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Surface States Due to Copper on Germanium

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Copper contamination from dilute aqueous solutions has previously been shown to produce fast surface states on germanium. These states comprise a recombination center close to midgap, with large capture cross sections for both electrons and holes, and trapping states at about 0.2 eV above and below midgap. The states are attributed to copper metal microcrystals that deposit on the surface.

INTRODUCTION

One of the long-standing problems in semiconductor surface research has been the attempt to understand the physicochemical origin of the fast surface states that are almost invariably found to exist on both atomically clean and chemically treated surfaces. On the latter type of surfaces there have been many studies of the effects of variations of the chemical treatment on the fast state energies, densities, and capture cross sections. The results of such studies have been summarized recently by Lax,[1] Watkins,[2] and Many[3] and will be discussed in a later section. In general, they have been interpreted in terms of a fairly well-defined set of energy levels, but there have been only fragmentary clues as to the origin of these levels.

The possible importance of trace impurities on the surface has probably been widely recognized, but only scantily investigated. The first work along such lines was that of Morrison,[4] who found that traces of Cu, Sb, and Ag in the etch or rinse water made the germanium surface more *p* type. Following this, the author[5] observed that, on germanium surfaces prepared in a way that appeared to remove a residual film left by the HF-containing etchant, brief exposure to a dilute cupric nitrate solution produced a large increase in the surface recombination velocity. At about the same time, Boddy and Brattain[6] obtained similar results on surfaces in contact with aqueous electrolyte solutions.

Thus, it has become clear that copper (and other contaminants) can indeed produce surface states on germanium. The present paper is concerned with the properties and origin of the states so produced.

EXPERIMENTAL METHODS

Field-effect measurements were made using the sample geometry previously described,[5] with four side arms for contacts so that etching could be carried out without introducing any foreign materials into the bath. However, full rather than "cut out"[5] dielectric spacers ($\frac{1}{2}$- or 1-mil Mylar) were used in the present work in order to increase the maximum induced charge density by more than an order of magnitude. This made the flatness of the sample much more critical and, in order to avoid rounding of the edges, the germanium slices were lapped to final thickness (a few mils) and polished through $\frac{1}{4}$-μ diamond grit before cutting out the samples. The cutting was done with an ultrasonic die while the slice was waxed between a glass plate and a thin cover glass. Then application of soldered connections to the ends of the side-arms and etching to a depth of a few microns to remove mechanically damaged material completed the preparation of the samples.

The etching was found always to degrade the surface planarity to some extent. In addition to a slight rounding of the edges to a radius of the order of 0.1 mm, there was an over-all roughness of a depth of several tenths of a micron, and localized etch pits of much greater depth. As a result, the measured capacitances between sample and field plates did not exceed 80 to 90% of the values calculated from the projected areas. The corresponding average air gaps amount to 1 to 2 μ. This is in agreement with the very few values that have been quoted in the literature.[7–9] The importance of attaining capacitances close to the calculated values is that only in this way can one be assured that the applied fields are reasonably homogeneous. In the present case, the variation in local field strength amounts to several tens of percents. The error thus introduced will be negligible at voltages where the field-effect curve is nearly linear, but may be appreciable in the vicinity of the conductance minimum, particularly when the latter occurs at a high voltage. The result will always be a widening of the minimum, hence an increase in the apparent density of surface traps in this region.

The present measurements were made on n-type samples with resistivities between about 15 and 25 Ω-cm. The samples were cut from Czochralski-grown crystals, selected for homogeneity, with major faces

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[1] M. Lax, *Proceedings of the International Conference on Semiconductor Physics* (Czechoslovakian Academy of Science, Prague, 1961), Paper M1.

[2] T. B. Watkins, *Progress in Semiconductors*, edited by A. F. Gibson (John Wiley & Sons, Inc., New York, 1960), Vol. 5, p. 1.

[3] A. Many, *Proceedings of the International Conference on Semiconductors, Rochester, 1958* [J. Phys. Chem. Solids **8**, 87 (1959)].

[4] S. R. Morrison, *Proceedings of the Second Conference on Semiconductor Surfaces* (Pergamon Press, New York, 1960), p. 214; also J. Phys. Chem. Solids **14**, 214 (1960).

