

Electrical resistivity due to dislocations in highly purified copper

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We have measured the specific dislocation resistivity in copper single crystals with low densities of dislocations ($\sim 10^7$ cm of dislocations per cm^3) introduced by bending. The dislocation density was estimated from etch-pit counts. Most of the specimens had residual resistivity ratios of about 40 000 before deformation, this high ratio being produced by oxidation. The specific dislocation resistivity was found to be $\sim 3 \times 10^{-19} \Omega \text{cm}^3$, estimated correct to within a factor of 2. We also looked for anisotropy of resistivity in fatigued single crystals and found none.

I. INTRODUCTION

The electrical resistivity due to dislocations in fairly heavily deformed copper has been determined many times (see, for example, Blewitt *et al.*,¹ Basinski and Saimoto,² Basinski *et al.*,³ Rider and Foxon,⁴ and Yoshinaga⁵). The generally accepted value for the resistivity per unit length of dislocation per unit volume is approximately $10^{-19} \Omega \text{cm}^3$.

On the other hand, Gantmakher *et al.*⁶ measured the resistivity of bent crystals of copper with lower dislocation density (10^7 – 10^8 dislocations per cm^2) and obtained a value of about $10^{-18} \Omega \text{cm}^3$. They attributed the discrepancy to the substantial correlation of the dislocations at high densities, more particularly to the superpositions of the long-range strain fields which tend to cancel their effects. Another possibility, they suggest, is that at high densities impurities may be captured by the dislocations thereby reducing the number of independent impurity-scattering centers.

Subsequently, Fedotov and Mezhov-Deglin⁷ studied the thermal conductivity of deformed copper samples and in a subsidiary experiment measured their electrical resistivity. They confirmed the finding of Gantmakher *et al.*, as did those of Kasumov *et al.*⁸

Since the disparity between the resistivity as measured at the two extremes of dislocation density is about a factor of 10 and since only a few sets of measurements (with almost identical experimental methods) showed this large discrepancy, we wished to repeat these measurements and determine the resistivity due to dislocations at comparatively low density (in the region of 10^7cm^{-2}) if possible, with the dislocation scattering the dominant mechanism. We also wished to determine the anisotropy of the resistivity.

The experimental requirements are severe. If the conventional value of $10^{-19} \Omega \text{cm}^3$ is correct, the resistivity due to dislocations at a density of 10^7cm^{-2} is $10^{-12} \Omega \text{cm}$. If the dislocation scattering is to be comparable with that due to residual impurities, the resistance ratio $R(300 \text{K})/R(4.2 \text{K})$ of the virgin copper must be about 2 000 000. With this ratio the mean free path of the electrons when the copper is cooled to low temperatures is about 8 cm, so that to avoid size effects the samples

would have to be impossibly large. Moreover, copper of such purity has never yet, as far as we know, been produced.

In any event, we were able, through oxidation, to produce single crystals with a residual resistance ratio of about 40 000. The mean free path is thus less than 2 mm and we used specimens whose cross-section was a square of side 4 mm. Thus corrections for size effects were small and negligible compared to other uncertainties in the experiments. Other specimens were purified with wet hydrogen (see Appendix).

The specimens were deformed by bending. After subsequent annealing and measurement of the resistivity change, the dislocation density was determined by etching the $\{111\}$ planes and counting the etch pits by means of both optical and electron microscopy. Experience showed that the largest uncertainty lay in finding the number of dislocations introduced.

In another set of experiments with fatigued crystals we looked for the anisotropy of the resistivity but were unable to detect any. Since these experiments are of a rather different nature from the first set, we have described them separately.

II. EXPERIMENTAL PROCEDURES

A. The copper crystals

The single crystals of copper were grown from Cominco 99.999%-pure plate copper and before oxidation had a residual resistance ratio of about 4000. The crystals were seeded and grown from the melt in prepurified graphite molds; they had dimensions $0.4 \text{cm} \times 0.4 \text{cm} \times 6 \text{cm}$. The axis of the crystals was about $[321]$; one pair of the long faces was close to the $\{111\}$ planes, chosen so that the number of dislocations could subsequently be determined by means of etch-pit counts. The direction of the axis of the crystal is chosen to be near the middle of the standard triangle (i.e., as far as possible from the principal symmetry directions), so that under deformation the resolved shear stress is greatest on a single glide system.

One batch of crystals was finally oxidized at a temperature of 1050°C ; this further lowered their resistivity and produced a residual resistivity ratio of about 40 000. Oth-

er crystals were heat-treated with wet hydrogen with the intention of removing carbon impurities; they had residual resistance ratios between 17 000 and 12 000. Details of the purification of the crystals are given in the Appendix.

