POSITRON ANNIHILATION IN COPPER ALLOYS

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The long-slit geometry has been used to measure the angular correlation of annihilation radiation from copper alloys. The alloys 0.975 Cu-0.025 Al, 0.95 Cu-0.05 Al, and 0.77 Cu-0.23 Ni display "necks" in momentum space. In units of the copper Fermi-surface neck, the measured neck radii of 1.3, 1.5, and 0.8, respectively, are consistent with the assumption that the energy-momentum relation is unchanged upon alloying.

Recent investigations[1-4] of annihilation radiation from oriented single crystals of copper and copper alloys have shown anisotropies which are apparently produced by "necks" where the Fermi surface (F.S.) makes contact with the [111] Brillouin zone boundaries. It therefore seems that the positron method, if applied with sufficient angular resolution, could provide useful data on changes in the F.S., and particularly in the necks, as copper is alloyed with other metals. Other methods[5] of studying these changes have been restricted to solute concentrations of about 0.1% or less, but the positron method imposes no such restriction; the only limitation lies in our ability to interpret the results. We have used the method to study the following alloys: 0.975 Cu-0.025 Al, 0.95 Cu-0.05 Al, 0.78 Cu-0.22 Zn, and 0.77 Cu-0.23 Ni. Decimals indicate atomic percentages in all constituents.

Our data were obtained by a "long-slit" angular correlation apparatus in which the angles were defined by slits 30 cm long and 1.0 mm wide, at a distance of 4.0 m from the sample. Single crystals of the above alloys, as well as a single crystal of pure Cu, were oriented with respect to the slits in such a way that the angle θ was proportional to the component of momentum parallel to the [110] axis (or, in one case, to the [111] axis). Our angular correlation curve for copper is in agreement with the results of Berko, Cushner, and Erskine,[1] who used the same geometry.

Each single-crystal sample was also used as the source of positrons; in each case about 1.5 Ci of Cu^{64} was produced in the sample by thermal-neutron irradiation. After irradiation the source sample was placed in a pocket constructed with identically oriented (nonirradiated) pieces of the same alloy crystal, so that all of the positrons were annihilated in the assembly in a volume whose width parallel to the selected momentum component was about 0.3 mm. The resulting angular-resolution function had a full width at half-maximum of about 0.3 mrad, for the momentum component in the selected direction. The whole assembly was cooled to liquid-nitrogen temperature in order to minimize the contribution of the positron to the momentum of an annihilating pair.

Figure 1 shows the angular correlation curve obtained for the [111] axis of the Cu-Ni alloy. Data for $\theta<0$ are folded over onto the data for $\theta>0$; the clear agreement between the two sets of points provides a good check on the experimental technique and on the treatment of the data—e.g., the correction for decay of the source. Each point near the peak represents about 60 000 coincidence counts, and the entire curve represents over four million coincidence counts.

Curves obtained for the other samples are similar in appearance to the one shown, but significant details of the curves are best displayed by plotting the slope of the angular correlation, as

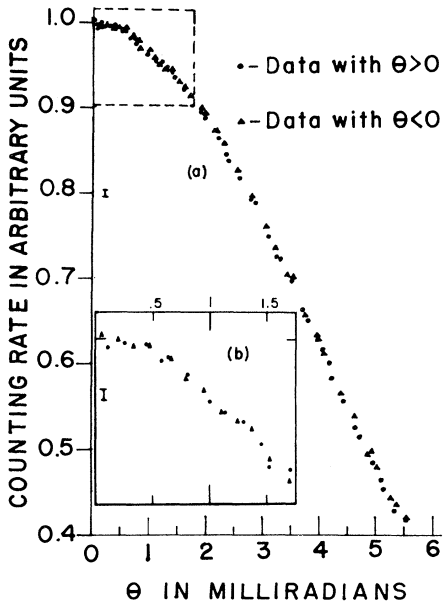

FIG. 1. (a) Angular correlation of annihilation photons along [110] planes in 0.77 Cu-0.23 Ni. (b) Region near $\theta = 0$ expanded, with neighboring points averaged for further clarity; each point represents over 110 000 counts.

shown in Fig. 2. Each point in Fig. 2 was found from the least-squares fit of a straight line to five consecutive points in the corresponding angular-correlation curve. Errors were calculated directly from Poisson statistics.