[5] D. R. Frankl, J. Electrochem. Soc. **109**, 238 (1962).

[6] P. J. Boddy and W. H. Brattain, J. Electrochem. Soc. **109**, 812 (1962).

[7] A. V. Rzhanov, Yu F. Novototskii-Vlasov, and I. G. Neizvestnyi, J. Tech. Phys. (U.S.S.R.) **27**, 2440 (1957) [translation: Soviet Phys.—Tech. Phys. **2**, 2774 (1958)].

[8] V. G. Litovchenko and O. V. Snitko, Fiz. Tverdogo Tela **2**, 591 (1960) [translation: Soviet Phys.—Solid State **2**, 554 (1960)].

[9] V. E. Primachenko and O. V. Snitko, Fiz. Tverdogo Tela **3**, 15 (1961) [translation: Soviet Phys.—Solid State **3**, 9 (1961)].

lying within a few degrees of a (111) plane. Preparation of the surfaces for measurement comprised the following steps:

(1) HF (48%) at room temperature for one minute, to remove any oxide; rinse in "pure" water (resistivity >15 MΩ-cm).

(2) 1% KOH at about 90°C for 1 to 5 min; rinse in pure water. This treatment was found[5] to remove the hydrophobicity and strong *n*-type bias left by the preceding step, and to make the surface sensitive to copper contamination.

(3) Either (a) 1 part per million $Cu(NO_3)_2$ solution at room temperature for one minute (these will be called "copper-treated" surfaces), (b) 3% KCN at about 50°C for 1 to 5 min, then rinse in pure water ("KCN-treated" surfaces), or (c) neither of these ("untreated" surfaces).

(4) Rinse in methanol and drain dry.

(5) Mount between field plates, measure capacitances to the individual plates and see that these agree within a few percent, and insert in the measuring chamber as soon as possible (i.e., within about 5 min).

Measurements of field-effect conductance and lifetime were made by the steady-state ac method previously described[5] in both dry nitrogen and vacuum of about 10^{-6} Torr. No difference was detected between the results in these two ambients. Comparisons were also made between results with "full" and "cut out" dielectric spacers. No difference was found over the range of amplitude of applied field strength that could be attained with the latter. However, the application of ac fields of higher amplitudes (with the full spacers) caused significant changes to occur in those surfaces prepared without copper, as will be described more fully in the following section. Measurements were made at 27.0°C on all surfaces and also at 2.0 and 52.0°C on the copper-treated surfaces. For the reason given in reference 5, the data were analyzed without any mobility correction for diffuse surface scattering.

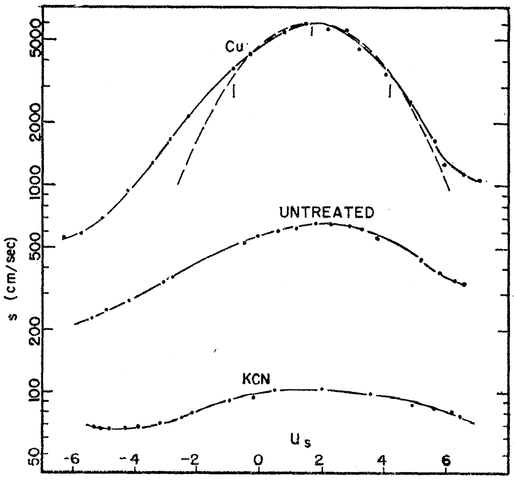

FIG. 1. Surface recombination velocity *s* vs normalized surface potential u_s for copper-treated, untreated, and KCN-treated Ge surfaces. Details of treatments are given in the text.

