Electrons of the vacuum surface of copper oxide and the screening of patch fields

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In the electron free-fall experiments of Witteborn, Fairbank, and Lockhart, the absence of the ambient electric fields due to the patch effect has been unexplained. Here we propose, and test against the experimental conditions, a model in which a double layer appropriate for screening is created by electrons captured from the vacuum on a copper-oxide film lining the drift tube. Necessary criteria turn out to involve: oxide thickness, number of electrons available, surface mobility of electrons, and electron-capture mechanism. We conclude that this model is a possible explanation of the results but the experiments to date remain ambiguous in its verfication.

I. INTRODUCTION

The report by Lockhart, Witteborn, and Fairbank[1] giving experimental evidence for a temperature-dependent surface shielding effect in copper, and the use of these results by LaRue, Fairbank, and Hebard[2] in order to eliminate electric-field-gradient effects in their levitation experimental search for quarks, has renewed interest in a controversial and unexplained series of experiments begun by Witteborn and Fairbank.[3-8] These original experiments were undertaken in order to measure the gravitational free fall of electrons. The gravitational force on an electron is extremely small compared with probable forces of magnetic or electrical origin, the electrical field equivalent of gravity being only $mg/q = 5.6 \times 10^{-11}$ V/m. A most complete description of the free-fall experiment and the experimental means employed to minimize undesirable forces have been recently reviewed by Witteborn and Fairbank.[8]

In this experiment electrons were constrained by a magnetic field to move vertically along the axis of a copper "drift tube," shown schematically in Fig. 1. In most of the experiments[6-8] and in Lockhart's temperature-dependent studies[1] the tube was about 1 m long with an inside diameter of about 10 cm. In the original experiments of Witteborn and Fairbank[6] at 4.2 °K their analysis indicated a *total* force on slow electrons in the tube of less than 0.09 mg implying an upward electrical force nearly balancing gravity. Lockhart's[1] analysis of his 4.2 °K data suggests an electric field of $(6 \pm 7) \times 10^{-10}$ V/m.

Whether or not the electric field inside this drift tube is really small enough for gravity to be observed on single electrons has been the subject of a lively theoretical debate.

Initially, Schiff and Barnhill[9] predicted that there would be an electric field of magnitude mg/q acting with an upward force and exactly cancelling the force of gravity for electrons within the tube, in agreement with the Witteborn-Fairbank result. The origin of this force was simply the equilibrium adjustment of the metallic electrons to gravity. Dessler *et al.*[10] proposed a much larger field of magnitude Mg/q exerting a downward force on an electron (where M is a mass typical of a metal ion). This field was derived from a calculation of the ionic displacements in the metal due to its gravitational compression. Herring[11] resolved the difference between these two calculations by showing that a proper treatment of the metal's elastic properties in the Schiff-Barnhill reciprocity-relation approach yielded the larger downward force found by Dessler *et al.*[10] of 10^{-7}–10^{-6} V/m. A review of the theoretical controversy,

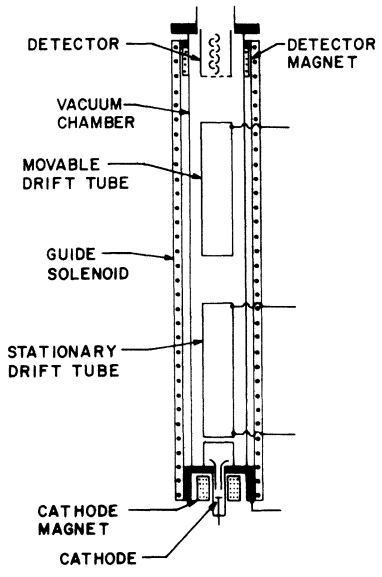

FIG. 1. Free-fall "drift-tube" apparatus used by Witteborn, Fairbank, and Lockhart. At issue is the degree of electric field screening within the negatively biased stationary drift tube.

including the contributions by Peshkin[12] and Harrison[13] and of the experimental determinations of the effect of stress on metal work functions by Beams[14] and Craig[15] has been given by Schiff.[16] Noting the discrepancy between the Witteborn-Fairbank result and theoretical expectation Schiff speculated, "It seems likely that ionic effects are shielded out by a surface layer that does not share the gravitational deformation of the underlying metal, so that only the electrons in the surface layer contribute to the electric field within the tube."[17]

Just such a mechanically decoupled surface layer was proposed in more concrete terms by Trammel and Rorschach.[18] They supposed the inner surface of the copper tube to be covered with a lush growth of copper whiskers producing an effective conducting surface with greatly reduced dependence on surface strain. Examination of the drift-tube interior[1] showed a thin oxide layer but no whiskers.