We have calculated a "theoretical" slope curve for the [110] direction in pure Cu; the curve, with our angular resolution folded in, is shown as the solid line in Fig. 2(a). The calculation was based on the Roaf[6] "four-term" F.S. for Cu. We assumed the wave function of each valence electron to be the sum of two plane waves, with wave vectors $\vec{k}$ and $\vec{k}+\vec{g}_{111}$, where $\vec{g}_{111}$ is a reciprocal lattice vector in the [111] direction; and we used first-order perturbation theory,[7] with the assumption of a 7-eV energy gap[8] at the [111] zone boundary, in order to find the amplitude of each plane wave. The inclusion of the second plane wave affects the result very slightly; the major effect is to produce the slight dip in the curve to the left of the peak, near $\theta = 4$ mrad. A similar dip is present in the measured slopes for copper. Other reciprocal-lattice vectors were not considered in the calculation, because the Roaf F.S. does not closely approach any other zone boundary.

We attempted to account for annihilations with core electrons by including in our theoretical angular distribution a core distribution found by fitting a Gaussian to the large-angle data of Berko, Cushner, and Erskine. The lack of fit between our theoretical and experimental slopes for copper may simply mean that our core function was incorrect.[9] Another possibility is that electron-positron correlations introduce a significant momentum dependence into the annihilation rate; such an effect has been studied only for annihilations in alkali matals.[10,11]

In spite of these uncertainties, one feature of the theoretical curve—the peak near $\theta = 1$ mrad—appears in the observed curves and has a direct interpretation. We have repeated the calculation using different core functions and different values for energy gap, but we find that the position of this peak is unchanged. This peak is a direct effect of the "neck" in the copper F.S., which comes about in the following way: Except for the effect of high Fourier components and core annihilations, an angular correlation measurement using the "long-slit" geometry essentially maps out cross-sectional areas of the occupied regions of k space in the first zone. (Figure 3 indicates an edgewise view of the slice of k space selected by a typical slit setting.) Near $\theta = 0$, these areas include a large contribution from the F.S. necks