B. The measurement of resistivity

The electrical resistivity of the samples was measured at liquid-helium temperatures by means of a superconducting thermal chopper (Edwards⁹) in a circuit as described by Basinski *et al.*³ The resistance of the specimens was typically about $10^{-9} \Omega$ and we were seeking to measure changes of about $10^{-10} \Omega$. With a measuring current of about 2 A, the detector thus needed a sensitivity of about 10^{-11} V or better. Provided the resistance in the circuit was low, we could achieve typically a sensitivity of about $5 \times 10^{-12} \text{ V}$.

In order to achieve this consistently, the resistance of the potential leads to the specimen had to be kept low. Moreover, the specimen had to be annealed after bending and before the final measurement of resistance. For this reason solder for the potential leads was unsatisfactory and we were unable to spot-weld to these bulky but mechanically soft copper samples without damage. Finally, we used sintered copper leads made from the same parent material as the sample and sintered to the sample during the oxidation process. The current leads were soldered to the end faces of the crystals. The ends of the specimen together with the current leads and all solder were removed by spark erosion before the annealing process. The connections to the potential leads and all solder were cut off; after annealing, the remaining parts of the sintered potential leads were used again. Thus the shape factor of the specimen was unchanged. The shape factor itself was determined both from measurements of the sample dimensions and by measurement of the room-temperature resistance. The low-temperature measurements were all made at the boiling point of liquid ⁴He.

At this temperature the resistivity of copper due to phonon scattering is $1.2 \times 10^{-12} \Omega \text{ cm}$ and we assumed that no correction was needed for this. The resistance of the specimens was checked at different values of the specimen current.

C. Production and counting of dislocations

The virgin crystals had approximately 10^5 dislocations per cm^2 . To introduce additional dislocations, the crystals were bent at liquid-nitrogen temperature on formers of suitable radius. The reason for bending at nitrogen temperatures was to ensure as far as possible that glide occurred on only one system. At low temperatures, easy glide (i.e., glide on a single system) persists to higher strains than at room temperature; nitrogen temperatures are convenient and reasonably satisfactory for this purpose.

Thereafter the crystals were annealed at a temperature of 350°C for 1 h to remove defects other than dislocations. We would have preferred to anneal the crystal at 750°C in order to remove as many dislocations as possible apart from those that are required to satisfy the geometry of the bend. Since, however, the crystals had been oxi-

dized to achieve a low resistivity, we decided that we dare not risk any change in the oxidation of the crystals and so kept the annealing temperature quite low.

The resistance of the crystals was measured again at liquid-helium temperatures after the bending and annealing. Then the number of dislocations was estimated by counting a representative sample. This was, we believe, the most critical, the most difficult, and the least accurate part of the experiment.

The crystal was first electropolished in ice cold nital (30% concentrated nitric acid and 70% methyl alcohol) at 4.5 V to remove about 0.1 or 0.2 mm of surface. The {111} surfaces were then etched in the solution recommended by Livingston¹⁰ for such surfaces; to obtain small etch pits the solution was kept at about -10°C and the etch time was in general less than 1 sec.

The crystals were then examined and photographed by optical microscope and scanning electron microscope. The optical microscope was used to survey comparatively large areas of the crystal surface. In particular, samples were examined from one edge of the crystal through the neutral section to the other edge (the neutral section is parallel to the bending axis and to the long faces and through the middle of the crystal). In bending the crystal, the regions away from the neutral section undergo more extension or more compression as the distance from the neutral section increases. Consequently, as might be expected and as was indeed found, the dislocation density tends to increase in these regions. Since the dislocation density is not uniform across the specimen, the distribution must be taken into account when estimating the average dislocation density. Optical micrographs gave the necessary distribution details, but the resolution available with this method is not high enough to ensure accurate etch-pit-density determination. For all specimens, scanning electron micrographs were therefore taken near the center of the crystal face, in the higher-density regions near the edges, and midway between these regions. The accurate etch-pit-density counts from scanning electron micrographs were used to calibrate the data from optical micrographs, by applying conversion factors obtained directly in the case of the three regions studied by both methods, and by interpolation elsewhere.

The photographs of specimen 2, taken as an example, sampled 2.2 mm out of the 4 mm across the crystal, admittedly in a slice only about $\frac{1}{4}$ mm wide. The number of dislocations counted in the sampling by optical microscopy was over 5000; the magnification used was 450.

