? (d) Are XPS spectra sensitive enough to distinguish critically among different theoretical band-structure calculations?

Experimental procedures are described and results presented in Sec. II. In Sec. III these results are compared with theory and addressed to the above questions.

II. EXPERIMENTAL

A gold single crystal of 99.9% purity was cut to provide samples with (100), (110), and (111) faces. These were polished, etched, and annealed. Spectra were taken at room temperature and in a sample chamber pumped to about 10^{-7} Torr, on a Hewlett-Packard ESCA spectrometer. This spectrometer

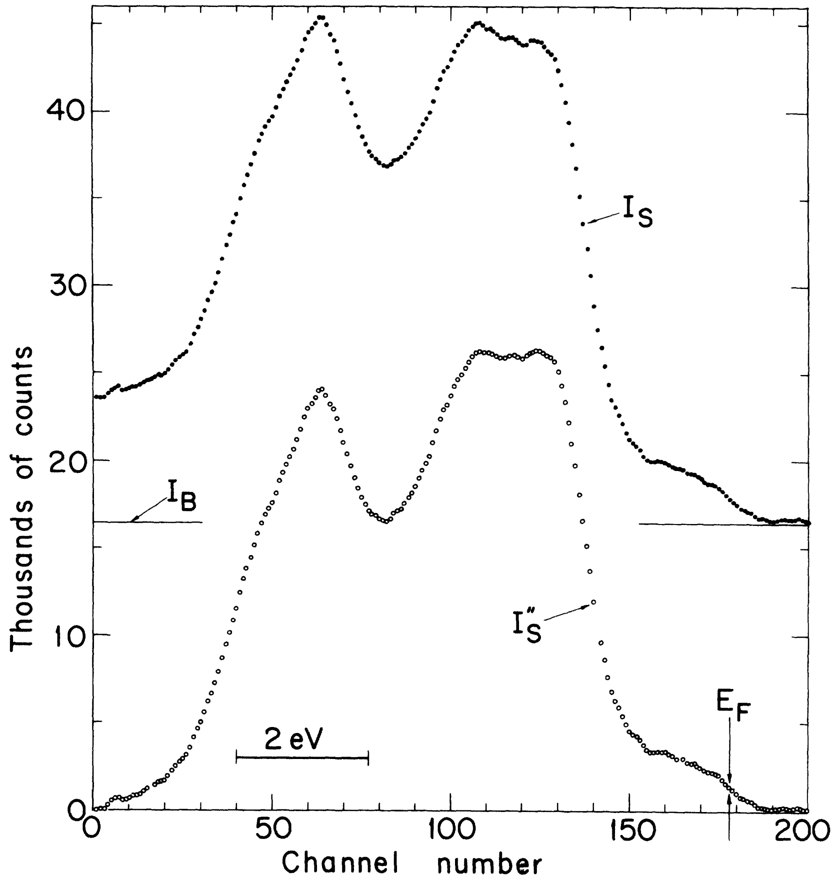

FIG. 1. X-ray photoemission spectrum of the gold valence bands before and after corrections for background and scattering.

employs monochromatized aluminum $K\alpha_{1,2}$ (1486 eV) radiation: It should in principle be possible to reduce the previously obtainable instrumental resolution[2,3] of 1.0 eV by a factor of 2 or more. The spectrum given below shows a definite improvement over earlier spectra. Although it is not possible to distinguish among various sources of broadening as yet, the apparent resolution obtained in this work is about 0.6 to 0.8 eV.

Under the above experimental conditions, which would be inadequate for most metals, gold is expected to retain a surface that is relatively free of adsorbed gases. That the active sample[4] was in fact predominantly gold metal was demonstrated by monitoring the Au $N_{\text{VI,VII}}$ doublet, which was very clean. In addition, the oxygen-1*s* line and carbon-1*s* line were barely detectable, whereas both are large in a sample which has a layer of oxide. More detailed surface studies under carefully controlled conditions are planned. Meanwhile, the rather conservative conclusions given below are believed to be justified in light of the sample conditions described above.

Spectra from specimens in the three crystal orientations were very similar. A (110) spectrum, which had the best statistical accuracy, was analyzed for comparison with theory. The data-reduction procedure consisted of three steps. First, the raw data were smoothed several times by the use of the relation

$$I_S(N) = \tfrac{1}{4}[I(N-1) + 2I(N) + I(N+1)] \quad . \tag{1}$$

Here $I_S(N)$ is the intensity in channel N after the smoothing operation. The main purpose of this step is the elimination of small systematic variations in intensity, of instrumental origin. These data were smoothed six successive times; this had only a negligible effect on spectral resolution. A plot of the result is shown in Fig. 1.

