Li-Mg, a Nearly Free-Electron Alloy*†

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The momentum distributions of electron-positron pairs annihilating in polycrystalline Li, $Li_{81}Mg_{19}$, and $Li_{42}Mg_{58}$ have been measured. The results show that the alloy is a good, nearly-free-electron metal with an electron concentration determined by counting one electron per Li atom and two per Mg atom. The data lead to speculations about the description of metallic electrons in this alloy.

INTRODUCTION

THE annihilation of positrons with electrons in metals usually occurs by emission of two photons at 180° to each other in the center of mass of the pair. The small departure from 180° in the laboratory system is directly proportional to the transverse (to the photon direction) component of momentum of the electron positron pair. Since the positron is probably thermalized,[1] a measurement of the angular correlation of the annihilation photons thus yields directly one component of electron momentum. The technique has been used to obtain information about the electron structure of metals and other crystals[2] although it cannot yield such details of the Fermi surface as are revealed by the usual low-temperature techniques, e.g., de Haas-van Alphen effect. However, for alloys some of the low-temperature techniques are less useful because the short mean free path of the electrons may prevent the establishment of orbits in a magnetic field. Thus, for alloys the positron annihilation technique should possess some advantages. The short lifetime of an electronic state is still long compared with the annihilation time (the time between the emission of the two annihilation photons). In fact, this technique may eventually have real promise for the measurement of the lifetime of some electronic states.[3]

We have chosen to test the technique with Li-Mg alloys. This alloy system is of interest because the addition of magnesium to lithium does not change the body-centered cubic structure or spacing (less than 1%) up to 70 at.% Mg.[4] The Fermi surface presumably expands steadily, with the addition of magnesium atoms to the alloy, until there is large contact with the first Brilluoin zone boundary at $(\frac{1}{2}, \frac{1}{2}, 0)$. If the energy gap in the alloy is comparable with that calculated for lithium,[5] there is probably no occupation of the second zone even with 70 at.% Mg.

EXPERIMENTAL RESULTS

Specimens of reagent grade lithium, and alloys,[6] Li_{81} Mg_{19} and Li_{42} Mg_{58}, with a flat face $\frac{1}{2}\times 1$ in., were mounted about $\frac{1}{2}$ in. below a positron emitter (4-mCi Na^{22} or about 40-mCi Cu^{64}). Two NaI (Tl) crystals behind lead slits 12 in.$\times$0.050 in., 100 in. from the specimen detected the annihilation photons. The electronics selected coincidences (about 10^{-7} sec resolution) in the two detectors and printed the total number received in a fixed time. The angle between photon directions was varied by raising and lowering the specimen. These arrangements are similar to those previously used.[7]

The coincidence count data when plotted against angle gives the usual inverted parabola of about $\frac{1}{2}$° base width plus "tails" at larger angles. We have plotted in Fig. 1 the modulus of the differences between adjacent points against their mean distance from the centroid of the angular correlation curve. It has been shown[7] that these "slopes" are proportional to $k\rho(k)$, where $\mathbf{k}$ is the wave vector and ρ is the isotropic density of occupation of $\mathbf{k}$ space. The statistical accuracy of the points has not been shown. It is sufficiently represented by the scatter of the points.

In the figure is also shown the size of the appropriate free-electron theory Fermi sphere drawn in a section of the first Brilluoin zone.

DISCUSSION

The lines drawn through (some of) the points have been constructed in three portions: the low-momentum region, near the Fermi cutoff, and the higher momentum region. For momentum less than 3×10^{-3} mc, a straight line was fitted by eye to the points. The probability of annihilation is not much velocity-dependent,[8] thus the straight-line fit is to be expected. It represents merely a constant density of occupation of k space for small k. For momentum above 6×10^{-3} mc a smooth line was drawn through the points consistent with the assumption that the higher momentum events are primarily annihilation with electrons of the ionic cores. The distribution of this higher momentum component was assumed to be continuous and smooth, and thus by

* Preliminary results were presented at the Baltimore Meeting, Bull. Am. Phys. Soc. **7**, 22 (1962).