The optical data on this specimen (bent to a radius of 7.2 cm about an axis parallel to the $[1\bar{1}\bar{1}]$ direction) gave counts of $\sim 1.7 \times 10^7 \text{ cm}^{-2}$ in the less dense regions near the middle of the crystal to over $2.5 \times 10^7 \text{ cm}^{-2}$ in the outermost regions. When these regions were in turn examined by the scanning electron microscope, the corresponding numbers were $\sim 2.5 \times 10^7$ and 10^8 cm^{-2} , i.e., a factor of 1.5 higher in the less dense region and a factor of 4 higher in the very dense regions.

The average density of dislocations in this crystal when bent was estimated to be $4 \times 10^7 \text{ cm}^{-2}$. The theoretical minimum demanded by the geometry is given by $n = 1/rb \cos\theta$, where b is the Burgers vector, θ is the an-

gle between the Burgers vector and the specimen axis, and r is the radius of curvature of the bend. Here $b = 2.55 \times 10^{-8}$ cm and $\theta = 40^\circ$. The equilibrium (minimum) number of dislocations is thus $7.7 \times 10^6 \text{ cm}^{-2}$, a factor of 5 smaller than that indicated by the actual count. Thus we conclude that unless the annealing after bending can be carried out at very high temperatures, the density of dislocations is considerably higher than the theoretical equilibrium number.

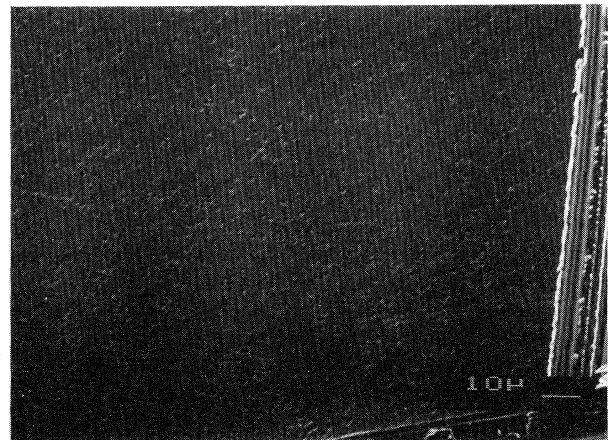
In specimen 3 with a lower density of dislocations, the optical and electron microscopes gave the same density for the middle region and differed by a factor of 1.3 at the edges. The average density was a factor of almost 2 higher than the ideal value. Scanning electron micrographs of three regions of specimen 3 (edge, middle, and intermediate) are shown for comparison in Fig. 1.

Several points should be mentioned in connection with conversion of the number of dislocation intersections with the $(1\bar{1}\bar{1})$ surface to an estimate for the dislocation-line density. Glissile dislocations must lie in $\{111\}$ planes and can therefore not lie parallel to the bending axis. In Fig. 2 the faces of the tetrahedron represent $\{111\}$ planes, and its edges represent $\langle 110 \rangle$ directions. For bending about $[1\bar{1}\bar{1}]$ the dislocation configuration involving minimum line length would be zigzags with components along $[1\bar{2}\bar{1}]$ and $[12\bar{1}]$. The ratio of this zigzag to a straight line along $[1\bar{1}\bar{1}]$ is $1/\sqrt{2}$, giving the minimum correction factor necessary from fcc dislocation geometry. For random dislocation distribution, there is a factor of 2 in the conversion from intersection density to line density. During bending about $[1\bar{1}\bar{1}]$ the above corrections apply in the region of the neutral axis, but in addition, towards the edges of the crystal some extension or compression takes place, introducing primary edge dislocations along $[1\bar{2}\bar{1}]$ for which the intersection to line density correction factor is $3/2\sqrt{2}$. It is well known, however, that plastic deformation introduces some dislocations with other line directions. Taking all of these factors into account, we felt it reasonable to apply an overall correction factor of $\sqrt{2}$ to the etch-pit count in order to arrive at a value for the dislocation-line density.