Despite the theoretical preoccupation with gravitationally induced gradients of work function, a far larger source of unwanted electric fields is the variation with crystallographic direction of the work function over the polycrystalline drift-tube walls. This is the "patch effect" and was an early concern of Witteborn's[5] for which he estimated potential variations of the order of 10^{-4} V. Even the clever whisker model of Trammel and Rorschach would be expected to show some patch effect due to randomness in whisker density and orientation.

In Sec. II we shall examine a different model for the elimination of electric fields within the drift tube. It involves screening by electrons bound to the copper oxide surface of the drift tube, an idea that has been independently suggested by Lockhart,[1] but which has heretofore not been quantitatively compared with the experiment.

II. SURFACE-ELECTRON SCREENING MODEL

If, in the course of the experiment, a variable contribution to the electric double layer on the inside walls of the drift tube is suitably spatially arranged, the undesirable fields may be "screened." Here we wish to examine the possibility that this screening is accomplished by electrons trapped on the vacuum side of the copper oxide tarnish film of the drift tube. The nature of the electronic surface states of a dielectric film on a metal substrate has been described by Cole.[19] In the present case, where the dielectric is most probably Cu_2O with a dielectric constant of 12, nearly all of the force attracting the electron to the surface is due to polarization of the dielectric with only a small perturbation from the metal substrate. The energy spectrum is free-electron-like for motion parallel to the surface but is quantized in discrete levels for perpendicular motion. For present purposes a satisfactory approximation to the bound states of the energy spectrum for perpendicular motion is the "hydrogenic" limit[20]

$$E_n^0=(-Z^2/2n^2)E_H, \quad Z=\tfrac{1}{4}(\epsilon-1)/\epsilon+1).$$

Thus ground-state electrons are bound by about 0.6 eV to the copper oxide surface.

For this to be a valid ground state, the lifetime with respect to decay by tunneling through the oxide into the copper must be long. And, if an appreciable number of these electrons are to be available for screening, this lifetime must also be long compared with times in which the surface can be charged by the experiment. Following Cole[19] the tunneling lifetimes of the ground state at -0.6 eV for three values of oxide thickness and two values of the oxide barrier height V_0 are given in Table I.

The oxide thickness is clearly a crucial parameter for a surface-electron screening model. In the most recent report Lockhart[1] mentions that an examination of the drift tube revealed a layer of copper oxide approximately 20 Å thick. According to Table I the oxide layer must be 30–40 Å thick to preserve surface electrons against tunneling. From the literature on the oxidation of copper[21] it seems probable that the oxide thickness exceeds 20 Å. (The 20 °C isotherm reported from the work of Miley[22] indicates an oxide thickness of 85 Å after 1 h.) Atmospheric tarnishing at room temperature is also extremely sensitive to the sulfide content of the atmosphere, thus Vernon[23] found a rate of 15 Å/day with 1 part in 6×10^8 of H_2S and 60 Å/day with 4 parts in 6×10^8 of H_2S in the atmosphere. One assumes that the sulfur content of the atmosphere is not so high that the tarnish becomes a mixed oxide sulfide.

Studies of the oxidation of different faces of a single crystal of copper[24] have shown that the growth is epitaxial and proceeds at sensibly different rates on the major crystallographic faces. We would infer from this that the oxide film on the polycrystalline drift tube has steps of several

TABLE I. Ground-state tunneling lifetimes, in seconds, for two barrier heights and three oxide thicknesses.

	20 Å	30 Å	40 Å
0.7-eV barrier	4.5×10^{-5}	5.8×10^{0}	7.1×10^{5}
1.7-eV barrier	1.1×10^{-1}	6.3×10^{5}	3.7×10^{12}

crystal lattice spacings between the various grains. It is conceivable that such steps could inhibit the lateral motion of surface electrons.

The screening depends upon the number and the spatial arrangement of the electrons in surface states. Consider a small region of the surface of uniform potential and double layer (a single patch) covered by an oxide film of thickness t and dielectric constant κ. The change in potential outside this region due to a surface-charge density of n electrons/m^2 will be

$$\Delta\phi = qnt/\kappa\epsilon_0 ,$$

the surface being characterized by a capacitance per unit area of $C' = \kappa\epsilon_0/t$ (0.035 F/m^2 for a 30-Å oxide film).

