plexity of the anisotropic superfluid state, and it may be unlikely that all aspects have been correctly treated here.

I would like especially to acknowledge the continued stimulation of my interest in this subject by C. M. Varma, and innumerable discussions with him. I want to thank D. D. Osheroff for patient discussions of the data, W. F. Brinkman for a remark on the validity of sum rules, and J. Serene for pointing out an error in Ref. 3.

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Valence Band of Mg_2Sn Determined by Auger and Photoemission Spectroscopy

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It is shown that Auger spectroscopy can be used to determine the density of valence states in compound semiconductors. We determined the density of valence states by this method in Mg_2Sn and find it in basic agreement with those which we obtained by x-ray– and uv-induced photoelectron spectroscopy. A comparison is made with the calculated Mg_2Sn valence band. The Mg_2Sn valence band obtained by Auger spectroscopy (involving the *KL* transition in Mg) is contrasted with the analogous spectrum for Mg metal.

Measurements of valence-band densities of states have recently been carried out by a number of authors using electron-emission spectroscopy.[1-5] Depending on the way the emitted electrons were originally excited, either by x-rays or far-ultraviolet radiation, the experimental methods are referred to as x-ray–induced electron-emission spectroscopy (XPS) (also called ESCA) and uv-induced electron-emission spectroscopy (UPS). Measurements with both methods have resulted in a number of experimental valence-band densities of states for several metals and semiconductors.[1-6]

Each of these methods has its advantages and drawbacks. These are caused mainly by differences of the depth of the surface layer which is sampled and by the effect of transition probabilities to the quasicontinuous final states. XPS measurements sample a deeper layer (~ 25 Å) than UPS (~ 5 Å) because of the higher velocity of the escaping electrons and are therefore more characteristic of the bulk properties: They should be preferred if simultaneously good resolution is obtained. On the other hand, with present experimental setups, the resolution is usually better for UPS measurements for which the condition of the surface plays a more important role. The second effect manifests itself as a dependence of the "nominal" valence-band density of states on the energy of the exciting uv radiation. However, as long as valence-band spectra obtained with 21- and 41-eV photons are similar, it is reasonable to conclude that the effects of absorption and of escape probabilities on the "nominal" density of valence states are negligible.

In this Letter we compare the above methods with a third way to measure the valence-band density of states which, in conjunction with other high-energy spectroscopic measurements, offers wide possibilities for the analysis of the valence bands, especially in compound semiconductors. This method is based on the Auger effect,[7] usually related to core states of atoms described by *WXY* (*W* denotes the core level where initially a hole is created by emission of an electron, *X* denotes the core level from which an electron is provided to fill the hole in the energetically deeper-lying *W* level, and *Y* the level from which another electron is expelled). If one of the two levels *X* or *Y* happens to be the valence band, one might expect Auger-emitted electrons with a kinetic energy distribution analogous to the density of valence states. The advantages of the XPS method are also maintained provided that the energies of the escaping electrons are in the keV range.

However, in contrast to the photoemission process in which the electron is directly emitted by the photon field, the Auger electron is emitted via the Coulombic interaction with other core electrons. In a compound material the charge density associated with the valence electrons may not be evenly distributed among the constituent atoms. The Auger process, which mainly samples the valence electrons around the emitting atom, is expected to be sensitive to any unequal sharing of the valence-electron cloud.

Because of the dissimilarities of the Auger and photoemission processes, we might expect matrix elements to produce significantly different electron energy distributions. We conclude from the present work that in covalent semiconductors this effect does not produce a significant deformation of the nominal density of valence states obtained with Auger spectroscopy. This has been shown recently[8,9] for the elements Si, Ni, and Cu, and we show that it also holds for compound semiconductors like Mg_2Sn.

The samples were dc sputtered on substrates at room temperature in a high-purity argon atmosphere at 25×10^{-3} Torr pressure. Their thicknesses were estimated to be above 1000 Å. Thicker films deposited at room temperature were found with x-ray diffraction to be polycrystalline. The samples were immediately transferred without breaking vacuum to the analyzing chamber, at a pressure of better than 5×10^{-10} Torr, and were measured. No traces of either carbon or oxygen contamination were found in the x-ray photoemission.