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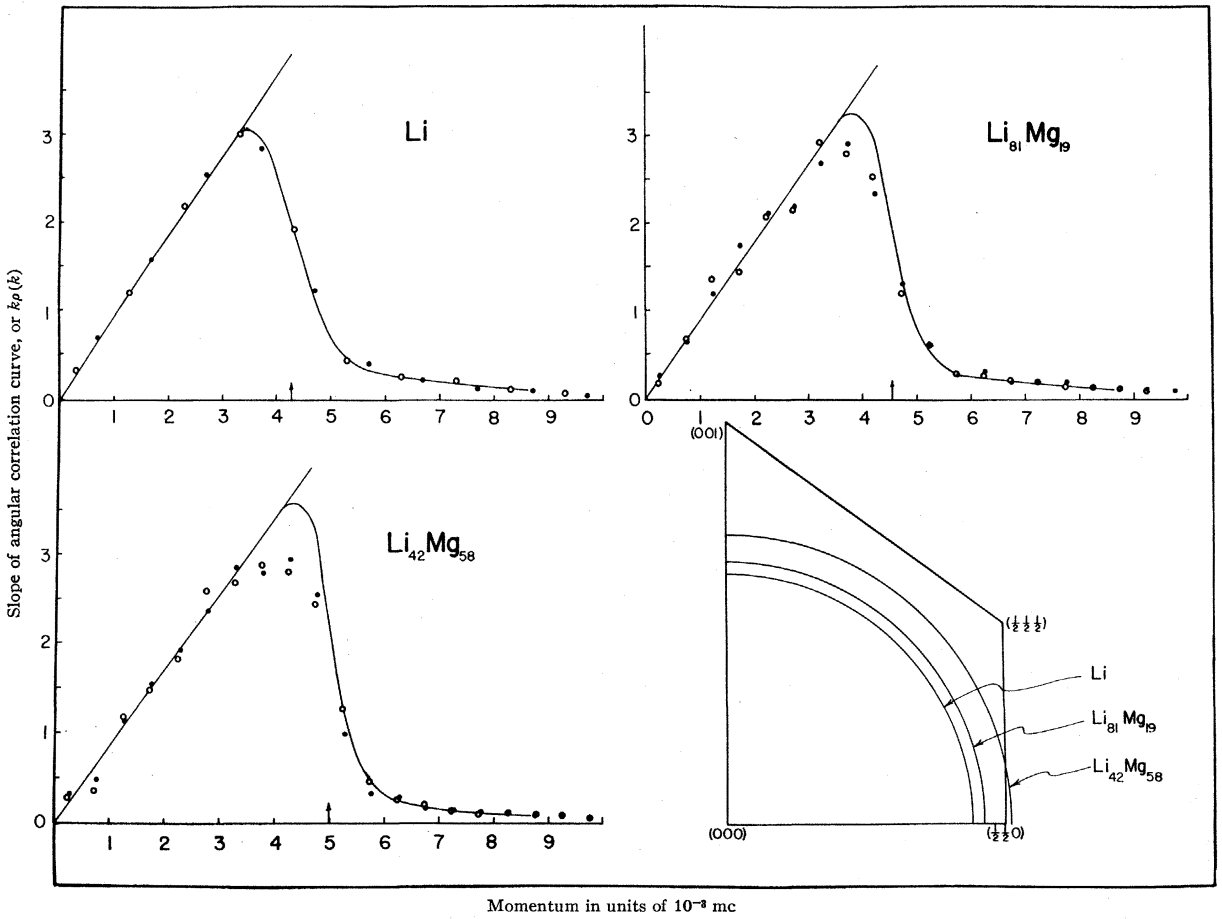

FIG. 1. Slopes of angular correlation data plotted against electron momentum for lithium and two alloys. The small arrows on the abscissa mark the positions of the Fermi momenta calculated from free-electron theory.

extrapolation separable from the conduction electron component in the region of the Fermi momentum. The decrease in intensity of this higher momentum component as a larger fraction of the lattice becomes Mg^{++} ions is to be noted. It implies that a larger fraction of the annihilations occur with conduction electrons than with core electrons even although the number of core electrons increases rapidly with the addition of magnesium.

Near the Fermi momentum the lines drawn on the graphs were calculated by assuming the momentum distribution of free-electron theory and taking into account instrument resolution. The instrument resolution was considered to be composed of two terms: (a) the geometrical resolution of slits and specimen thickness, and (b) the velocity of the positron, assumed to be in thermal equilibrium with the lattice and to have a free-particle mass. This calculated curve gives a good fit to the lithium data and a poor fit to the alloy data.

The good fit for lithium is somewhat fortuitous because the penetration of beta particles into this very light metal has not been established. The mean penetration is expected to be about 0.025 in. or half the slit width. Thus, the geometrical resolution of the instrument cannot be well defined. Unfortunately, because of this uncertainty, the data for lithium cannot be used to determine the anisotropy in the Fermi surface. If the good fit is not accidental the data imply an almost spherical Fermi surface.