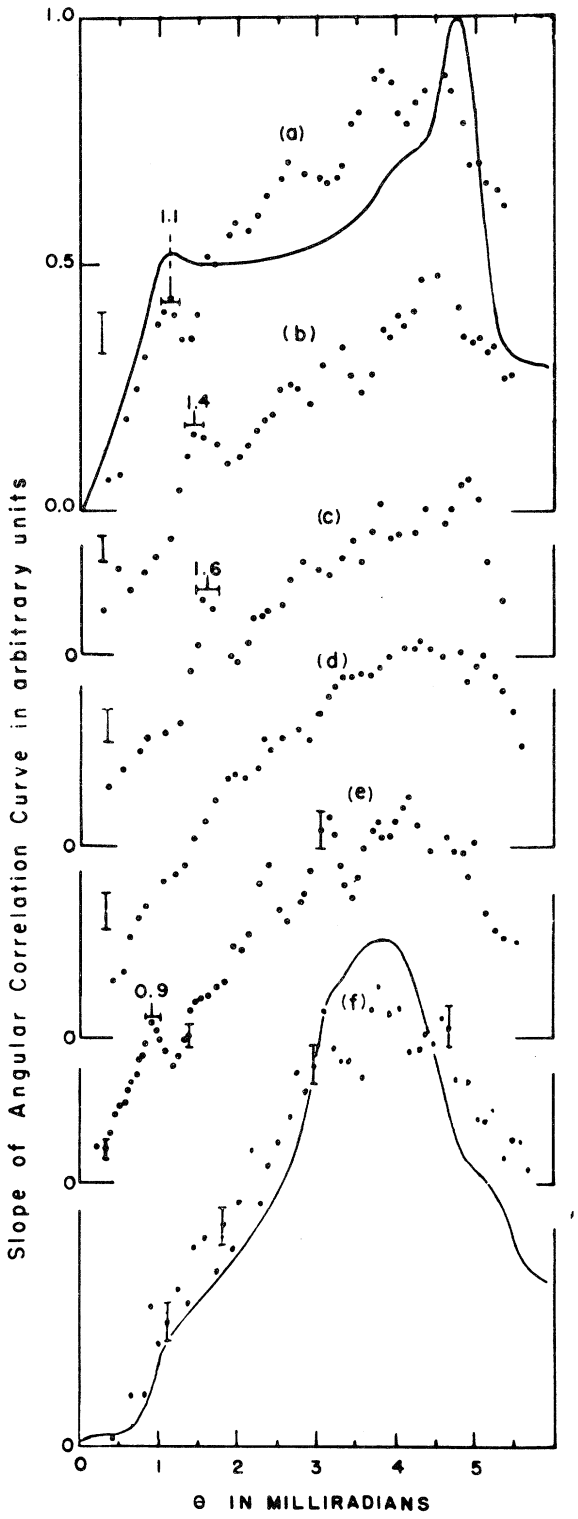

FIG. 2. Negative of slope of angular correlation curves for copper and copper-rich alloys. (a) Pure Cu, [110], with solid line showing result of theoretical calculation; (b) 2.5% Al, [110]; (c) 5.0% Al, [110]; (d) 22% Zn, [110]; (e) 23% Ni [110]; (f) 23% Ni [111], with solid line showing theoretical curve for Cu[111].

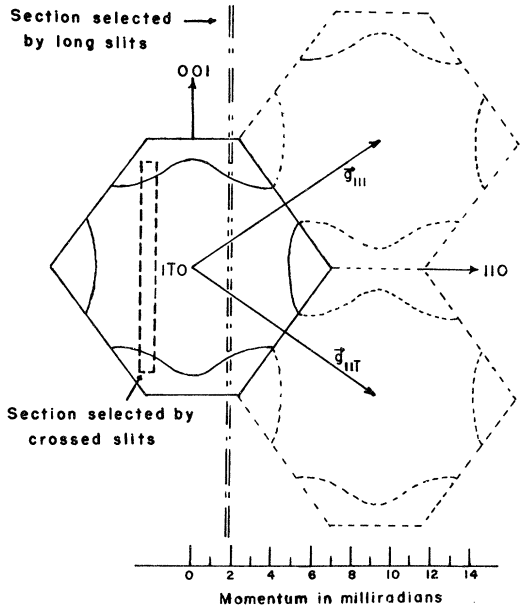

FIG. 3. Cross section through origin of k space perpendicular to $[1\bar{1}0]$ direction in Cu; abscissa is in units of $(\hbar k/mc)\times 10^3$. Dashed lines show sections selected by different geometries.

at four of the [111] planes, but the contribution of these necks to the cross-sectional area (perpendicular to the [110] axis) is a rapidly decreasing function of θ, and beyond $\theta = 1$ mrad the necks are no longer present. Thus the cross-sectional area decreases rapidly with θ until the necks disappear, after which this area decreases at a much slower rate, so that there is a peak in the curve of slope versus θ at the angle corresponding to the neck radius. The position of the peak in the experimental points for Cu agrees perfectly with the theory.

Thus by plotting the data as in Fig. 2 we have an unambiguous way to determine the edge of the F.S. neck. When we apply this method to the alloys we find similar indications of a neck in all except 0.78 Cu-0.22 Zn. The indicated values of 1.4 ± 0.15 mrad and 1.6 ± 0.15 mrad, for the neck radii in 0.975 Cu-0.025 Al and 0.95 Cu-0.05 Al, respectively, are in good agreement with the neck radii calculated from the "rigid-band" model[8] for the corresponding electron-to-atom ratios (1.05 and 1.10, respectively).

