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Electron Scattering at a Rough Surface

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The lifetime of electrons in a skipping trajectory is limited by an occasional diffuse-surface-scattering event that removes the electron from a given quantum energy level. For elastic transitions between surface states, the scattering rate Γ_s is predicted to become larger with increasing magnetic field as H^2. Such increasingly nonspecular surface reflection has been observed in a series of Ga and Sn samples with deliberate and controlled surface roughness.

I. INTRODUCTION

THE observation of sharp resonant microwave transition between electron states skipping along a metal surface by periodic specular reflection[1] provides definitive evidence for a high degree of "specularity" of a properly prepared metal surface. As shown recently by Nee, Koch, and Prange,[2] a careful consideration of line shapes and linewidths of the resonance signals is expected to allow a detailed examination of electronic reflection at the metal-vacuum interface. Resonance signals are due to electrons on a single narrow strip on the Fermi surface, and one obtains a measure of specular scattering for this specific group as a function of the angle of incidence.

In the presence of surface irregularities, the lifetime of an electron in a particular surface-state trajectory is limited by an occasional diffuse-reflection event that scatters the electron into a new trajectory. This adds to the frequency width of the corresponding quantum state and results in a broadening of the resonance signal. Characteristic of diffuse surface scattering of surface-state electrons is that it is expected to be magnetic-field-dependent,[1,2] with the most pronounced effect on the high-field resonance peaks of the oscillation spectrum.

Despite optimistic theoretical forecasts that surface scattering should be readily identifiable from an examination of the impedance oscillation spectrum, the detailed fits of theory to the experimental curves[2,3] showed little or no evidence for significant departure from perfect specular reflection at a carefully prepared surface. Examination of the experimental curves obtained to date made it patently clear that the ordinary bulk scattering effect due to phonons or impurities predominantly determined the line shape. The very minor influence of diffuse scattering in the indium data discussed in Ref. 2 could easily be masked by approximations made in the numerical calculations, especially the assumption of a cylindrically symmetric Fermi surface. It is for this reason that in the present experiments we have made an effort to study diffuse surface scattering by deliberate and controlled roughening of the sample surface. We have aimed to verify the magnetic field dependence of the surface scattering that had been predicted and discussed in recent publications.[1,2,4]

II. THEORY OF SCATTERING FROM A ROUGH SURFACE

A quantum-mechanical derivation that treats the rough surface as a perturbation has been sketched by Prange and Nee[1] and has recently been considered in more detail by Singhal.[5] Similar discussions of the problem are contained in papers by Fischbeck and Mertsching[6] and by Kaner *et al.*[7] We briefly describe and quote here the essential results only to motivate the reader for an understanding and appreciation of the experimental results that we have obtained.

The electron skipping along a smooth metal surface ($z=0$) is described as a quantum state with momentum K_i parallel to the surface and a quantum number n that is related to its quantized maximal depth of penetration z_n. The rough surface is taken to wobble about $z=0$ in a statistical manner, such that the correlation function of the height of the surface is

$$\langle f(r_0)f(r_0+r)\rangle_{\mathrm{av}}=a^2e^{-r^2/L^2}, \tag{1}$$

where a^2 represents a mean-square height and L represents a characteristic separation of irregularities on the surface. In the presence of surface roughness, the (K_i,n) state experiences an occasional nonspecular reflection event and is scattered elastically to a state with quantum number n' and a new momentum K_f parallel to the surface. This new state as in Fig. 1 belongs to a triangular potential well with a different $z=0$ intercept, but essentially the same slope when $(K_i-K_f)/K_i$ is small. The matrix element for such transitions is proportional to the strength of the Fourier component of the surface roughness at the scattering vector K_i-K_f. In addition, it contains the factor $(d\phi_n/dz)(d\phi_{n'}/dz)|_{z=0}$, i.e., the normal derivative at the surface of the one-dimensional wave function that

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[1] R. E. Prange and T. W. Nee, Phys. Rev. **168**, 179 (1968).

[2] T. W. Nee, J. F. Koch, and R. E. Prange, Phys. Rev. **174**, 758 (1968).

[3] J. F. Koch and J. D. Jensen, Phys. Rev. **184**, 643 (1969).

