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Fermi Surfaces of Some Dilute Hume-Rothery Alloys

P. T. Coleridge and I. M. Templeton
Division of Physics, National Research Council of Canada, Ottawa, Ontario K1A 0R6, Canada

(Received 15 March 1982)

In dilute alloys, in contrast to pure metals, the measured Fermi-surface volume is too small to accommodate all the electrons. In dilute copper-based heterovalent alloys the discrepancy increases as the solute valence increases but the *anisotropy* of the Fermi-surface changes is found to be approximately rigid-band-like in all alloys. These results are explained quantitatively in terms of the Fermi surface being determined by only those electrons which are scattered coherently.

PACS numbers: 71.25.Hc, 71.55.Dp

In pure metals the Fermi-surface volume is usually considered as being defined by the total number of electrons in the metal. More precisely it is defined as the volume of the constant energy surface corresponding to the chemical potential or Fermi energy in the metal. The equivalence of the two definitions follows from a theorem of Luttinger[1] which was proved for interacting electrons in a periodic potential. Disordered alloys, however dilute, are not periodic and so it is not immediately clear how the Luttinger theorem should be extended to alloys. The concept of the Fermi surface can be extended to alloys by including a self-energy term describing the interaction between conduction electrons and the impurities.[2] However, there remains the question of how the volume of the Fermi surface is related to the total number of electrons in the alloy. For dilute alloys this is equivalent to considering how the rate of change of Fermi-surface volume, $\Delta V/c$, where c is the concentration of impurities, is related to the valence difference ΔZ, defined as the number of extra conduction electrons per solute atom.

A sensitive and accurate probe of Fermi-surface dimensions is the de Haas–van Alphen (dHvA) effect. In very dilute alloys (of order 0.01 at.%) the Landau level broadening is sufficiently small that signals can be observed and changes in the dimensions of the Fermi surface (defined as above) can be measured by using high-precision techniques.[2,3] Although the measurements require a high magnetic field the effect of this on the Fermi-surface dimensions is significant only in the quantum limit.[2] For the particularly simple case of a rigid-band model the change in cross section ΔA for each extremal orbit is given by

$$c^{-1}\Delta A/A_0=\tfrac{2}{3}(m_c/m_{\text{th}})\Delta Z, \qquad (1)$$

where A_0 is the free-electron cross section, and m_{th} the thermal mass. The anisotropy of the area changes is just proportional to m_c, the cyclotron mass of each orbit. If the small anisotropy of the electron-phonon enhancement is ignored, experimental values can be used for m_c and m_{th}. When experimental results are compared with this simple theory two distinct kinds of breakdown of the model may occur. Firstly, if the Luttinger theorem is invalid the total change of volume of the Fermi surface will no longer be given by $c\Delta Z$. Secondly, the band structure of the alloy may differ from that of the pure metal; then the *anisotropy* of the Fermi-surface changes

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TABLE I. Area changes for copper-based alloys. The measured changes for five symmetry direction orbits, corrected by scaling for changes in lattice constant, are expressed in terms of the rigid-band changes expected for $\Delta Z = 1$.

	Cu(Zn)	Cu(Al)	Cu(Si)	Cu(Ge)	Cu(P)
⟨111⟩ belly	1.01 ± 0.03	1.79 ± 0.03	2.29 ± 0.05	2.6 ± 0.2	1.9 ± 0.2
⟨111⟩ neck	0.84 ± 0.08	1.73 ± 0.04	2.22 ± 0.05	2.3 ± 0.1	1.7 ± 0.2
⟨100⟩ belly	1.03 ± 0.02	1.77 ± 0.02	2.24 ± 0.05	$2.3_5 \pm 0.3$	$1.9_5 \pm 0.2$
⟨100⟩ rosette	0.99 ± 0.02	1.77 ± 0.06	2.15 ± 0.05	2.3 ± 0.2	$1.6_3 \pm 0.1$
⟨110⟩ dogsbone	0.96 ± 0.02	1.79 ± 0.03	2.29 ± 0.1	$2.3_5 \pm 0.2$	$1.6_4 \pm 0.1$
Average (ΔZ^*)	0.97	1.77	2.24	2.4	1.77

will deviate from rigid-band behavior and the area changes, ΔA, will not be proportional to the cyclotron masses.