The second data-reduction step was background subtraction. The position of the Fermi energy was easily identified in the raw spectrum by a step in the intensity (it was also established by the decelerating voltage of the electrostatic spectrometer). The spectral intensity was very constant above this energy. This intensity I_B was taken as background and was subtracted from the intensity throughout the valence-band energy range (i.e., for $-9.5 \leq E - E_F \leq 1$ eV). The intensity in channel N after this correction is denoted by $I'_S(N)$. Thus

$$I'_S(N) = I_S(N) - I_B \quad . \tag{2}$$

This correction is always necessary for x-ray photoemission spectra. The background in most spectrometers arises largely from photoelectrons that are ejected by high-energy bremsstrahlung and that undergo subsequent energy loss in the sample. This source of background is not present in the Hewlett-Packard spectrometer, because of monochromatization of the exciting radiation, but contributions from detector noise remain.

The final data-reduction step was a correction for inelastic scattering. In earlier work,[2] this correction was made by the use of a response matrix. For the present data a simpler procedure was possible, because there were no satellite x-ray peaks and a correction was necessary only for a constant inelastic tail.[5] In making the correction it was observed that the spectrum returned to a constant level at kinetic energies below those of the valence bands. This level was somewhat higher than the base line above the valence levels. The difference was assumed to arise entirely from valence-band photoelectrons that were inelastically scattered before leaving the sample. This interpretation has been qualitatively well established by earlier work,[2] but it could be slightly wrong in detail. Even if it is, however, the corrected spectrum would be only slightly affected, and the interpretations given below would not be affected.

The inelastic-scattering correction was made by subtracting from $I'_S(N)$ a quantity proportional to the valence-band area at higher energies to give $I''_S(N)$, under the condition $I''_S(0)=0$. Here the double-prime notation denotes the intensity after correction for scattering, and channel 0 represents an energy just below the valence bands. Thus

$$I''_S(N)=I'_S(N)-I''_S(0)\left(\sum_{N'>N} I'_S(N')\Big/\sum_{N'>0} I'_S(N')\right). \quad (3)$$

This equation should in principle be iterated, but iteration was unnecessary for the gold spectrum because the correction was small. Figure 1 shows I_S and I''_S together, to indicate the effect of data reduction on the spectrum.

III. COMPARISON WITH THEORY

The final corrected spectrum I''_S should be closely related to the density-of-states function $\rho(E)$ that may be obtained by sampling procedures from band-structure calculations. An XPS spectrum is not expected to be affected significantly by the final-state density of states (as is the case in UPS), because at energies in the 1.5-keV range the density of states should be essentially featureless. There are other reasons that a direct comparison of I''_S and $\rho(E)$ may not be valid. These were discussed in some detail earlier.[2] The conclusion was drawn that it would be difficult to estimate the extent to which I''_S should resemble $\rho(E)$. The approach taken below is simply to plot the two together for comparison.

Nonrelativistic band-structure calculations give density-of-states histograms differing from I''_S so much that there is no value in plotting them. Such a plot was made earlier for platinum.[2] The good agreement of the two-peak form of I''_S with relativistic band-structure calculations appears, on the other hand, to establish immediately that relativistic effects must be considered in discussing the band structure of gold. This has been pointed out earlier by Christensen and Seraphin[6] and by Smith,[7] among others.

Six theoretical results are available for the relativistic band structure of gold. Sommers and Amar[8] used the Korringa-Kohn-Rostoker (KKR) approach. They did not give $\rho(E)$, so a direct comparison with I''_S is not possible. It is clear, however, that their results give a valence bandwidth considerably larger than the experimental width. This has been attributed by Christensen and Seraphin[9] to the use of $\frac{2}{3}$ Slater exchange by Sommers and Amar. Indeed, in another KKR calculation, Connolly and Johnson[10] used full Slater exchange and obtained a smaller valence bandwidth that agrees well with experiment.

None of the presently available band-structure calculations is close enough to *ab initio* quality that a single feature (such as $\frac{2}{3}$ vs full Slater exchange) can be definitively isolated by comparison with experiment. Thus, the comments below on the superior agreement with experiment of band structures based on full exchange are empirical observations, rather than assertions that full exchange is really better. Because of the possibility of cancellation of errors in existing calculations, $\frac{2}{3}$ exchange may ultimately prove to be preferable.