Of course the fundamental assumption of the rigid-band model—that the dependence of the energy of a state upon its k vector does not change upon alloying—is an approximation only. There is some question as to the meaning of a F.S. in an alloy, when the periodicity of the lattice potential is destroyed by the appearance of foreign ions at random lattic points. A change in the lattice potential must change the relation between E and $\vec{k}$ to some extent, and if a foreign metal is introduced randomly in a large enough concentration the whole F.S. would become "smeared out" as a result of these changes. This effect would appear in our results as a more smoothly varying distribution; the momentum distribution would become more isotropic, and the peak caused by the F.S. neck would disappear.

It is clear from our data that this smoothing out does not happen at concentrations of Al up to 5%. Certainly to some degree of approximation we can still represent electronic states in an alloy as vectors in k space, and we can use the positron method to determine the occupation of those states. Our results, up to 5% concentration of Al, indicate that the rigid-band model provides a useful way to determine which states become occupied as the electron-to-atom ratio (e/a) increases, up to $e/a = 1.10$. These results complement the findings of Chollet and Templeton[5] in the range $1.000 < e/a < 1.001$.

The 0.78 Cu-0.22 Zn curve does appear to be smoothed out; Fig. 2(d) is quite straight between 0 and 2 mrad. But this result is inconclusive, because the F.S. neck, if it still exists in such a nondilute alloy, would have a radius of about 2 mrad for $e/a = 1.22$, according to the rigid-band model. It happens that there is a slight change in slope in Fig. 2(d) near 2 mrad, but we do not claim any significance for this.

The findings for 0.77 Cu-0.23 Ni deserve special mention, because in Cu-Ni alloys the value of e/a has been in doubt. Mott in 1936 proposed[12] that the nickel atoms in such an alloy add zero valence electrons to the conduction band, for Ni concentrations up to 40%. Recent experiments have indicated[5,13] that this scheme does not give the correct e/a ratio for such alloys, and that each Ni atom up to 0.1% concentration adds about 0.4 electrons to the conduction band, if the results[5] are interpreted on the basis of the rigid-band model. Our results are also in disagreement with the Mott proposal. If the peak at 0.9 mrad [Fig. 2(e)] is interpreted as an indication of a neck edge, we can compute from the rigid-band model that each Ni atom is contributing 0.8 electrons to the conduction band. Of course we have no way to determine whether this neck is in contact with the zone boundary, but we have collected many more counts in this region of the curve, in order to confirm conclusively the existence of

this peak, and to measure its position accurately. It is interesting to note that there is no smoothing effect on our curve even at this large concentration of solute; this may be an indication that the assignment of 0.8 conduction electrons per nickel atom is reasonable, for in that case the nickel ions would closely resemble copper ions and would cause only slight perturbation of the lattice potential. We have also studied the same alloy crystal oriented in such a way as to obtain the momentum distribution along the [111] axis; the results [Fig. 2(f)] confirm our findings and indicate a great anisotropy in the momentum distribution.

These are the first published results on positron annihilation in copper alloys by the "long-slit" method. Previous papers[3,14] have reported results obtained by the "crossed-slit" and the "collinear-point" geometries. In contrast to our findings, these results have been in disagreement with the rigid-band model (and with each other), and no explanation has been presented for the neck radii which they have observed. Fujiwara, Sueoka, and Imura[3] reported a decrease in neck radius as Al concentration increased from 2.6 to 5.7%, followed by a large (100%) increase at 10.6% Al. The decrease at 5.7% was much greater than the assigned error in the measurement. But Williams, Becker, and Petijevich[14] reported only a 30% increase in neck radius when copper was alloyed with 30% zinc. Without a thorough investigation of the details of these experiments it is difficult to explain the contradiction, but we wish to point out some reasons for confidence in our own results, and for our preference for the long-slit geometry.

The long-slit geometry permits a tremendous increase in solid angle, for detection of the gamma rays with a given angular resolution relative to one axis. This increase in solid angle amounts to a factor of 100 or more over a "collinear-point" geometry; the factor is smaller, but still greater than 10, for long-slit versus "crossed-slit" geometry.