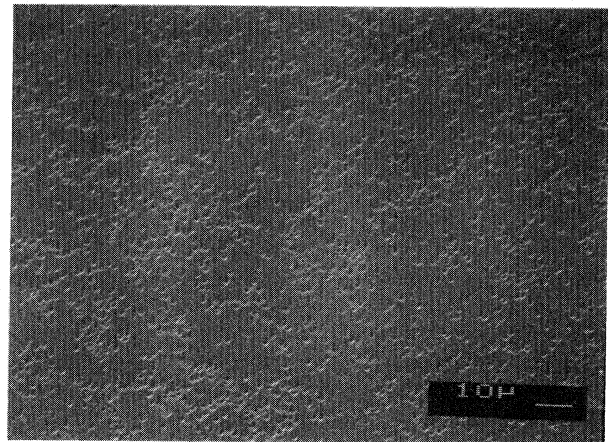
III. EXPERIMENTAL RESULTS

The experimental results are summarized in Table I, which gives details of the specimens, the change in resistivity on bending, the spread of dislocation densities derived from counting, the estimated average densities, and the resistivity per unit length of dislocation per unit volume. Note that in going from the average density to the change in resistivity per unit length of dislocation per unit volume (the last column) we have incorporated the factor $\sqrt{2}$, whose origin was explained at the end of Sec. II C. The experiments in specimen 1 were somewhat preliminary in that the counting of dislocations was from random regions, rather than from systematically chosen samples across the breadth of the specimen. Secondly, we improved the sensitivity of the resistance measurements before making measurements on the remaining samples.

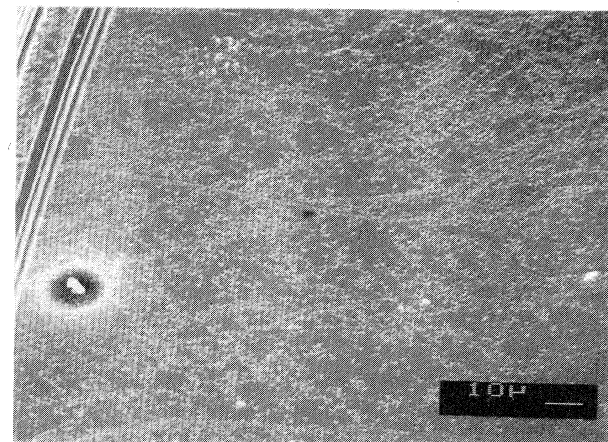
The change in resistance and hence in resistivity is accurate to better than 10%, but the number of dislocations



(a)



(b)



(c)

FIG. 1. (a) Electron micrographs of edge pits in specimen 3 showing how the density of dislocations increases from the center of the specimen; (b) through an intermediate position; (c) to the edge of the specimen. Scratches in the photographs were produced after etch pitting and were used to identify the same areas for optical and electron microscopy. The specimen surface was inclined 45° to the optical axis of the microscope.

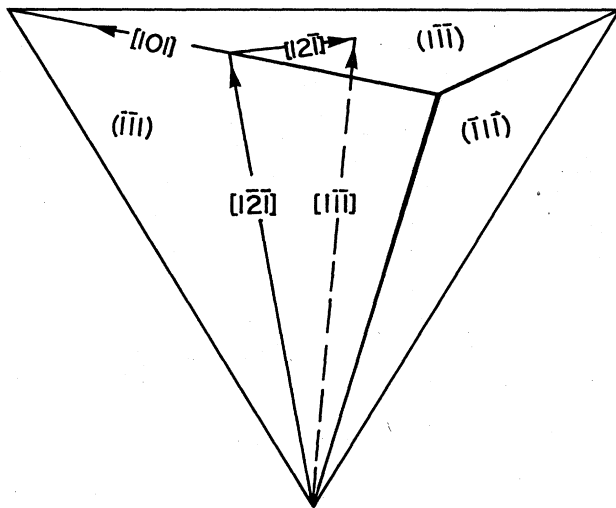


FIG. 2. Geometry of slip in fcc metals. Glide planes are represented by faces of the tetrahedron, and possible Burgers vectors by its edges. Dashed line, bending axis and required mean dislocation line direction. To satisfy Nye's conditions the required dislocations must be along $[1\bar{1}\bar{1}]$ and have $[101]$ Burgers vector; this can be achieved by the addition of segments along $[12\bar{1}]$ and $[12\bar{1}]$.

involved is uncertain to a factor of about 2. This is because the dislocation density is not uniform and sampling on a scale to improve this uncertainty would be an immense task. The increase in density towards the edges of the crystal, although expected, is bigger than we anticipated. This arises partly because the crystals are grown in graphite molds which introduce some imperfections mainly in the form of subgrain boundaries. These could be avoided by treating the molds with soot before use, but this might cause serious contamination of the crystals and impede the effects of oxidation. We thus have to compromise between crystal perfection in terms of dislocations and crystal perfection in terms of impurity scattering. For our present purpose the best compromise seemed to be to have a high residual resistance ratio.

For the final value for the resistivity due to dislocations we find $\sim 3 \times 10^{-19} \Omega \text{ cm}^3$. This result should be accurate to within a factor of 2. The nonuniformity of the distribution of dislocations is not big enough to seriously alter the current distribution and no correction for this has been made.