Suppose we entertain the idea that surface electrons provide a screening double layer for the patch fields at distances from the surface comparable to patch dimensions. This would require that roughly half of the drift-tube inner surface have an electronic double layer producing a potential change of about the amplitude of the patch potential variation (the order of tenths of volts). The total number of electrons required will be somewhat greater than 3×10^{15} for the 1-m drift tube. Since the tunnel cathode is operated at about 1 pulse of 10^9 electrons every second it would take *all* of the electrons for 1000 h of operation to produce a small-scale screening of the patch fields.

Fortunately this small-scale screening of the patch fields is not required or detectable in the free-fall experiment. The variation of electrostatic potential outside a perfectly regular array of patches (such as a checkerboard for a two-patch model) falls off exponentially with argument $(-2\pi z/X)$, where z is distance from the surface and X is a patch dimension.[25] The fields due to a regular array are thus negligible on the drift-tube axis. The fields that need to be screened are those arising from slight irregularities in the patch distribution on the scale of the tube radius. Witteborn[5] recognized this and derived a simple statistical two-patch model for the potential fluctuations $\Delta\Phi$ on the axis of the drift tube of radius a due to a random arrangement of patches with potentials $\pm\phi$ on a "checkerboard" with squares of dimensions X:

$$\Delta\Phi = \sqrt{\tfrac{3}{8}}\,(X/a)\phi .$$

Thus for $X = 40$ μm, $a = 5$ cm, and $\Phi = 0.1$ V, we have $\Delta\Phi \cong 5 \times 10^{-5}$. From the nature of the derivation this result would imply random axial-field fluctuations with magnitudes of about $\Delta\Phi/2z$ or 5×10^{-4} V/m. The number of electrons required to screen these random fields is only a small fraction of that required to completely screen the patch fields. A rough estimate of this number is obtained by assuming that about half of the area of the drift-tube surface would require a potential change of $\Delta\Phi$. Thus

$$N = q^{-1}\Delta\Phi C'(0.15\ \text{m}^2) = 1.6 \times 10^{12} .$$

It is conceivable that *this* many electrons can be accumulated on the walls of the drift tube during the course of hours of operation.

Two regimes for the spatial distribution of the surface electrons are distinguished by whether they are free to move on the oxide surface. If they are, their distribution should be describable by a surface Fermi level (not coincident with that of the copper substrate because of the negligible tunneling). If they are not, electron position is determined by the dynamics of the capture mechanism.

Let us consider the case of a two-patch model in which the metal has a random patchwork of two work functions covered by a uniform layer of oxide. How are electrons distributed on this surface in equilibrium with respect to lateral motion? At first one might suppose that the low-work-function high-potential patches would have equal probabilities of occupation. However, the potential at the oxide vacuum interface is the sum of the electric double layer at the metal surface *and* the integral of the normal electric field in the oxide. In the absence of surface electrons this normal electric field originates solely from the boundary conditions imposed by the patch distribution. Thus a high-potential (low-work-function patch) in a region dominated by low-potential patches has a lower oxide-surface potential than one in a region of predominantly high potential. Electron states on the high-potential patch in the high-potential region will have lowest energy and will fill first in surface thermal equilibrium. This is just what is needed in order to decrease (screen) the large-scale electric field between the regions.

A simple quantum effect prevents this surface equilibrium screening from completely eliminating electric fields. The electron populations of two regions will be in balance when there is equality of the surface Fermi levels. The surface Fermi energy consists of the electrostatic potential and also a term derived from the filling of the available surface levels according to Fermi statistics. The dependence on Fermi level of the density of a degenerate two-dimensional electron gas is

$$\frac{\partial n}{\partial \epsilon_F} = \frac{4\pi m}{h^2} ,$$

from which we obtain the change in surface po-

tential due to a change in Fermi level (in electron volts) as

$$\frac{\partial\Phi}{\partial(\epsilon_F/q)}=\frac{q^2}{C'}\frac{4\pi m}{h^2}\,.$$

For our typical C' of 0.035 this turns out to be about 19. Thus the difference of potential between two regions can be reduced by at most this factor of about 20 if the screening electrons are in equilibrium between the two regions. (If the screening is by a nondegenerate gas the derivative of potential with respect to Fermi level is even smaller.)

No such limit applies to nonmobile electrons, their location for screening being totally dependent upon the efficiency of the capture process.