[4] J. F. Koch, Physik Kondensierten Materie **9**, 148 (1969).

[5] S. P. Singhal (private communication).

[6] H. J. Fischbeck and J. Mertsching, Phys. Status Solidi **27**, 345 (1968).

[7] E. A. Kaner *et al.*, Zh. Eksperim. i Teor. Fiz. **55**, 931 (1968) [English transl.: Soviet Phys.—JETP **28**, 483 (1969)].

describes the periodic z motion of the electron. In Fig. 1, we have sketched both real-space skipping trajectories and the corresponding energy-level diagram to allow the reader to visualize the type of scattering process that we have in mind. The magnetic-field dependence of the scattering rate is contained in the $d\phi_n/dz|_{z=0}$ terms. From the known surface-state wave function,[1] we have

$$d\phi_n/dz|_{z=0}=(2KeH/\hbar)^{1/2}, \qquad (2)$$

where K is the local radius of curvature of the Fermi surface at the point where the electron is skipping about. This expression is independent of n and varies as $H^{1/2}$. The total scattering rate by the Golden-rule formula will be a sum of the square of the matrix element over all possible final states, so that we should expect the surface scattering rate $\Gamma_{n,s}$ to be

$$\Gamma_s \propto (K^2H^2). \qquad (3)$$

This result should apply when diffuse scattering amounts to only a gentle deviation from specularity, so that it makes sense to talk of scattering from one shallow surface trajectory to another. Alternatively, if, as has been done in Ref. 2, one considers large-angle scattering events, the final state more appropriately may be taken as an essentially field-independent plane-wave state. This results in a linear dependence of Γ_s on magnetic field. In either case, the surface scattering rate is expected to increase with the strength of the magnetic field.

A little reflection will convince the reader that the dependence of the scattering on the slope $d\phi/dz|_{z=0}$ is really to be expected. The energy of a given surface state is determined from the boundary condition that the wave function vanish at the surface. If, as is the case for a rough surface, the surface wobbles about $z=0$, then one should expect a level broadening dependent on the gradient of the wave function at the surface. Alternatively, we may choose to interpret $d\phi_n/dz|_{z=0}$ as something proportional to the angle of incidence of the corresponding classical trajectory. This is apparent when one recalls that ϕ_n is an oscillatory function. In that case, the field dependence as in Eq. (3) appears to predict increased scattering with steeper angles of incidence to the surface. The dependence on K only reproduces the usual classical hand-waving argument that long-wavelength electrons (and hence small K, such as in Bi) are more likely to be specularly reflected.

The finite lifetime of the surface state due to both diffuse surface scattering and the usual phonon and impurity collisions that account for the bulk mean free time τ is reflected in a quantum-mechanical energy width $\hbar\Gamma_n$ of the surface state. The frequency width Γ_n is the sum of the bulk relaxation frequency $1/\tau$ and surface scattering rate $\Gamma_{ns}(H)$. The mean width $\Gamma_{nm}=\frac{1}{2}(\Gamma_n+\Gamma_m)$ of a pair of surface state appears in the denominator of the impedance derivative formula,[1,2] i.e.,

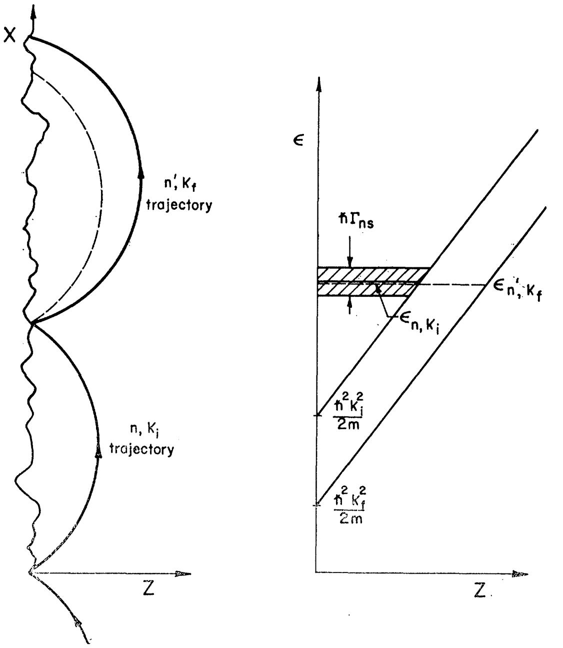

FIG. 1. Trajectories and energy-level scheme for a surface electron scattered elastically from quantum state (n,K_i) to (n',K_f). $\hbar\Gamma_{ns}$ is the energy-level width that results from such diffuse-scattering events.