However the crossed-slit geometry suffers from a further disadvantage. In using this technique, one narrows the angular resolution along the long axis of the slit to about 5.5 mrad, which means that the selected slice of k space (dashed line in Fig. 3) is just equal in vertical extent to the volume enclosed by the F.S. But the resolution function is not square but triangular—that is, the counting efficiency falls linearly to zero, from the center of the slice to the end of the slice—so as this slice is moved along the [110] axis the number of occupied states which it selects varies in a complicated way, and it is not immediately obvious how one can correlate peaks in the observed angular distribution with necks in the F.S. No analysis has been presented which indicates that this problem has been solved. On the other hand, the vertical resolution function in our long-slit geometry has a base width of 150 mrad, so that the triangular shape of the resolution function causes a variation of only a few percent in counting efficiency over the entire zone.

The collinear-point geometry does not introduce the same difficulties of analysis, but it still suffers from the tremendous loss of counting efficiency. Of course the contribution from the F.S. necks is a large percentage of the total counts in this case, but the reduction in "noise" is accompanied by such a huge reduction in "signal" that the advantage is questionable. In order to recapture some of the "signal," Williams et al.[4] used a horizontal resolution of 1 mrad, over three times the width of our horizontal resolution (Fig. 3). With a resolution of 1 mrad one can certainly see whether F.S. necks are present, but it is doubtful if one can determine the radius of the neck to the accuracy needed in order to obtain useful comparisons of different alloys, especially when such a small number of counts is obtained. If one had an accurate model for the shape of the neck in each alloy, one might be able to do this, but the only model available is the rigid-band model, whose predictions were contradicted by these investigators' own results.

On the other hand, it seems clear from the width of the peaks displayed in Fig. 2 that our error assignments are conservative and that we have an accuracy sufficient to see the differences between the various alloys.

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STUDIES ON NONMETALS DURING IRRADIATION: THE GROWTH AND DECAY OF F CENTERS IN KCl AT 20°C †

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In KCl the F center versus dose curves obtained by making absorption measurements during gamma-ray irradiation differ considerably from those made by irradiating a crystal and then transferring it to a spectrophotometer. When the source is "turned off" the absorption drops abruptly for approximately 30 min and more slowly thereafter. The growth is accurately described by a sum of three saturating exponential terms and one linear term; the decay by the sum of four decreasing exponentials.

In the last ten or fifteen years there have been numerous studies on the radiation-induced color centers in various crystals, particularly in the alkali halides.[1,2] With very few exceptions, these studies have been made by irradiating samples in an x-ray or gamma-ray source and then transferring them to a spectrophotometer for measurement. However, one set of experiments utilized a facility for making optical absorption measurements while the sample was irradiated with Co^{60} gamma rays at relatively low dose rates.[3] These measurements showed that in KCl the F center versus dose curves obtained at room temperature could be resolved into several saturating exponential components. Also, after the source was "turned off" the coloring decreased and these decay curves could be separated into three or four exponentially decreasing components. However, the maximum dose rate available for most of these measurements[3] was approximately 3×10^3 R/hr and, since the maximum coloring increases with dose rate, the total induced absorption was small. Recently it became possible to make optical-absorption measurements as often as every ten seconds on samples while they were being irradiated at dose rates up to 5×10^5 R/hr, i.e., at dose rates 100 times larger. Summarized below are the more obvious new results obtained at the higher rate. The experimental equipment will be described separately.

A typical F center absorption versus time curve, obtained while a Harshaw KCl crystal was being irradiated at a dose rate of approximately 10^5 rad/hr at room temperature, is shown in Fig. 1. Compared to similar curves made at low dose rates or by irradiating a sample at similar rates and then transferring it to a spectrophotometer for measurement, the initial coloring rate is at least ten times higher, the transition from the initial rapid increase to the plateau occurs in a much shorter time, and once the plateau is reached the curve is precisely linear with a small slope. The insert in Fig. 1 shows, on a semilog plot normalized to unity, the difference between the data and the curve made by extrapolating the linear portion to $t = 0$. The insert shows that this difference can be resolved accurately into three saturating exponential components. The entire growth curve, then, can be accurately described by the expression

$$\alpha_F(t) = \sum_{i=1}^{3} \alpha_{F0i}(1 - e^{-a_i t}) + \alpha_L t. \quad (1)$$

The following parameters were obtained from