It is reasonable to assume that the surface electrons are mobile at high temperatures and do not come to surface equilibrium at low temperatures. A model for the surface conductivity may be obtained starting with a two-dimensional Richardson equation for the surface particle current over a barrier $\Delta\phi$ above the Fermi level

$$\Gamma=\frac{2(2\pi m)^{1/2}(kT)^{3/2}}{h^2}\,e^{-q\Delta\phi/kT}\,.$$

This may be converted to a surface conductivity considering barriers a distance l apart and the contribution of an applied field to the barriers, thus

$$J=q\Delta\Gamma=\frac{lq^2 2(2\pi mkT)^{1/2}}{h^2}\,e^{-q\Delta\phi/kT}E$$

or

$$J=\sigma_s E\ (\mathrm{A/m})\,.$$

The corresponding time constant for the equilibration of a region of dimension d is

$$\tau=Cd^2/\sigma_s\,.$$

In order to see if this time constant for surface equilibrium is relevant to the experiments we inquire as to the barrier height $\Delta\phi$ which would produce a time constant $\tau=3600s$ at $T=100$ °K for a region of size d, equal to the drift tube radius (0.1 m) containing patches of size $l=4\times10^{-5}$ m ($C'=0.035$ as before). We obtain $\Delta\phi=0.17$ V. This is perhaps a bit larger than one might expect from the patch work-function differences but is close enough for us to be convinced that surface equilibrium is attained in experimental times at room temperature but is not approached at liquid-helium temperatures.

In order to understand screening by electrons which lack surface mobility, we must propose a mechanism by which they are captured by the walls at just the right places. At first glance it is difficult to see how electrons arrive at the inner walls of the drift tube at all. In the guiding magnetic field of 7–20 G,[6] the radius of the cyclotron orbit of an electron emitted at the peak of the 3000 °K energy spectrum of the tunnel cathode is only a few millimeters. The diameter of the central part of the drift tube into which electrons are injected is determined by those magnetic field lines which thread the controlling aperture above the cathode. Since the field in the cathode region is 3000 G and the controlling aperture is 1 mm, this diameter is about

$$(3000g/10g)^{1/2}\times1\ \mathrm{mm}=17\ \mathrm{mm}\,.$$

Thus with no other perturbations, the injected electrons appear to be localized to the center, 2 or 3 cm of the 10-cm diam drift tube, and will pass right through if they have sufficient axial momentum.

For any appreciable number of electrons to reach the walls it is our hypothesis that there are some random fluctuations of the potential along the axis, such as would be expected due to the patchy nature of the copper work function. It is also essential to recognize that the 1-msec pulse of injected electrons is quite long compared with even very slow electron-transit times. An electron that is captured is then one whose axial component of momentum is insufficient to surmount an axial potential barrier and which after turning back toward the cathode suffers an energy-losing collision with an upward moving electron so that it cannot surmount a lower potential barrier and is therefore trapped. Once trapped its progress toward the wall may be quite slow, governed by the cross-field drift in the guide magnetic field and whatever radial patch fields it encounters. This process keeps trapping electrons in the regions of positive potential on the axis. The rate of capture should decrease as the potential fluctuations become screened out by electrons on the walls. In particular, at the lowest temperatures where there is no surface mobility, a relatively complete cancellation of axial potential fluctuations should be obtainable given enough time.

In light of our estimate of 1.6×10^{12} electrons to screen the *random* fields in the drift tube, this capture process would have to operate with an efficiency of about 1.5% for 30 h (10^5 pulses of 10^9 electrons each). If the drift tube is kept at liquid-helium temperature this charge could be accumulated over several experimental "runs."

In addition to the fields arising from a patchy work function is the field due to the gradual gradient of work function due to gravitational compression of the drift tube and also the applied fields produced in the experiments by passing

small currents through the drift tube. For the present model of screening these two long-range fields should appear only as slight biases on the patch fields and hence should be screened to the same extent provided that there is sufficient time for the differential-capture process to operate.

III. COMPARISON WITH EXPERIMENT

Lockhart *et al.*[1] provide a summary of the ambient fields observed in drift-tube experiments at 300 °K, 77 °K, and in the range 4.2–10 °K. Figure 2 is from their publication. It is tempting to ascribe the relative success of low-temperature screening to the freeze out of a surface transport mechanism such as we have discussed in Sec. II. In all of the experiments the fundamental quantity measured has been the time-of-flight (TOF) distribution of electron arrivals at the detector at the top of the tube(s) after the cathode pulse. A parameter which could be systematically varied in taking these distributions was an applied drift field—an axial field in the drift tube produced by passing a small current from end to end in the walls of the tube. The true response of the screening mechanism to this applied field is crucial to our understanding.