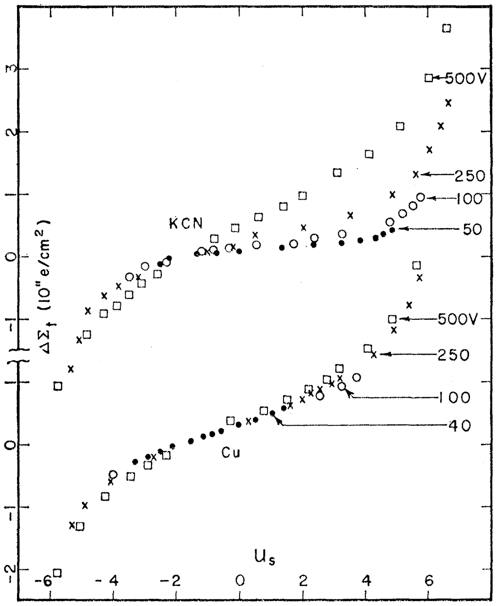

FIG. 2. Trapped charge density (electrons/cm²) vs u_s for copper- and KCN-treated surfaces. Numbers at right are amplitudes of ac voltage applied to field plates. Note shift of ordinate scales.

In addition to the field-effect measurements, radioactive tracer analyses of the amount of copper deposited by the treatment described above were made by J. Cosgrove, and examinations by electron microscopy and electron diffraction were carried out by C. F. Tufts.

EXPERIMENTAL RESULTS

Field-Effect Measurements

Figure 1 illustrates the effects of the various surface treatments on the surface recombination velocity *s* as function of the normalized surface potential u_s. (u_s denotes, as usual, the energy difference between the Fermi level and the intrinsic Fermi level at the surface, in units of *kT*.) The results are quite similar to those obtained previously,[5] except that the range of u_s values has been considerately extended. It is clear that the copper treatment results in a considerable increase in *s*, whereas the KCN treatment, which was designed to remove any residual traces of copper and other heavy metals, decreases *s*. As in the earlier work, the reproducibility in the *s* values obtained on the copper-treated and the untreated surfaces was rather poor; however, the KCN treatment gave excellent reproducibility.

The dashed curve in Fig. 1 shows the fit of the data on the copper-treated surface to the Stevenson-Keyes formula,[10] which is expected to hold when the surface recombination proceeds mainly via a single type of

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[10] D. T. Stevenson and R. J. Keyes, Physica **20**, 1041 (1954).

recombination center. The short vertical lines mark the two values of the recombination center energy that would lead to this curve. It is seen that the data can be fitted to the theoretical form reasonably well near the maximum, but the deviations in the wings indicate an additional "background" of other recombination centers. On the untreated and especially the KCN-treated surfaces, this background makes a relatively greater contribution.

Figure 2 illustrates the trapped charge density (electrons/cm^2) as function of u_s for a copper-treated and a KCN-treated surface at 27°C. In both cases, the data represent the first runs made after preparation of the surfaces, and were made in order of increasing voltage amplitude. It is seen that the KCN-treated surface is highly sensitive to the ac field in that marked increases in the density of trapping states are caused by application of relatively small voltage. Similar effects have been noted by others[11–13] on surfaces prepared in other ways. The copper-treated surfaces, on the other hand, were virtually insensitive to the highest fields that were applied. The untreated surfaces were generally intermediate between these extremes.

The insensitivity of the copper-treated surfaces to field-induced changes makes it possible to obtain reliable trapping data over a wide range of surface potentials. The results obtained at three temperatures are illustrated in Fig. 3. These curves should, if the fast-state distribution is a discrete one, fit a sum of Fermi-Dirac functions of the form

$$\Delta\Sigma_t(u_s)=N_i[1+\exp(u_s-u_{ti})]^{-1}, \qquad (1)$$

where Σ_t = density (cm^{-2}) of electrons trapped in fast surface states, N_i = density (cm^{-2}) of states having energy E_{ti}, and

$$u_{ti}=(E_{ti}-E_i)/kT.$$

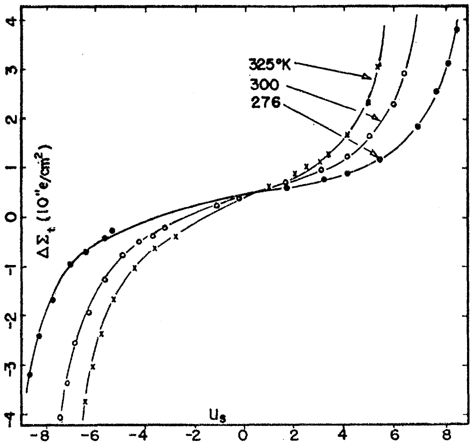

FIG. 3. Trapped charge density (electrons/cm^2) vs u_s for a copper-treated surface at three temperatures.