IV. DISCUSSION

The results show that the resistivity due to dislocations does not appear to change significantly with the density of dislocations. There could be a trend which our accuracy does not reveal, but the trend is not on the scale suggested by the results of Gantmakher *et al.*⁶ Some dependence of resistivity on purity is to be expected because of departures from Matthiessen's rule.

The main reasons for the discrepancy between our findings and those of Gantmakher and his colleagues can perhaps be inferred from Table I. If you take the value of the ideal dislocation density (column 7) and use this to calculate the normalized resistivity, the specimens 1, 2, 3, and 4 give, respectively, 10^{-18} , 10^{-18} , 9×10^{-19} , and $1.5 \times 10^{-18} \Omega \text{ cm}^3$. These are to be compared to the Gantmakher *et al.* value of $2.2 \times 10^{-18} \Omega \text{ cm}^3$. (All these numbers omit the geometrical factor $1/\sqrt{2}$ which, as discussed earlier, should be applied to all of them.) The remaining discrepancy is then a factor of only about 2, which we attribute to the different annealing temperatures used here as compared to those of Gantmakher *et al.* On sample 5 we made a direct comparison of the two annealing temperatures and found that after annealing for 1 h at 100°C , an additional anneal of 1 h at 350°C reduced the resistance by a factor of 1.8.

We suspect therefore that the difference between our results and those of Gantmakher *et al.* may arise mainly from taking the ideal, equilibrium value for the dislocation density instead of the actual, counted value, which is very different. We find it hard to believe that the crystals in the work of Gantmakher *et al.*, which were annealed at only 100°C for 1 h, could approach the ideal number as obtained by Livingston,¹⁰ whose crystals were annealed at 1060°C for 3 d. The same comments apply to the measurements of Fedotov and Mezhev-Deglin.⁷

A further feature that makes it unlikely that the specimens in the work of Gantmakher *et al.* could have the ideal density is that the tensile axis chosen was not favorable for slip on one system. This would inevitably lead to more rapid multiplication of dislocations during the deformation. Gantmakher *et al.* report that they did control experiments in which "the dislocations were displayed by etching" and found the same results as Livingston. They give no further details. Our experience is that optical microscopy alone at densities above about 2×10^7 is quite misleading, and that although the dislocations may be distributed reasonably uniformly in the central regions

TABLE I. The residual resistivity of specimens before and after bending to specified radii together with the corresponding dislocation densities.

Specimen	$10^{-3}\rho(300 \text{ K})/\rho(4.2 \text{ K})$	Bending radius (cm)	ρ_0 ($10^{-11} \Omega \text{ cm}$)	$\Delta\rho$ (4.2 K) due to bending ($10^{-12} \Omega \text{ cm}$)	Range of dislocation counts per (10^7 cm^{-2})	Estimated average density (10^7 cm^{-2})	Ideal density (10^6 cm^{-2})	$\Delta\rho$ per unit length for unit volume ($10^{-19} \Omega \text{ cm}^3$)
1	39	5.3	4.3	8.5	1.1–2.7	1.8	10	3.0
2	43	7.2	4.0	8.1	2.5–10.0	4.0	7.7	1.4
3	45	19.8	3.8	3.6	0.35–1.7	0.75	4.0	3.3
4	16.8	7.2	10.0	11.8	0.85–6.0	2.8	7.7	3.0

of the crystals their uniformity diminishes and their density increases towards the edges. Thus the ideal theoretical number provides no real guidance.

Kasumov *et al.*⁸ did measure both the resistivity change due to dislocations and estimate their density by etch-pit techniques and by examination with an electron microscope. Not enough details of the etch-pit measurements are given to comment on these, but the dislocation substructure shown in their Fig. 2 appears to be inconsistent with the substructure to be expected from the experiments as described. Since the only pure edge dislocations of the orientation shown would have a Burgers vector normal to the foil, they could not therefore have been introduced by bending.

V. ANISOTROPY OF RESISTIVITY

A. Experimental

The resistivity due to dislocations should be highly anisotropic, provided that the dislocations themselves are strongly oriented in some given direction. We have looked for this effect in fatigued crystals in which the dislocations had a very definite predominating direction. The crystals which were the same as those used in bending, except that they were 5 cm in length, were fatigued in tension-compression at low constant plastic strain amplitude ($\pm 1.2 \times 10^{-3}$) at room temperature in the presaturation region. This treatment produces a dislocation substructure (the matrix) consisting of cells, or veins, of densely packed dislocations of predominantly primary edge type (see, e.g., Basinski *et al.*¹¹) with dislocation axes $[101]$, $[\bar{1}\bar{1}1]$, $[1\bar{2}\bar{1}]$, which would coincide with the principal axes of the conductivity.