At high temperatures where surface charges are mobile, it would seem that the applied field should be screened to the same extent as the ambient patch fields. The TOF data for 300 °K presented by Lockhart[26,27] is peculiar in its asymmetry. In Fig. 3(a) we show Lockhart's logarithmic plot of the data and in Fig. 3(b) a *linear* plot of the same data. We would surmise that the true maximum in TOF intensity lies off scale to the right. Such a result seems possible where mobile electrons on the tube walls have moved asymetrically

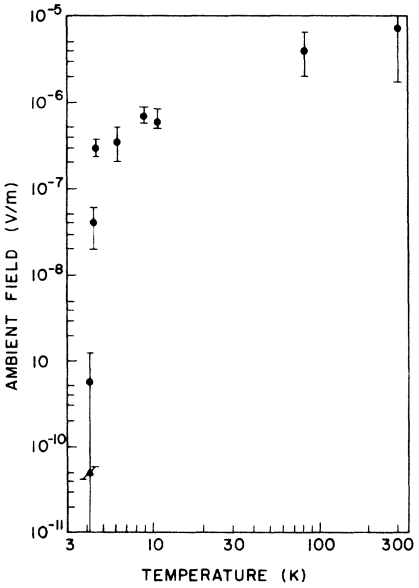

FIG. 2. Ambient electric field in the drift tube at different temperatures from Lockhart *et al.* (Ref. 1).

to the ends under the influence of the unequal positive potentials outside the ends of the drift tube. This accumulation of electrons at the ends may account for the failure to screen the small applied-axial fields. As far as we know, the 77 °K results are similar to the 300 °K data.

At temperatures from 4.2 to 10 °K, screening appears to be effective and we assume that charge carriers are not mobile on the copper-oxide surface.

Since it would appear that given time enough an applied field should be screened as effectively as the ambient fields, it is important to ascertain how often the applied field was changed and how symmetrically about zero. Apparently[8] field changes were made every 10 min in experimental runs lasting for days. There is reason to believe

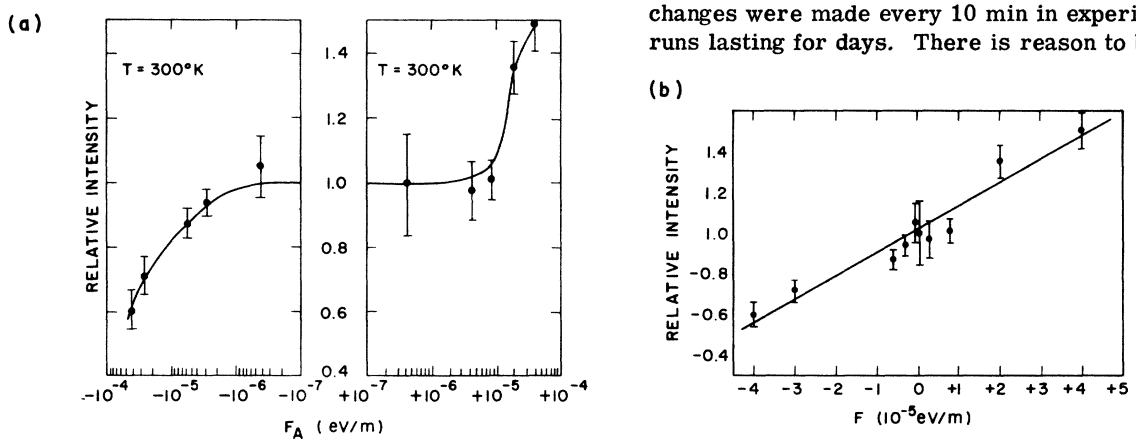

FIG. 3. (a) Time-of-flight data at 300 °K as plotted by Lockhart (Refs. 26 and 27). Relative intensity is the ratio of the slow (late) electron count at the applied field to that at zero applied field. (b) Same data replotted against a linear abscissa scale. In both cases the solid line is only a "guide for the eye."

that fields of both signs were used in the Witteborn studies and in Lockhart's first 4.2 °K study. However, in Lockhart's investigation between 4.3 and 11 °K only upward forces (several values) were applied. There have also been some differences in the data analysis. Late arriving electrons (those that had tarried awhile in electrostatic traps) seem to play a larger role in the later Lockhart analysis—although they are certainly a part of Witteborn's five-parameter fitting function.[8] Thus it seems possible that the various differences in observed ambient field below 11 °K represent perturbations by the methodology.