For the denser alloys the penetration of positrons is no better known but it is smaller and thus less important. The calculated cutoff is therefore reasonably well known. The lack of fit is obvious and puzzling.

By attributing to the electrons or the positrons a short lifetime one can, through the uncertainty relation, obtain a smear in k space at the Fermi cutoff. However, any smearing obtained in this manner is nearly symmetrical in the sense that the decrease in occupation of states below the Fermi surface is roughly the same as the increase in occupation of states a corresponding displacement (in k) above the Fermi surface. However the lack of fit is anisotropic about the free-electron Fermi surface. Thus, a short mean free path alone cannot account for the data.

Another possibility to account for the lack of fit arises from the presence of the zone boundary at $(\frac{1}{2}, \frac{1}{2}, 0)$. It will certainly distort the Fermi surface. In

the Li_{81} Mg_{19} specimen the surface probably bulges and may touch the zone boundary. If the nearly free-electron theory (two plane waves) is applicable, the bulge would result in an appreciable tail above k_{ZB} and some diminution below k_{ZB} but still above k_f, the free-electron radius. Thus the cutoff should be sharper on the lower side and more gradual on the higher momentum side. The opposite is observed. In the Li_{42} Mg_{58} specimen the smear caused by the zone boundary should be approximately symmetric about k_f. The data show a strong asymmetry which is thus still unexplained.

One effect of alloying the two metals could be to smear the Fermi surface in the manner described by Edwards[9] for spatial disorder in liquids. Such smearing should also be symmetrical, however, and thus cannot account in full for these data.

We are finally led to speculate that the shape of the cutoff is influenced by the alloy nature of the metal but in another way. We suggest that the pile up of electric charge around the magnesium ions must be described by electron wave functions which have Fourier components widely dispersed through k space. These higher momentum components are not easily "seen" in this experiment. The resultant diminution in occupation of k space within the Fermi surface seems to occur preferentially for $k \gtrsim \frac{2}{3}k_{ZB}$, this being the maximum value of k for which the linear relation is observed in the figure. It is not unreasonable to suppose that those electrons with a half-wavelength approximately equal to an atomic spacing are the ones required to heap up charge around the Mg^{++} ions. We hope that this speculation can be checked by a calculation of electron wave functions in such a metal alloy.

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Dispersion of the Index of Refraction Near the Absorption Edge of Semiconductors*

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A simple method is used to calculate the contribution of the rapid rise in optical absorption near the absorption edge of semiconductors to the index of refraction near the edge. Other contributions to the index are also estimated. The results give qualitative agreement with the results obtained for PbS by Riedl and Schoolar, and very good agreement with Marple's prism measurements of the index for GaAs. Some applications to injection lasers are discussed. The temperature and pressure dependence of the index of refraction near the absorption edge is estimated, and agrees well with experimental results for GaAs.

I. INTRODUCTION

THE absorption edge of a semiconductor is usually a region of very rapidly rising absorption. It is a direct consequence of the dispersion relation[1] between the real and imaginary parts of the complex index of refraction that this rapid rise in absorption will lead to structure in the index of refraction near the photon energy of the absorption edge. We shall examine this structure using both numerical absorption data and a number of simple models for the absorption near the edge. We find that there is rapid dispersion of the index of refraction near the edge, and in some cases a peak in the index. However, the total variation of the index near the absorption edge is small in the semiconductors which we consider. For that reason the effect has only occasionally[2] been considered in detail heretofore.

The development of injection lasers, which have narrow emission lines near the absorption edge, has provided a sensitive tool for studying the dispersion of the index of refraction near the edge, and has motivated this work. The application to lasers is discussed specifically in Sec. V. In Sec. II we give the relevant dispersion relations, and show how they can most conveniently be used to treat the variation of the index near the absorption edge. In Sec. III we present a number of simple models, and in Sec. IV we apply these methods to obtain results for GaAs and PbS which are in fair to excellent agreement with experiment. In the last section, we show how the same methods used to describe the dispersion of the index also give a good description of the effect of temperature or pressure

* A brief account of this work was presented at the St. Louis meeting of the American Physical Society, in March 1963 [Bull. Am. Phys. Soc. 8, 201 (1963)].

[1] See, for example, F. Stern, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1963), Vol. 15, p. 327.

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