The measurements were performed with a Vacuum Generators ESCA III system equipped with a He lamp capable of producing the He I (21.2 eV) and He II (40.8 eV) lines, and an Al x-ray source, which was also used to excite the Auger electrons. A carbon filter was placed in the uv beam so as to enhance the He II line with respect to the He I. The instrumental resolution for the x-ray photoemission, including the width of the excitation line, was 1.5 eV. For the uv photoemission, it was better than 0.35 eV.

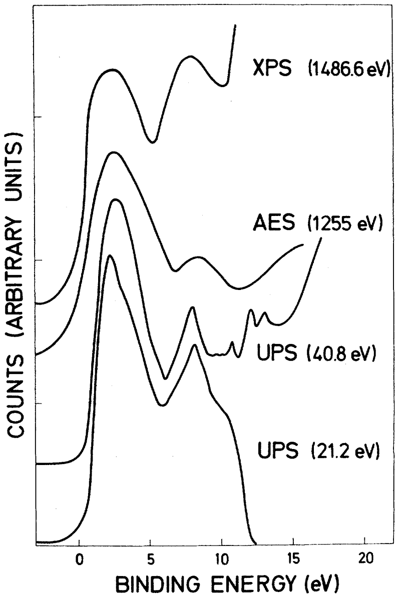

FIG. 1. Comparison of XPS , AES, and UPS curves of Mg_2Sn showing the valence-band structure and the background due to inelastically scattered and secondary electrons. The energy scale represents the binding energy with respect to the top of the valence band as determined by XPS. The other curves have been shifted such that their first maximum coincides with that of the XPS measurement.

Figure 1 shows the uncorrected electron energy distribution curves of Mg_2Sn for the x-ray-induced photoemission (XPS), the Auger electron emission (AES), and the uv photoemission with 21.2- and 40.8-eV photons (UPS). The parentheses on the photoemission curves indicate the energy of the incident photons, and that for the Auger process indicates the energy of the approximate onset of the Auger electrons. All of the curves have been displaced so that the positions of their peaks fall at the some binding energy. The zero position of the binding energy was determined from calibrated XPS measurements. In all cases these is a rising background with increasing binding energy, produced by electrons that have undergone inelastic collisions before escaping the sample. The energy-loss distribution following the core levels in the XPS measurements rose slowly and smoothly to a peak at ~14 eV; thus, no structure from the inelastic electrons in expected to contribute to the electron emission from the valence bands. In the 40.8-eV curve, the structure at binding energies greater than 11 eV is associated with the Sn *d* bands arising from lines of higher energy in He II. This part of the structure will be discussed elsewhere.[10]

The four curves in Fig. 1 exhibit strong similarities. The similarities are made even more striking after the contribution of the inelastic electrons is removed, as has been done in Fig. 2. The corrections were made by subtracting a constant times the area under the emission curves, normalized at a point which was taken to represent the bottom of the valence band. This procedure must be considered as an approximation, introducing uncertainties in the determination of the valence band. Thus, the existence of a gap that attains a zero value, and the precise relative proportions of the valence-band peaks, cannot be conclusively established. However, the similarities in the curves suggest that matrix-element effects are unimportant, that the procedure used to remove the inelastic electrons is at least qualitatively adequate, and that the curves well represent the valence-band density of states.

The valence bands calculated for Mg_2Sn are similar to those of germanium, as would be expected from the similarity in the electronic structure of these two materials. The main differences arise from the absence in Mg_2Sn of the degeneracies required along the X-W line of the Brillouin zone by the nonsymmorphic nature of the germanium space group. In the absence of these degeneracies, a gap develops between the lowest s-like valence band and the three upper p-like bands. This gap appears clearly in the photoemission curves of Fig. 2 between the two peaks at 2.2 and 7.9 eV. The calculated band structure yields rather flat p-like bands with almost completely flat portions at the edge of the zone between X, W, and K.[11] These flat portions, with a centroid at about 2.0 eV below the top of the valence band, should produce the first peak of Fig. 2. The spread in these bands is about 2 eV, which is also compatible with the width of the observed peaks. Following the same considerations we find that the second peak should occur 7.3 eV below the top of the valence band, i.e., below the onset in photoemission. This conclusion is also supported by our experimental results. The curves, after accounting for the resolution of the x-ray and Auger curves, show that the width of the valence band is about 9 eV, in agreement with theoretical calculations.[11]