To detect any anisotropy in the electrical resistivity at low temperatures, we attached potential leads (by sintering) to the four corners of the crystal approximately in a plane normal to the axis of the crystal. If these leads were accurately in place, measurements between one such lead and its two neighbors would measure the transverse voltages and, hence, the transverse electric fields in the specimen when a current flows along the crystal axis. Measurement of the potential on the fourth lead would test the self-consistency of the two other measurements. A further potential lead on a corner of the crystal but some distance away from the others allowed us to measure the longitudinal field and so normalize the transverse fields. In this way we could test for any anisotropy; if the resistivity is isotropic, the transverse fields should be zero.

Since, however, we cannot accurately position the electrodes as assumed above, a preliminary experiment at room temperature (where the resistivity is essentially isotropic) enables their effective positions to be determined. Thus the measurements at helium temperatures where the dislocation resistivity is dominant can be corrected for any departures of the electrodes from their ideal positions in the normal plane. In specimen 9 we had two sets of electrodes in different transverse planes so that the internal consistency of the results could be further checked. The results are summarized in Table II. This shows the two transverse resistivities R_x and R_y with the z axis in the longitudinal direction, i.e., that of the current flow.

TABLE II. Transverse components of the resistivity of fatigued specimens, together with the associated transverse and longitudinal electric field strengths.

Specimen	$\frac{R(293\text{ K})}{R(4.2\text{ K})}$	Correction		Correction		R_x ($10^{-10}\ \Omega$)	δR_x ($10^{-10}\ \Omega$)	Measured R_y ($10^{-10}\ \Omega$)	Correction to R_y ($10^{-10}\ \Omega$)	δR_y ($10^{-10}\ \Omega$)	R_z ($10^{-10}\ \Omega$)	E_x ($10^{-10}\ \text{V cm}^{-1}$) for 1 A	E_y ($10^{-10}\ \text{V cm}^{-1}$) for 1 A	E_z ($10^{-10}\ \text{V cm}^{-1}$) for 1 A	E_x/E_z	E_y/E_z
		Measured R_x ($10^{-10}\ \Omega$)	to R_x ($10^{-10}\ \Omega$)	to R_x ($10^{-10}\ \Omega$)	to R_y ($10^{-10}\ \Omega$)											
6	1860							2.27	3.38	-1.11	23.5		-2.8	56.5		-0.05
7	3420	0.93	1.24	-0.31				3.10	2.68	0.43	19.8	-0.8	1.1	31.7	-0.03	0.03
								0.83	0.64	0.19	19.8		0.5	31.7		0.02
8	1290	0.61	-1.14	1.75				3.90	3.34	0.55	64.1	4.4	1.4	86	0.05	0.02
		-1.89	-2.03	0.14							64.1	0.4		86	0.05	
9	896	3.32	3.06	0.25				3.37	4.42	-1.05	71.3	0.63	-2.6	118	0.005	-0.02
		-0.40	-0.97	0.57				6.15	6.02	+0.13	71.3	1.4	0.3	118	0.01	0.003
		-5.20	-5.09	-0.11							71.3	-0.3		118	-0.003	

Notice that the corrections to R_x and R_y due to the inaccurate placing of the potential probes are comparable to R_x and R_y themselves. Columns 10, 11, and 12 give the two transverse fields, E_x and E_y , and the longitudinal electric fields E_z . The final two columns give the ratios E_x/E_z and E_y/E_z which thus serve as a measure of the relative strengths of the transverse fields. They are all less than 5%, but if you look at the results within one sample (e.g., specimen 9) you see that some have opposite signs and are zero within the experimental error.

Note that in these *fatigued* specimens the resistivity due to the dislocations is several times higher than any residual impurity resistivity. These specimens are, however, of no value for determining the specific resistivity due to dislocations, because it is not possible to *count* the dislocations.

B. Discussion

It seems to be accepted, on theoretical grounds, that if we have pure edge dislocations, electrons traveling in the direction of the dislocation line will not be scattered (e.g., Dexter¹², Hunter and Nabarro¹³, and Martin and Ziman;¹⁴ see also the discussion by Nabarro¹⁵). This is because the periodicity of the lattice in this direction is not disturbed by the dislocation. Consequently, there should be a large anisotropy of electrical resistivity.

The experimental results given in Table II indicate, however, that within our experimental error there is no anisotropy in the resistivity. Notice, in particular, the final two columns which list E_x/E_z and E_y/E_z . These indicate that any transverse field is less than our experimental error of ~5%. This means that the anisotropy in resistivity is less than about 10%, which is quite astonishing. If the average residual resistance ratios of the fatigued and virgin crystals are, respectively, ~3000 and ~40000, there should be an anisotropy of resistivity of order 10.

