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VOLUME DEPENDENCE OF THE ELECTRONIC STRUCTURE OF Cu₂Mg

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Résumé.- Nous avons mesuré plusieurs sections de la surface de Fermi de Cu₂Mg en fonction de la pression et nous comparons les résultats à des calculs de structure de bandes où l'on fait varier le volume.

Abstract.- We have made measurements of the pressure dependence of several cross sections of the Fermi surface of Cu₂Mg and compare them with a volume dependent band structure calculation.

The pseudobinary Laves systems are the classical examples of alloys in which the structure is widely accepted to be determined by the electron concentration. Since these systems constitute the most common structures assumed by binary combination of metals (over 220 known examples to date) it is of considerable interest to understand their electronic properties and the relation of these properties to the structural details and phase diagrams.

Cu₂Mg is the prototype cubic Laves structure. As the electron concentration e/a is increased by addition of higher valence additives replacing the Cu, the density of states determined by heat capacity /2/ and by susceptibility /3/ measurements is observed to rise sharply to a maximum near e/a = 1.45 and then fall precipitously until the phase transition (near e/a = 1.75) from cubic to the MgNi₂ type structure. Since the initial work of Laves and Witte /4/ over forty years ago, it has been more or less accepted that the peak in the density of states occurred when the Fermi surface contacts the (311) Brillouin zone face /2/. The subsequent drop in the density of states as e/a increases toward the phase change is said to correspond to filling zones which is interrupted by another peak corresponding to contacting the (222) face. Heine and Wearie /5/ have argued from pseudo-potential considerations that these ideas are in difficulty.

In this study we report direct measurements of the Fermi surface as a function of hydrostatic pressure and an APW band structure as a function of interatomic spacing which give for the first time a direct measurement of details of the electronic structure at the Fermi surface which can be related to the experimental anomalies.

The Fermi surface of Cu₂Mg has been investigated using pulsed field and torque de Haas-van Alphen techniques by Wagner and Gordon /6/. These investigators compared their results with a valence-eight free-electron Fermi surface and found some similarity but no general correspondence. They observed an anomalously large effective mass for a small sheet attributed to a second band hole surface predicted that this sheet might be important in alloying and pressure studies. We used samples with a nominal resistance ratio of 25. De Haas-van Alphen frequencies were determined using the field modulation technique /7/ in a 55 kOe superconducting solenoid. Pressures were generated in He and derivatives of Fermi surface cross sections determined in both fluid /8/ and solid /9/ He by shifting individual oscillations of a given frequency. The pressure derivative dμF/dP is then given by B=MB/ΔP where B is the magnetic induction and ΔM is the shift in field of the oscillation with a change of pressure ΔP.

The pressure results are summarized in Table I. We have employed the orbit nomenclature of Wagner and Gordon. Free-electron scaling, the filling of the same fraction of the Brillouin zone as it increases in size with increasing pressure,
contributes a factor given by 2/3 the volume compressibility /10/.

Table I

Pressure derivatives of cross sections of the Fermi surface of Cu2Mg. The orbit designations are from Reference 5. The pressure derivatives are in units of 10^{-6} kbar^{-1}. Free electron scaling value is 7.1 in these units.

<table>
<thead>
<tr>
<th>Cross section</th>
<th>Field Orientation</th>
<th>Frequency (eV)</th>
<th>d(\sigma)/dP (10^{-5} eV^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>F_2</td>
<td>111</td>
<td>6.7 x 10^5</td>
<td>-300(\pm 100)</td>
</tr>
<tr>
<td></td>
<td>110</td>
<td>7.1 x 10^5</td>
<td>-300(\pm 50)</td>
</tr>
<tr>
<td>F_{4,7}</td>
<td>100</td>
<td>1.45 x 10^7</td>
<td>-2 (\pm 1)</td>
</tr>
<tr>
<td>F_9</td>
<td>100</td>
<td>7.1 x 10^7</td>
<td>8 (\pm 1)</td>
</tr>
</tbody>
</table>

For Cu2Mg this contribution is 7.1 x 10^{-6} kbar^{-1}. With the very limited data we have so far, we see that only the largest cross section observed, F_9, behaves even qualitatively as predicted by free-electron considerations. Of particular significance is the very large negative derivative observed for the F_2 cross section. As pointed out by Wagner and Gordon this sheet has associated with it a remarkably large effective mass (m^*/m_o=0.35) with respect to its size which is \(\approx 10^{-3}\) of the area of the maximum cross section of Fermi sphere.

We have calculated the electronic energy band structure of Cu2Mg at both normal volume and reduced volume using the APW method /11/. The potentials were derived from a superposition of atomic potentials /12/.

Based on these energy band calculations, we confirm the assignments of Wagner and Gordon of F_6 to the sixth band electrons. Similarly we concur with the association of F_2 to second band holes centered at \(\Gamma\) derived from the empty \(\Gamma\) 15 states. This state is triply degenerate and is bonding p-like on the magnesium and copper. From the calculations of Cu2Mg with reduced lattice constant we find a large energy shift for this state of +1 Ry compared with a free-electron value of \(-1.12\) Ry. The measured small size of this orbit means that \(\Gamma\) 15 is close to the Fermi energy, \(\approx 0.05\) Ry, in contrast to the band prediction of .02 Ry. This difference is not unreasonable in view of the approximations involved in the band calculations. If we adjust the states at \(\Gamma\) 15 down by \(-0.015\) Ry, the second band hole surface will be of correct topology and size. Similarly, adjusting the states along \(<111>\) by \(-0.025\) Ry one can get rid of both the third band arms (nests) and fourth band arms due to the flatness of these bands. Neither we nor Wagner and Gordon were able to observe these nests which should give rise to prominent dH-vA oscillations if analogies with AuGa_2 /13/ and the free-electron model hold. These are in fact the states associated with the (311) planes in the free-electron picture which are presumed to account for the anomalies in the susceptibility and heat capacity. The increase in the density of states upon increasing e/a from 1.33 to 1.45 seems more likely to be associated with the 5th band maximum at some center \(<111>\) and with the second band maximum at \(\Gamma\).

The observation of orbits on the fourth band surface, F_7 and F_{4,7}, with weak angular variation, in particular along \(<110>\), is strongly indicative of lack of \(<111>\) arms. These orbits too would have negative pressure derivatives which would be much smaller due to the fact that the intersection of the Fermi energy with the bands along \(<111>\) and \(<110>\) is further from \(\Gamma\) reflecting the larger area. The band structure results predict both fifth and sixth band electron surfaces centered at X although the origin of F_{6,7} is uncertain but since it is large and scales with the Brillouin zone with pressure, it is not a crucial test of a band structure model. Although more analysis is needed we believe the above interpretation is the most consistent with the band calculations and the pressure derivative results.

Summarizing, our model with very small adjustments in the positions of the calculated bands yields i) closed 2nd and 3rd band holes at \(\Gamma\) with a very large negative pressure derivative; ii) closed 3rd and 4th band hole surface at \(\Gamma\) with small negative pressure derivatives. This picture is in good agreement with our observations. The anomalies in the density of states related properties are not associated with intersection of the Fermi sphere with the (311) planes since in our model these states are already filled consistent with the closed nature of the 3rd and 4th band sheets. Rather the increase in the density of states with increasing electron/atom ratio stems from 5th and 2nd band maxima near the point \(\Gamma\) in the Brillouin zone.
References

/7/ Stark, R.W. and Windmiller, L.R., Cryogenics 8 (1968) 272.