Three relativistic-augmental-plane-wave (RAPW) calculations of the valence-band structure of gold have been reported. Ramchandani[11] used full (1), $\frac{5}{6}$, and $\frac{2}{3}$ Slater exchange, and concluded that full exchange was best. On comparison of his density-of-states histograms with I''_S, it is obvious by inspection that his full-exchange results are in reasonable agreement with I''_S, while the other two are not even remotely similar. Kupratakuln,[12] on the other hand, has done essentially the same calculation, also with full, $\frac{5}{6}$ and $\frac{2}{3}$ exchange, and has concluded that the best results are obtained with an exchange coefficient of $\frac{19}{24}$. Detailed comparisons of the two sets of results show that they are in serious conflict, with Kupratakuln's results showing extreme sensitivity to the exchange coefficient and his "$\frac{19}{24}$" band structure being in reasonably good agreement with Ramchandani's full-exchange results. Christensen and Seraphin[9] have also reported an RAPW calculation, with full Slater exchange. The

TABLE I. Comparison of gold d-band parameters.

Description	ΔE_B(eV)[a]	ΔE_d(eV)[b]	$E_F - E_d$(eV)[c]	Ref.
KKR	0.79	5.25[d] (5.18)	1.89[d] (1.93)	10
RAPW	0.54	5.54 (5.58)	1.56 (1.41)	11
RAPW	0.78	4.90 (4.92)	2.21 (2.20)	12
RAPW	0.85	5.07 (5.12)	2.17 (2.04)	9
Interpolation	0.92	5.67 (5.64)	2.34 (2.18)	13
Experiment	···	5.24	2.04	This work

[a] FWHM of the Poisson broadening function by which theoretical band-structure histograms were multipled.

[b] FWHM of the d band.

[c] Energy difference from Fermi level to a point half-way up the higher-energy d-band peak.

[d] Values in parentheses were taken from smoothed curves. Values without parentheses were evaluated before smoothing. The accuracy is 0.1 eV.

energy bands in this case resemble Ramchandani's full-exchange results and Kupratakuln's "$\frac{19}{24}$"-exchange results much more closely than the $\frac{5}{6}$- or $\frac{2}{3}$-exchange results of the former or the full or $\frac{2}{3}$ results of the latter. Apparently, Kupratakuln has used a different Slater-exchange-coefficient scale factor than the authors of Refs. 8–12.

Smith and Traum[13] have simulated a relativistic band structure by an interpolation scheme due to Hodges, Ehrenreich, and Lang[14] and Ehrenreich and Hodges.[15] This scheme inserts spin-orbit coupling into nonrelativistic band-structure results.[13]

Theoretical $\rho(E)$ functions are reported as histograms. As such, they cannot be readily compared with experimental spectra, because the latter are broadened by instrumental resolution and relaxation effects.[2] For this reason the theoretical histograms were broadened before the comparison was made. First, the histogram was converted into digital form by measuring the lengths of the bars in the published histograms. Next, broadening was done by a smoothing operation similar to that given in Eq. (1). The operation was repeated until the theoretical $\rho(E)$ was judged to resemble I_S'' most closely, for each case. Table I lists ΔE_B, the full width at half-maximum height (FWHM), for the (optimized) broadening applied to each theoretical curve. It can be inferred from the fact that the broadening was optimized in each case that the effective experimental resolution from all sources is in the 0.6- to 0.8-eV range. Also listed are ΔE_d, the full width at half-maximum height of the d bands, and $E_F - E_d$, the energy difference between the Fermi energy and a point on the higher d-band peak that is half the peak height. The last two quantities were evaluated before and after broadening, to ensure that the broadening process did not distort their values.

Finally, each broadened theoretical $\rho(E)$ curve was multiplied by a scale factor that made it about the same average height as I_S''. Each $\rho(E)$ is plotted with I_S'', separately, in Figs. 2–6.

IV. DISCUSSION

Cursory inspection of Table I and Figs. 2–6 shows that the over-all agreement between theory and experiment is good. The quality of agreement varies sufficiently, however, to favor some of the theoretical curves over others, and to draw some useful conclusions.