$$\frac{dZ}{dH}\propto\frac{d}{dH}\int dk_y v_x \sum_{n,m}\frac{\alpha_{nm}^2}{\omega-\omega_{nm}+i\Gamma_{nm}(H)}. \qquad (4)$$

For a detailed derivation and discussion of calculated results we refer the interested reader to the references and note here only that α_{mn} is a matrix element of the microwave electric field between the surface-state wave functions, ω is the experimental frequency, and ω_{nm} is the quantum-mechanical difference frequency $\epsilon_n-\epsilon_m/\hbar$ of a pair of surface energy levels with energies ϵ_n and ϵ_m.

Referring to the impedance formula quoted above, we can readily predict the consequences of the field-dependent scattering term Γ_{ns}. With increasing magnetic field, we expect the resonances to be broadened and diminished in amplitude relative to resonance peaks occuring at lower magnetic field. The calculations carried out by Nee, Koch, and Prange[2] (using Γ_s proportional to field H) explicitly confirm this expectation. Field-dependent surface scattering has a characteristically different effect on the resonance spectrum than the bulk relaxation time τ, making it possible in principle to identify both contributions in a given experimental curve.[4]

III. EXPERIMENTAL NOTES ON SURFACE PREPARATION

The experimental work has been done on high-purity single-crystal samples of Ga and Sn, with some ha

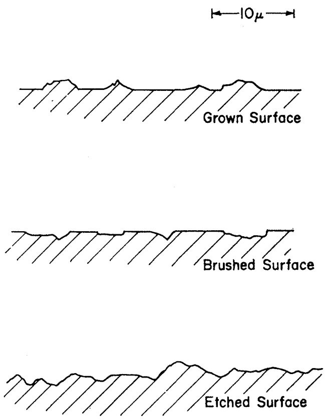

FIG. 2. Surface profiles achieved with various preparation techniques. The scale of heights and separations of surface perturbations is approximate.

hearted and largely unsuccessful attempts at In. Ease of sample preparation, as well as a desire to choose a material with exceptionally long mean free path in order to have predominantly surface scattering, figured in the choice of Ga. This is in spite of the relative complexity of the signals observed in this material. We chose Sn as a second material for this work because it can be etched chemically to a uniform degree of roughness.

Single-crystal Ga samples were grown from the melt in a mold with specially prepared rough-surface glass faces. The glass substrates had been roughened by sandblasting with a fine grit or, alternatively, by optical grinding with a diamond paste. The severity of roughening was determined by both grit size and duration of blasting or grinding (Fig. 2). When examined under a microscope, the sandblasted surface shows a uniform distribution of typically micron-sized pits with varying average separation and depth. For the very lightly roughened substrates there are remaining flat portions with linear dimensions of several microns between successive pits. Optical grinding with micron-sized diamond paste tended to produce long scratches. With proper care, the crystal surface, when grown from the melt, was found to produce a reasonable facsimile of the rough substrate. The height of dimples on the Ga surface we suspect is somewhat less than the depth of corresponding pits in the substrate surface. While we admit the experimentally rough surface to be only a poor approximation to the smooth statistical distribution envisioned by the theoretical model, we nevertheless would like to quote a mean height a and correlation length L to characterize a typically rough Ga sample. With pits on the order of $1\,\mu$ deep, 4 or $5\,\mu$ in diam, and spaced roughly $10\,\mu$ apart, we arrive at an estimate for mean height $a\sim0.2\times10^{-4}$ cm and length $L\sim6\times10^{-4}$ cm to describe an average degree of roughness that should correspond to something like surface II for the data in Fig. 4. We estimate the lightly roughened surface (surface I) to have roughly $\frac{1}{2}$ the mean height and twice the correlation length, while the roughest of the surfaces discussed with reference to Fig. 4 would have twice the mean height and $\frac{1}{2}$ the value of L of the average sample. Since we limit our studies in this paper to qualitative observations, these estimates of roughness should suffice to give an impression of the surface characteristics. The upper part of Fig. 2 shows an "idealized" view of what the surface looks like for the as-grown samples.