Kasumov *et al.*⁸ found a considerable anisotropy of resistivity (a factor of between 2 and 3) in bent specimens. There is, however, not enough detail to be sure the effects they describe are real. We note that the mean free path of the electrons is very close to the size of the specimen and that size effects could have been important in the results. In addition, as we have stressed, bent samples are not homogeneous, and when the resistivity due to dislocations is dominant this inhomogeneity can have large effects; the resistance of the strip depends on where it is cut from the bent specimen.

From our own experiments we conclude that the dislocations introduced by fatigue show no anisotropy of resistivity greater than 10%. One factor that might be relevant to this result which is not considered in conventional theories is inelastic scattering by dislocations. If this is important it would show up in the temperature dependence of the resistivity since it must ultimately vanish as the temperature is lowered. This can therefore be tested experimentally.

Watts¹⁶ has recently suggested that an "atomistic" model of scattering from dislocations might produce scattering that is approximately isotropic since it could in-

duce large changes in the component of the electron k vector parallel to the dislocation line by Bragg reflection. He has, however, not yet developed the idea in detail.

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APPENDIX: PURIFICATION OF COPPER

In order to obtain pure material from which to grow the single crystals, we experimented with the electrolysis of commercial copper and found that this was a very effective way of removing iron. It is generally recommended¹⁷ that, as an electrolyte, one should use copper nitrate, not sulfate, for fear of leaving traces of sulfur as an impurity in the deposited copper. In our experience, however, copper deposited from copper nitrate solution was powdery, porous, discolored, and very likely to form dendrites. As a consequence, there is a large surface area which allows impurities to be physically absorbed, and these impurities can then be taken into solution when the copper is melted. Copper electrodeposited from copper sulfate solution, on the other hand, was dense, bright, and in generally good condition for melting.

Analysis by mass spectrometer showed that most, and possibly all, of the iron impurity was removed by electrolysis. We checked this further by adding radioactive ⁵⁹Fe to the electrolyte and testing for radioactivity in the deposited copper. This measurement indicated that the concentration of iron was reduced by a factor of 8×10^{-7} . This was further tested by electrolyzing a solution of copper sulfate and iron sulfate with about 30 at. % Fe. The iron in the deposited copper was estimated from the residual resistivity to be less than 1 ppm.

The residual resistance ratio of the electrolyzed copper was typically 4000 to 5000, never higher. We were convinced that the remaining impurity was not iron but might have been silicon or carbon. Schroeder¹⁸ told us that he had reduced the residual resistivity of copper by using vitreous graphite instead of the conventional form of graphite crucible, implying that carbon might well be the dominant residual impurity. This would explain why the residual resistance ratio of crystals grown from different batches of copper was so reproducible—usually in the range 1000–2000.

Consequently, we tried treating the single crystals with wet hydrogen. This process consists of bubbling ultrapure hydrogen gas through water and then over the copper crystal which is maintained at a temperature between 1025 and 1050 °C in a transparent silica tube. The process took about 5 d. The objective is to convert the carbon to CO and so remove it; this process is a standard one for

decarburizing iron.

The wet-hydrogen treatment improved the residual resistance ratio in one batch from about 1000 to 17 000. The fact that this treatment reduced the concentration of impurity in solution in the copper is further evidence that

the residual impurity is not iron since iron would *not* be affected by the wet-hydrogen reaction. It is important to pump out any residual hydrogen from the specimen by heating in a good vacuum at 1050 °C until the residual gas is removed.

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¹T. H. Blewitt, R. R. Coltman, and J. K. Redman, in *Conference on Defects in Crystalline Solids* (The Physical Society, London, 1955), pp. 369–82.

²Z. S. Basinski and S. Saimoto, *Can. J. Phys.* **45**, 1161 (1967).

³Z. S. Basinski, M. Sahoo, and S. Saimoto, *Acta Metall.* **25**, 657 (1977).

⁴J. G. Rider and C. T. B. Foxon, *Philos. Mag.* **16**, H33 (1967).

⁵H. Yoshinaga, *Phys. Status Solidi* **18**, 625 (1966).

⁶V. F. Gantmakher, V. A. Gasparov, G. I. Kulesko, and V. N. Matveev, *Zh. Eksp. Teor. Fiz.* **63**, 1752 (1972) [*Sov. Phys.—JETP* **36**, 925 (1973)].

⁷A. O. Fedotov and L. P. Mezhov-Deglin, *Fiz. Tverd. Tela (Leningrad)* **24**, 207 (1982) [*Sov. Phys.—Solid State* **24**, 114 (1982)].