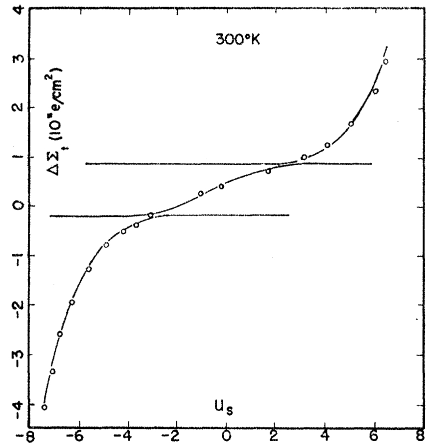

FIG. 4. Illustration of the fitting of a trapping curve to Eq. (1).

To make such a fit completely unique, one would require data covering a much wider range of surface potential than was obtained in these (or any other) experiments. The customary procedure in the past has been to choose one of the E_{ti} on the basis of auxiliary evidence obtained from the surface recombination data and, with this as a starting point, to work outward in both directions along the trapping curve.[14] Such a procedure was usually necessitated by the lack of pronounced "structure" in the trapping curves. The resultant fit was often quite unsatisfactory near the ends of the curves, although the introduction of additional terms could, of course, have remedied this.

In the present case, a more straightforward procedure is possible, owing to the pronounced changes in slope observable in Fig. 3. The rapidly increasing portions of the curves near the ends quite clearly suggest the presence of trapping states with u_t values slightly beyond the experimental u_s range, and it is indeed found that intervals of 4 or 5 kT at each end can be well fitted by a single term of the form (1). When the contributions of these terms are subtracted from the data, there remains a region of increasing trapped charge density near the middle of each curve, and this can be moderately well fitted by one additional term. The quality of fit is illustrated in Fig. 4.

The energy levels deduced in this way are plotted as dots in Fig. 5. It is seen that the energies are all temperature independent within the experimental uncertainties of about $\pm\frac{1}{2}kT$ for the upper and lower levels and $\pm 1kT$ for the middle level. This is in contrast with most previous work, in which the energies deduced appeared to vary with temperature.

The crosses in Fig. 5 denote approximate values of

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[11] A. Rzhanov, N. M. Pavlov, and M. A. Selezneva, J. Tech. Phys. (U.S.S.R.) **28**, 2645 (1958) [translation: Soviet Phys.—Tech. Phys. **3**, 2419 (1958)].

[12] V. G. Litovchenko and V. I. Lyashenko, Fiz. Tverdogo Tela **1**, 1609 (1959) [translation: Soviet Phys.—Solid State **1**, 1470 (1960)].

[13] Y. Margoninski, Phys. Rev. **121**, 1282 (1961).

[14] A. Many and D. Gerlich, Phys. Rev. **107**, 404 (1957).

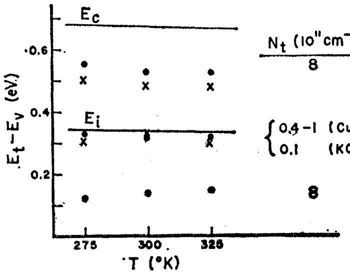

FIG. 5. Dots represent energies of surface states deduced from trapping data. Crosses represent possible energies of recombination states deduced from recombination data. E_v and E_c are the energies of the top of the valence band and the bottom of the conduction band, respectively.

the two energies that can be deduced from the surface recombination data, as illustrated in Fig. 1. In general, the recombination data were not as reproducible as the trapping data. Nevertheless, the accuracy was sufficient to permit a clearcut choice between the two possibilities: as seen in Fig. 5, the *lower* of the two possible values agrees, at each temperature, much better with one of the E_t values deduced from the trapping data than does the upper. Thus, we conclude that the recombination centers lie quite close to the middle of the gap. This is again in contrast with most previous work, in which, following Many and Gerlich,[14] the upper of the two possible values has been chosen, placing the recombination level about 5 kT above midgap.[15]

The densities of the states on the copper-treated surfaces were somewhat poorly reproducible from treatment to treatment. For the recombination center, N_{t2} ranged from about 4×10^{10} to 1×10^{11} cm^{-2} as indicated in Fig. 5. The maximum surface recombination velocity, s_m, also varied over about a 3:1 range, though not in good correlation with N_{t2}. The s curve shown in Fig. 1 represents roughly the upper limit of the range of variation. There were, in the course of several dozen treatments, two exceptional cases in which the copper-treated surfaces had s_m values considerably below the usual range; one of these resulted from the first treatment given to a new sample and the other from a copper treatment following a KCN treatment. In both cases, subsequent copper treatments gave normal results.