The Hume-Rothery alloys,[4] i.e., heterovalent solutes in noble-metal hosts, are an attractive system in which to investigate these effects because the crystal structure appears to be controlled by the electron/atom ratio and this suggests that the rigid-band model might be a good approximation. Results have been obtained in Cu(Zn),[5] Cu(Al),[6] Cu(Si), Cu(Ge),[7] and Cu(P) alloys. The maximum impurity concentration in each alloy ranged from 0.01 at.%, in Cu(P), to 0.1 at.%, in Cu(Zn). Impurity-impurity interactions would appear as a quadratic concentration dependence of the dHvA frequencies and, in the absence of clustering, should be extremely small for these concentrations. In each system at least two impurity concentrations were used and there was no evidence of a concentration dependence that was not linear within experimental error. The results can therefore be considered typical of the single-impurity limit. Lattice distortion, i.e., a change of lattice constant on alloying, complicates comparison with theory so that the series of alloys was chosen with some regard to minimizing these effects. The maximum lattice-constant change is 0.094% per at.% [for the Cu(Ge) system][8] and all results have been corrected for lattice distortion, to first order, by scaling the measured frequencies to the lattice constant in the alloy.

In each alloy the area changes, $\Delta A/c$, for five symmetry direction orbits vary by a factor of about 3. It is convenient to express the results as the effective valence difference required to give the area changes according to Eq. (1). These values, shown in Table I, are approximately constant for each alloy indicating that the *anisotropy* of the Fermi-surface changes is close to rigid-band behavior. This means that for each alloy a single average value, ΔZ^*, provides a fair description of all the area changes and in this case, the total change of the Fermi-surface volume is given rather accurately by ΔZ^*. However, only for the smallest values is ΔZ^*, plotted in Fig. 1, equal to the actual valence difference and for Cu(P) the discrepancy is a factor of more than 2. The experimental results show rather clearly that for large valence differences, i.e., for strong impurity potentials, the Luttinger theorem breaks down and that the Fermi-surface volume does not account for all the conduction electrons in the alloy.

This deviation between the measured Fermi-surface volume and the number of electrons in the alloy is, it should be noted, a smooth function of the increasing strength of the impurity potential and so it is difficult to attribute it to

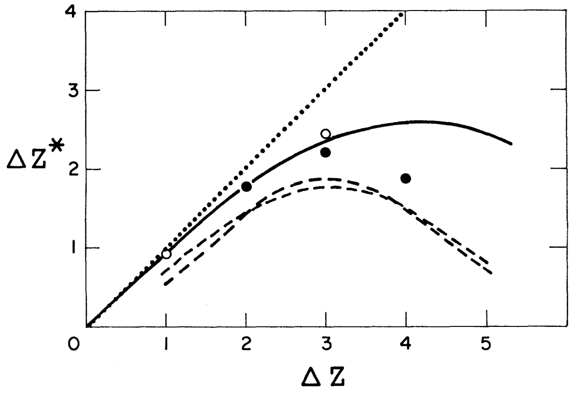

FIG. 1. Change in Fermi-surface volume expressed as an apparent valence difference ΔZ^* for Cu(Zn) and Cu(Ge) (open circles) and Cu(Al), Cu(Si), and Cu(P) (solid points). The dotted line is the simple rigid-band model and the solid line the coherent-scattering rigid-band model. The dashed lines are deduced from phase shifts calculated in Ref. 9.

the appearance of bound impurity states in the alloys of larger valence difference as has been suggested by Prasad and Bansil.[10] Such an explanation would require not only that $\Delta Z^* \lesssim 1.5$ for Cu(Ge) but also would imply a discontinuous change of ΔZ^* between Cu(Al), which has no bound state, and Cu(Si) and Cu(Ge) which have.[9] Indeed a clear distinction should be drawn between the localized density of states inside the impurity cell and the propagating or coherent states which determine the alloy Fermi surface.[2,11] The existence of the Fermi surface (as shown for example by the observation of dHvA signals) depends on the extent to which the impurity atoms scatter the Bloch states of the host metal coherently, i.e., in the forward direction. Dependent though this is on the strength of the impurity potential, for any alloy system there is a concentration of impurities sufficiently small that a Fermi surface can be observed. At the Fermi surface the change Δk (measured normal to the surface) of the *coherent* states is given by[2]