The ratio of the total strength observed for the upper band to that of the lower band should be 3 if the transition probabilities involved can be assumed independent of binding energy. This conclusion agrees well with the results for x-ray photoemission. The uv and Auger data yield a somewhat higher ratio. The Auger spectrum is somewhat broader than both the uv and x-ray photoemission curves, and since the resolution of the energy analyzer was 0.6 eV for the XPS and AES measurements, the extra broadening is not due to instrumental effects. The energy of the Auger electrons at the top of the valence band is given by precisely the difference measured between the K and $L_{\text{II},\text{III}}$ levels (1253.2 eV),[10] suggesting that the transition involved is a KLV (V for valence) variety and that the valence electrons adequately screen the hole in both the Auger and photoemission processes, thus permitting a close correspondence between the photoemission and Auger energies to exist. The absence of peaks corresponding to Mg $K\alpha$ excitation from the core levels demonstrates that we are not observing internal photoemission.[12]

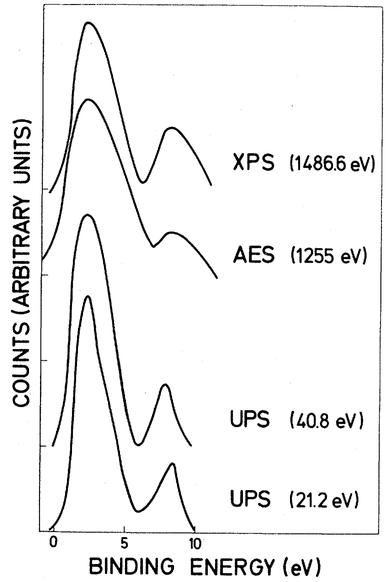

FIG. 2. Comparison of the valence-band structure of Mg_2Sn as determined in Fig. 1 after subtraction of the background.

It was found that the Auger emission was about 3 times stronger than the x-ray photoemisson of the valence band. The total strength of the KLV emission was also found to be about $\frac{1}{10}$ of the strongest KLL magnesium Auger transitions.

The KLV emission spectrum of pure Mg metal was also measured and consisted of a single peak only, roughly equivalent to the 2.2-eV peak of Mg_2Sn.[10] It exhibited, however, a steeper rise at low binding energies, its maximum occurred at 2.0 eV, it decayed more gradually towards higher binding energies, and it had a full width at half-maximum of 4.2 eV.

The fact that the valence-band density of states of Mg_2Sn is apparently measurable by AES is not a trivial matter. X-ray emission measurements have been made[13] on related compounds and different Mg-Al alloys, and the emission bands corresponding to electron recombination between valence band and L shells of Mg or Al have not at all reflected a similar situation. In both cases, the soft-x-ray spectra of the alloys indicated that one fraction of the valence band electrons recombined with the Al core and another—with a different energy distribution—with the Mg core. This difference is not due to orbital selection rules which govern the soft-x-ray emission.

We were able to examine the total valence-band density of states with Auger electrons. The results were very similar to those obtained with x-ray and uv photoemission. Similar electron-emission measurements for Mg_2Ge and Mg_2Si, together with the energies of the core levels of all these materials, will be reported in a future publication.[10]

It has been shown that the x-ray and uv photoemission and Auger-emission curves are similar for Mg_2Sn, suggesting that each represents rather well the density of states of the bulk material.

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Problems in Strong-Scattering Binary Alloys*

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We present results of model calculations based on two different approximations which were both intended to be improvements over the coherent potential approximation. We show that both approximations yield nonphysical solutions; specifically, they predict average Green's functions which contain singularities on both the upper and lower halves of the complex energy plane. We conjecture that nonanalytic behavior will occur generally in high-order approximations to the average Green's function.

We report numerical calculations based on two very different extensions of the coherent potential approximation (CPA). One is based on the corrected cumulant scheme of Yonezawa[1] as developed by Nickel and Krumhansl[2]; the other is based on the cluster approach of Butler and Kohn[3] developed to include self-consistency as outlined by Butler.[4] Our calculations of the average Green's function for binary alloys are carried out not only for real energies but for complex energies as well. It is this extension into the complex energy plane that makes these calculations unique and shows absolutely unambiguously that the solutions of the equations for the average