For the KCN-treated surfaces, much less detailed information is available, owing to the changes caused by the measuring field. However, from the curve denoted by solid dots in Fig. 2, representing the data taken at the lowest voltage amplitude, it is evident that the slope in the vicinity of $u_s=0$ is much lower than that of the copper-treated surfaces. The value of N_{t2} calculated from this slope is about 1×10^{10} cm^{-2}, or a factor between about 4 and 10 lower than on the copper-treated surfaces. Furthermore, if the states at the energies E_{t1} and E_{t3} found for the copper-treated surfaces are present at all, their concentrations must be lower by a factor of at least 5. On the other hand, s_m is reduced by a much larger factor, between about 20 and 60 (see Fig. 1). This disparity suggests that not all of the states at E_{t2} are recombination centers, i.e., that there are two kinds of states close to midgap. It is, of course, not certain that these have exactly the same energy, since the trapping data are inadequate to resolve two closely spaced levels. However, they must lie within about 0.05 eV of each other, since otherwise the agreement between the trapping and recombination data would be impaired.

The lack of knowledge of the number of actual recombination ceters makes it impossible to determine the capture cross sections of the centers introduced by the copper treatment. We may, however, obtain *lower limit* estimates by inserting the N_{t2} value obtained from trapping into the Stevenson-Keyes recombination formula.[10] The results, for electron and hole capture, respectively, are

$$\sigma_n=2\times10^{-14}\ \text{cm}^2,$$

$$\sigma_p=4\times10^{-12}\ \text{cm}^2.$$

Thus, the centers appear to be of much greater than atomic dimensions.

RADIOACTIVE TRACER ANALYSES

Tracer measurements were made by J. Cosgrove of these Laboratories on slices of high-purity germanium treated exactly as described above and also with higher concentrations of $Cu(NO_3)_2$ (3 and 10 ppm) and KOH (3 and 5%) and other times of reaction ($\frac{1}{3}$ and 3 min) with the KOH. The results showed that the amount of copper deposited during the 1-min dip was, very roughly, proportional to the $Cu(NO_3)_2$ concentration and only slightly dependent on the KOH concentration and time. The standard treatment (1 min in 1 ppm solution) deposited about 10^{14} Cu atoms per cm^2, or almost the equivalent of a monolayer. This is in general agreement with published results.[16]

It was also observed in the course of these measurements that steps 1 and 2 of the standard treatment did not completely remove copper once it had been deposited on the germanium. KCN, however, did remove all detectable traces. These observations may explain the variability found in the field effect on copper-treated and untreated surfaces; probably the latter still contained variable amounts of contamination which could influence not only the immediate measurements but also those after subsequent treatments.

ELECTRON MICROSCOPY AND DIFFRACTION

The finding that the number of Cu atoms deposited by the standard treatment was several thousand times greater than the number of surface states produced suggested the possibility that the copper deposition was highly nonuniform. Electron microscope and electron diffraction observations made by C. F. Tufts of these

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[15] The energy value previously given by the author [Bull. Am. Phys. Soc. 7, 179 (1962)] was obtained in this way, and should be disregarded.

[16] V. S. Sotnikov and A. S. Belanovskii, Zhur. Fiz. Khim. 35, 509 (1961).

Laboratories on about a dozen samples, gave fairly strong evidence that this was, indeed, the case. The results were, in brief, as follows:

(1) The copper-treated samples were usually covered with "globules" about 100 Å in diameter and 10^{11} to 10^{12} per cm^2 in number, whereas on the blanks prepared in parallel with the samples through all steps except the $Cu(NO_3)_2$ dip, the number of such globules was at least an order of magnitude smaller. The higher number of globules was found on about half the samples treated for 1 min in 1-ppm solution (the standard treatment used in the field-effect studies) and on all the samples treated for 5 min in 1 ppm or for 1 min in 10-ppm solution.