Our estimate of the time required to trap a sufficient number of electrons on the surface (at least 30 h of operation after cooling to liquid-helium temperatures) suggests that very definite "learning curve" behavior should have been obvious for the low-temperature TOF spectra. This effect does not appear to be explicitly mentioned in the experimental reports.[1,5,6,27]

Finally, the electrons which are observed to come from traps during the measurement interval provide an unresolvable uncertainty for any screening theory. Thus, if these traps are caused by slight variations in the potential near the axis of the drift tube of the sort that promote capture of surface electrons then a few electrons in these traps can *themselves* give rise to screening fields which may be substantial in terms of these experiments. We feel compelled to conclude that while surface screening producing nearly vanishing electric fields remains a possibility as an explanation of the appearance of very late electrons in the TOF spectra, its hallmarks, a long buildup time, and the ability to screen the applied fields (given time), have not been sought or unequivocally observed in the experiments.

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[1]J. M. Lockhart, F. C. Witteborn, and W. M. Fairbank, Phys. Rev. Lett. 38, 1220 (1977).
[2]G. S. LaRue, W. M. Fairbank, and A. F. Hebard, Phys. Rev. Lett. 38, 1011 (1977).
[3]W. M. Fairbank, F. C. Witteborn, and L. V. Knight, Science 144, 562 (1964).
[4]F. C. Witteborn, L. V. Knight, and W. M. Fairbank, in *Proceedings of the Ninth International Conference on Low Temperature Physics*, edited by J. G. Daunt, D. O. Edwards, F. J. Milford, and M. Yaqub (Plenum, New York, 1965), p. 1248.
[5]F. C. Witteborn, thesis (Stanford University, 1965) (unpublished).
[6]F. C. Witteborn and W. M. Fairbank, Phys. Rev. Lett. 19, 1049 (1967).
[7]F. C. Witteborn and W. M. Fairbank, Nature (Lond.) 220, 436 (1968).
[8]F. C. Witteborn and W. M. Fairbank, Rev. Sci. Instrum. 48, 1 (1977).
[9]L. I. Schiff and M. V. Barnhill, Phys. Rev. 151, 1067 (1966).
[10]A. J. Dessler, F. C. Michel, H. E. Rorschach, and G. T. Trammell, Phys. Rev. 168, 737 (1968).
[11]C. Herring, Phys. Rev. 171, 1361 (1968).
[12]M. Peshkin, Ann. Phys. (N.Y.) 46, 1 (1968); and Phys. Lett. A 29, 181 (1969).
[13]W. A. Harrison, Phys. Rev. 180, 1606 (1969).
[14]J. W. Beams, Phys. Rev. Lett. 21, 1093 (1968).
[15]P. P. Craig, Phys. Rev. Lett. 22, 700 (1969).
[16]L. I. Schiff, Phys. Rev. B 1, 4649 (1970).
[17]L. I. Schiff, Proceedings of the Fifth International Conference on Gravitation and the Theory of Relativity, Tbilisi, USSR, 1968 (unpublished).
[18]G. T. Trammell and H. E. Rorschach, Phys. Rev. B 2, 4761 (1970).
[19]M. W. Cole, Phys. Rev. B 3, 4418 (1971).
[20]M. W. Cole, Phys. Rev. B 2, 4239 (1970).
[21]For a review, see, Henry Leidheiser, Jr., *The Corrosion of Copper, Tin, and Their Alloys* (Wiley, New York, 1971); or A. Röunquist and H. Fischmeister, J. Inst. Met. 89, 65 (1960–1961).
[22]H. A. Miley, J. Am. Chem. Soc. 59, 2626 (1937).
[23]W. H. J. Vernon, Trans. Faraday Soc. 23, 113 (1927).
[24]F. W. Young, Jr., J. V. Cathcart, and A. T. Gwathmey, Acta Mettal. 4, 145 (1956).
[25]C. Herring and M. H. Nichols, Rev. Mod. Phys. 21, 185 (1949), see Appendix IV.
[26]J. M. Lockhart, F. C. Witteborn, and W. M. Fairbank, in *Proceedings of the Fourteenth International Conference on Low Temperature Physics*, edited by M. Krusins and M. Vuorio (Elsevier, New York, 1975), Vol. 4, p. 274.
[27]J. M. Lockhart, thesis (Stanford University, 1976) (unpublished).