Connolly and Johnson's results (Fig. 2) for $\rho(E)$ follow the experimental curve very closely. The d-band widths are in essentially perfect agreement. The position of Connolly and Johnson's d bands is 0.1 to 0.2 eV closer to E_F than the experimental value. The spectral shapes are very close (perhaps surprisingly so), with the smaller low-energy peak showing slightly poorer agreement than the high-energy peak. The more intense component of the low-energy peak lies at −5.7 eV (theoretical) vs −6.15 eV (experimental). Even if the d bands were lowered in energy to coincide over all better with experiment, the experimental intensity of the smaller component of the lower-energy peak would be much smaller than theoretical. This may in part be a consequence of some admixture of s-like character, which would imply a lower photoemission intensity than that of d electrons. The very good over-all agreement in this case indicates that the relativistic KKR method can yield very good results for the gold d bands. Full Slater exchange was used in the Connolly and Johnson calculation, giving correct d bandwidths, while the Sommers and Amar KKR calculation, with $\frac{2}{3}$ Slater exchange, gave bands that were far too wide. Thus full Slater exchange would appear to be preferable in a relativistic KKR calculation on gold. The imposition of self-consistency restraints might reverse this con-

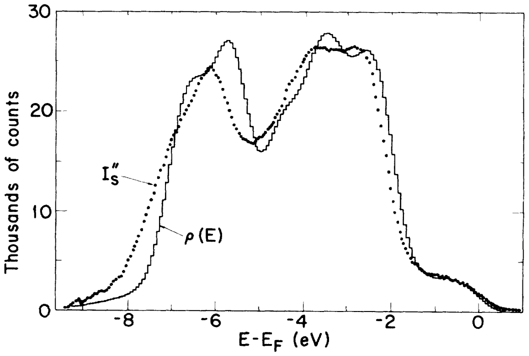

FIG. 2. Comparison of I_S'' with broadened density-of-states function $\rho(E)$ from the relativistic KKR band-structure calculation of Connolly and Johnson (Ref. 10).

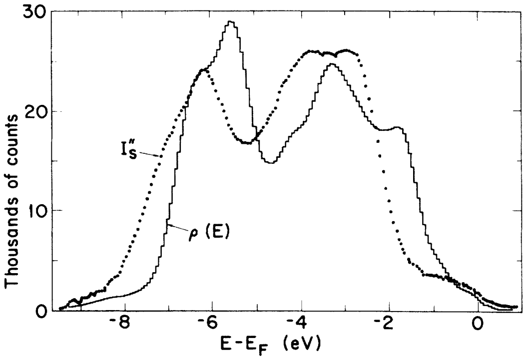

FIG. 3. Comparison of I_S'' with broadened density-of-states function $\rho(E)$ from RAPW band-structure calculation of Ramchandani (Ref. 11).

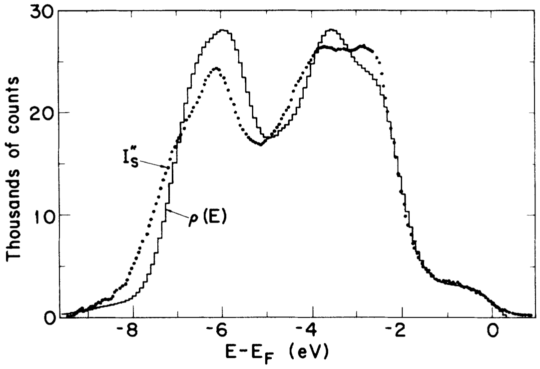

FIG. 5. Comparison of I_S'' with broadened density-of-states function $\rho(E)$ from the RAPW band-structure calculation of Christensen and Seraphin (Ref. 9).

clusion.

Although the same principal features of the valence *d* bands are visible in Ramchandani's RAPW calculation (Fig. 3), detailed agreement is absent. Christensen and Seraphin have attributed the lack of agreement between Ramchandani's calculation and their own (both RAPW, with full exchange) to the use by Ramchandani of a matrix too small to achieve convergence.

Kupratakuln's RAPW results, with $\frac{19}{24}$ exchange, are fairly close to experiment (Fig. 4), but his *d* bands are too narrow. Because his exchange scale factor appears to differ from that of the other calculations, little more can be said about this result.

The full-exchange RAPW curve of Christensen and Seraphin (Fig. 5) follows the experimental spectrum about as well as did that of Connolly and Johnson. The former appears to reproduce the *d*-band position slightly better, while the latter has a slight edge in regard to *d* bandwidth. Both, however, show very good agreement with experiment. If the experimental spectrum can be made slightly sharper in the future, it may become feasible to make a detailed analysis of the components of each of the two main peaks in terms of individual energy bands.