(2) The samples with large numbers of globules showed, in electron diffraction, a pattern of diffuse rings superimposed on the sharp Laue spot and Kikuchi line pattern of the germanium. In the case of the 5-min dip, an additional sharp ring pattern, unambiguously identified as due to copper metal, was present. The blanks gave no significant reflections other than the Laue spots and Kikuchi lines of the germanium.

DISCUSSION

The results presented in the preceding section strongly suggest that the copper treatment can deposit on the germanium surface microcrystals of copper metal, each containing $\sim 10^4$ atoms. Based on the relative numbers of fast surface states and microcrystals so produced, it appears likely that the latter are the entities giving rise to the former, although the mechanism by which this might come about is not apparent. The failure to obtain perfect (i.e., completely featureless) blanks in the microscopy studies suggests that a small amount of contamination is either deposited accidentally during the preparation or remains on the sample from some previous source. This may well be the reason why surfaces completely free of surface states were not obtained in this work.

The conditions for nucleation of the microcrystals on virgin surfaces are still somewhat uncontrollable. Apparently the standard treatment used in this work lies about on the borderline of the nucleation conditions. This can account for the absence of large numbers of globules on some of the microscopy samples and the failure to obtain the usual high s values on two of the field-effect samples given this treatment. Presumably the nucleation takes place on some sort of "active sites" on the surface, since a relatively fixed number form. It may be speculated that these same sites are, in the absence of copper, responsible for the creation of new trapping states under the influence of the applied field.

The present results are, in the main, in excellent accord with the results on germanium surfaces in contact with aqueous electrolytes obtained recently by Boddy and Brattain.[6] These authors too found that traces of copper (and other heavy metals) produced surface states, and in roughly similar though somewhat smaller densities, about 10^{11} trapping states and 2×10^{10} recombination centers per cm^2. They found the densities to be independent of the copper concentration in the solution, though the time of formation was not, and they suggested that the states were due to isolated copper atoms in "certain select sites." In view of the present results, it would seem that their states, too, could be due to copper metal microcrystals.

Another point of agreement is the assignment of the recombination center energy to the *lower* of the two possible values deduced from the s curve. In both cases, the reason is essentially the same: The trapping (or, what is equivalent, surface state capacitance) data simply leave no room for a state at the upper value. It will be recalled than Many and Gerlich[14] chose the upper value on the basis of the *relative* temperature independence of the quantity $(E_t - E_i)$. It would seem, however, that the *absolute* temperature independence of E_t would be a better criterion, and on this their data provide little basis for choice, since the upper value changes by 0.031 eV and the lower by 0.036 eV over the 23-deg temperature interval investigated. In contrast, the present data show both values to be sensibly constant over a 50-deg range. Most subsequent workers have followed Many and Gerlich in the use of the upper value as a starting point in the fitting of trapping data. However, a re-examination of much of the published data suggests that an equally good or better fit could be obtained by starting with the lower value.

A major point of difference with the results of Boddy and Brattain concerns the energies of the trapping states. They find a single state with density $\sim 10^{11}$ cm^{-2} about 0.05 eV above midgap and, most surprisingly, find little or no trapping near the extremes of the accessible u_s range. It may, of course, be the case that the electrolyte interface differs in some essential respect from the dry surface, or that the (100) surfaces which they used behave differently from the (111) surfaces used here, although if it is true that the surface states are due to copper microcrystals nucleated at defect sites, then one would expect fairly similar behavior. Another possible explanation is that the time constants of the outer states are too long for them to be able to follow the microsecond pulses employed by Boddy and Brattain, although this, too, seems implausible in view of the well-known high-frequency data of Montgomery.[17] For the time being, therefore, this difference must remain unresolved.

ACKNOWLEDGMENTS

It is a pleasure to give thanks for the work of C. F. Tufts on electron microscopy and diffraction and J. Cosgrove on radio-tracer analysis described in this paper. Thanks are also due to P. J. Boddy and W. H. Brattain for discussion of their results prior to publication.

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[17] H. C. Montgomery, Phys. Rev. **106**, 441 (1956).