$$\Delta k = (\hbar v_{\vec{k}})^{-1}\,\mathrm{Re}\Sigma(\vec{k}), \tag{2}$$

where $v_{\vec{k}}$ is the velocity and $\Sigma(\vec{k})$ the appropriate self-energy. In the dilute limit this is given by the forward-scattering T matrix of the impurity which, for a dilute-alloy Korringa-Kohn-Rostoker model, can be written[2]

$$\Sigma(\vec{k}) = cT_{\vec{k}\vec{k}} = c\textstyle\sum_l [t_l(\vec{k})/I_l]\sin\varphi_l \cos\varphi_l, \tag{3}$$

where $t_l(\vec{k})/I_l$ are the appropriately normalized coefficients in the pure-metal wave-function expansion, and φ_l are the Friedel[12] or generalized[13] phase shifts which represent the extra eigenstates in the alloy and which are constrained by the Friedel sum rule to account for the added states, i.e.,

$$\Delta Z = (2/\pi)\textstyle\sum_l (2l+1)\varphi_l. \tag{4}$$

The Friedel phase shifts are the sum of two terms, the phase shift differences between impurity and host phase shifts, which characterize the impurity potential, and a back-scattering phase shift which includes the multiple scattering by the host lattice of the outgoing partial waves.

A rigid-band version of this model can be constructed with $\Delta Z = 1$ by finding three phase shifts ($\varphi_l = 0.177,\ 0.2455,\ 0.130$) which have the correct Friedel sum and which reproduce, within 0.2%, the rigid-band area changes[14] predicted by Eq. (1). By integrating Δk over the Fermi surface it can be shown that the rate of change of Fermi-surface volume is then given by

$$c^{-1}\Delta V/V_0 = \Delta Z^* = (2/\pi)\textstyle\sum_l (2l+1)\sin\varphi_l \cos\varphi_l. \tag{5}$$

If for larger values of ΔZ the values of φ_l are just increased in proportion to maintain the correct Friedel sum [Eq. (4)] the anisotropy of the area changes remains approximately rigid-band-like but, as the $\sin\varphi_l \cos\varphi_l$ terms saturate, the calculated values of ΔZ^*, shown in Fig. 1 by the solid line, deviate increasingly from the simple rigid-band behavior. We call this a coherent- or forward-scattering version of the rigid-band model and, except for the case of Cu(P), it provides a remarkably good description of the experimental results.

Friedel phase shifts for these alloys have recently been calculated from first principles with use of a self-consistent density functional approach.[9] Corresponding values of ΔZ^* for the third and fourth rows, calculated according to Eq. (5), are shown as dashed lines in Fig. 1. While they are all approximately 0.4 lower than the experimental values they mirror accurately the rate of drop off at high values of ΔZ. This deficiency of 0.4 corresponds almost exactly to a similar discrepancy in the Friedel sum of the calculated phase shifts and presumably occurs because the calculation was made with any change of potential restricted to the impurity cell and with the phase shifts evaluated at the muffin-tin radius of that cell. To recover the extra charge requires a more complex calculation in which charge transfer and perturbation of the surrounding host atoms are also considered. Such a calculation would undoubtedly increase the value of ΔZ^* by approximately the same amount as the Friedel sum and hence would provide an extremely good fit to the experimental data.

It is interesting to note that although the Fermi-surface changes are not rigid-band-like, in the sense that the volume change depends both on the number of electrons added and the type of impurity, the total change in the density of states, given in the dilute limit by the Friedel phase shifts, does seem to be approximately independent of the impurity type. This is consistent with the Hume-Rothery behavior in the alloys because the total density of states provides the driving force determining the crystal structure and this, unlike the Fermi-surface changes, depends only on the electron/atom ratio and not the type of impurity.

In conclusion, de Haas–van Alphen experiments in dilute Hume-Rothery alloys show that the Fermi-surface volume is too small to accommodate all the electrons in the alloy, i.e., the alloys do not follow the Luttinger theorem. The results are not consistent with a concentration-dependent Fermi surface in which some of the impurity states are localized and removed from the Fermi surface. They are, however, explained well by a rigid-band type of model but with the Fermi surface containing only the coherently or forward-scattered states. It is emphasized that the volume discrepancies are linear in concentration and appear not when the impurities are sufficiently concentrated to interact with each other but when the scattering potential is sufficiently strong to provide an appreciable fraction of incoherent scattering. The discrepancies are then of the same order of magnitude as the impurity concentration.

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