The interpolated band-structure results of Smith and Traum (Fig. 6) give a good representation of the experimental spectrum at high energies, but bandwidth is about 0.4 eV larger.

In an earlier paper,[1] it was predicted that valence-band ultraviolet photoemission spectra, which vary strongly with energy, should approach XPS spectra as the photon energy is raised. This prediction is nicely confirmed for gold by comparing the spectra of Eastman and Cashion[16] between 10.2 and 26.9 eV and the (low-resolution) 40.8-eV curve by Eastman[17] with the present results. The good agreement between the spectra for 40.8- and 1486-eV photons, together with their agreement with theoret-

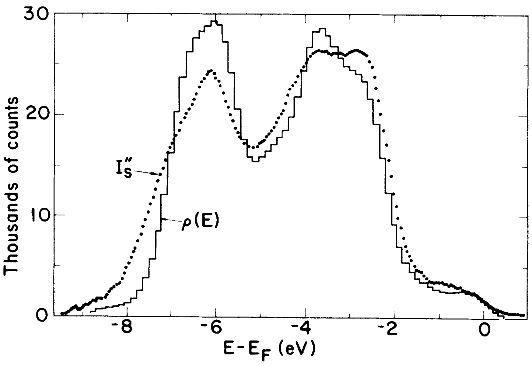

FIG. 4. Comparison of I_S'' with broadened density-of-states function $\rho(E)$ from the RAPW band-structure calculation of Kupratakuln (Ref. 12).

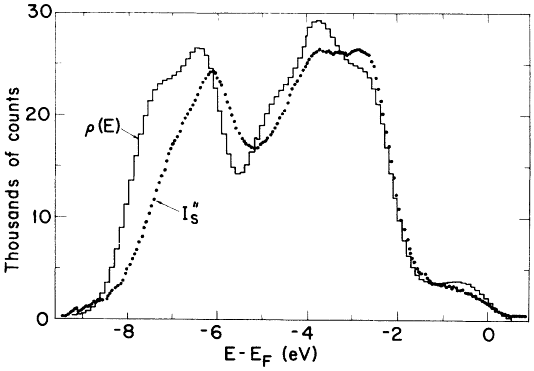

FIG. 6. Comparison of I_S'' with broadened density-of-states function $\rho(E)$ from the interpolated-band-structure calculation by Smith and Traum (Ref. 13).

ical $\rho(E)$ curves, strongly suggest that "matrix-element modulation"[18] of these spectra is a small effect. The reason for this is not well understood.

ACKNOWLEDGMENTS

Dr. A. Malera was most helpful in running many gold spectra on the Hewlett-Packard ESCA spectrometer. Professor G. Somorjai generously provided a gold crystal and instructions on how to prepare it. Mrs. Winifred Heppler prepared the specimens and, together with Mrs. Penny Fink and James Davis, assisted in data reduction. The author also had helpful discussions and/or communication with Professor Marvin Cohen, Dr. Dean Eastman, Dr. Neville Smith, and Professor J. W. D. Connolly.

[†] Work performed under the auspices of the U. S. Atomic Energy Commission.

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Monotonic Behaviors in Semimetals in Strong Magnetic Fields

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In sufficiently strong magnetic fields, all except the lowest of the Landau levels of electrons or holes in a semimetal may have crossed over the Fermi level. At sufficiently low temperatures, the probability of an electron or a hole being in the levels other than the lowest one then becomes negligibly small. Under these conditions, the motion of the charge carriers is essentially of one degree of freedom. Associated with such motion, the density of the charge carriers, the chemical potential, the total energy, the magnetic moment, and the specific heat exhibit monotonic variations in an increasing magnetic field. A theoretical analysis is presented to show these monotonic behaviors. Both zero temperature and low temperature are considered. The condition and the behavior of a magnetic-field-induced semimetal-semiconductor transition are discussed and compared with experimental work. A possible specific-heat anomaly is indicated.

I. INTRODUCTION

Semimetals are characterized by the energy overlap of the conduction band (electrons) and the valence band (holes). In the presence of a magnetic field, the energy levels of both electrons and holes are quantized. These quantized Landau levels move relative to the band structure when the magnetic field intensity changes. In a sufficiently strong magnetic field, the energy levels other than the lowest one in either band may have crossed over the Fermi level (chemical potential); therefore, most