⁸A. Yu. Kasumov, Ch. V. Kopetskii, L. S. Kokhanchik, and V. N. Matveev, *Fiz. Tverd. Tela (Leningrad)* **23**, 271 (1981) [*Sov.*

Phys.—Solid State **23**, 151 (1981)].

⁹G. J. Edwards, *J. Phys. E* **4**, 299 (1971).

¹⁰J. D. Livingston, *J. Appl. Phys.* **31**, 1071 (1960).

¹¹S. J. Basinski, Z. S. Basinski, and A. Howie, *Philos. Mag.* **19**, 899 (1969).

¹²D. L. Dexter, *Phys. Rev.* **86**, 770 (1952).

¹³S. C. Hunter and F. R. N. Nabarro, *Proc. R. Soc. London, Ser. A* **220**, 542 (1953).

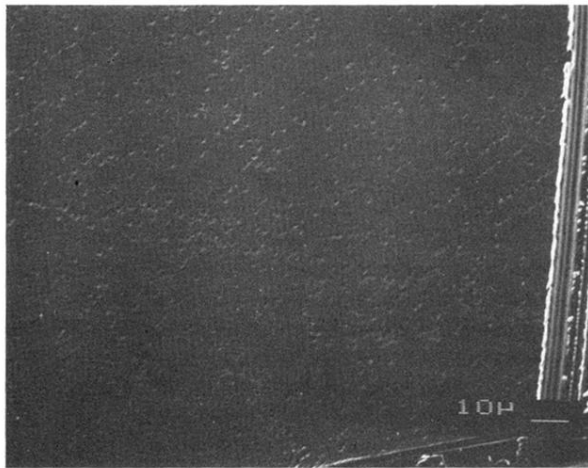
¹⁴J. W. Martin and J. M. Ziman, *J. Phys. C* **3**, L75 (1970).

¹⁵F. R. N. Nabarro, *Theory of Crystal Dislocations* (Clarendon, Oxford, 1967).

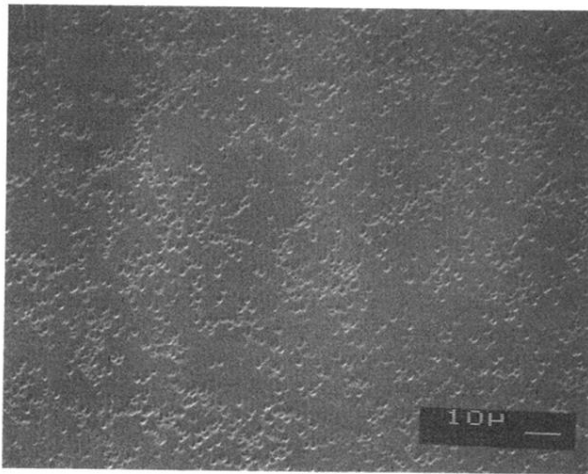
¹⁶B. R. Watts, in *Proceedings of the 17th International Conference on Low Temperature Physics*, edited by U. Eckern, A. Schmid, W. Weber, and H. Wühl (Elsevier, Amsterdam, 1984), pp. 1099–1100.

¹⁷F. Blanié and J. Le Héricy, *C. R. Acad. Sci.* **275**, C67 (1972).

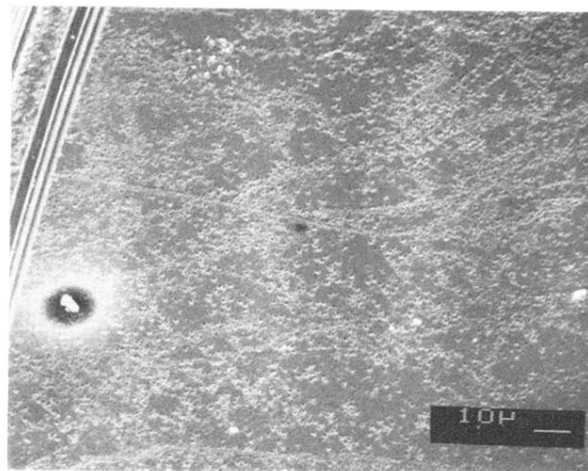
¹⁸P. A. Schroeder (private communication).



(a)



(b)



(c)

FIG. 1. (a) Electron micrographs of edge pits in specimen 3 showing how the density of dislocations increases from the center of the specimen; (b) through an intermediate position; (c) to the edge of the specimen. Scratches in the photographs were produced after etch pitting and were used to identify the same areas for optical and electron microscopy. The specimen surface was inclined 45° to the optical axis of the microscope.