An alternative approach that we have used is to mechanically "roughen" an initially smooth crystal surface by a light random brushing with a very soft fine-textured camel-hair brush. This achieves a dense random-crisscross pattern of shallow scratches about $1\,\mu$ wide as sketched in Fig. 2. We felt very unsure initially about results obtained with scratched samples, because of the possibility that mechanical working of the surface would reduce the mean free path in the surface layer. These fears proved unfounded when the data turned out substantially the same as for the grown samples and showed predominantly the effects of diffuse surface scattering.

Chemical etching and corrosion of a surface should prove an interesting alternative approach to producing various degrees of roughness. From our point of view, however, the technique leaves much to be desired. In working with In crystals, we suffered from an all-or-nothing syndrome. A crystal exposed to a dilute atmosphere of HNO_3 and HCl vapor in a jar would show no tarnishing at all until the concentration was increased to a critical point, where we ended up with such severe etching that the signal disappeared completely. Another undesirable feature was that the lightest etches were completely nonuniform, with some patches of surface heavily etched and others not at all. We have, however, had some measure of success with Sn samples. We start with a relatively severe but uniform etch using HCl vapor and subsequently electrolytically repolish the specimen for varying

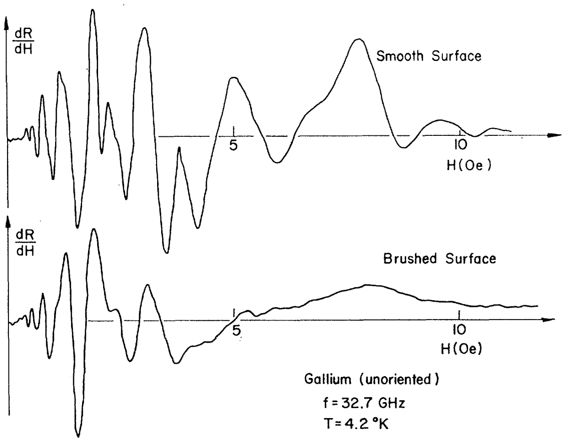

FIG. 3. Effect of "brushing" treatment of the Ga sample.

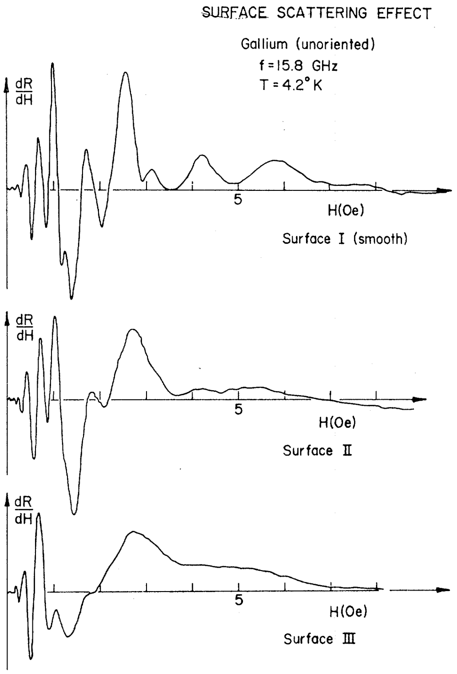

FIG. 4. Sequence of recorder traces for increasingly rough surfaces at a frequency of 15.8 GHz.

lengths of time. This method produces a more or less statistically uniform roughness, except for a tendency of the surface structure to align with crystal axes, as characteristic of blaze planes. Again this approach was suspect because we feared chemical contamination of the surface layer by diffusion. The results, however, bear out predominantly the effects of surface scattering.

IV. EXPERIMENTAL RESULTS

We turn now to a consideration of the experimental data obtained from "rough-surface" samples to examine the evidence for the predicted field-dependent diffuse surface scattering.

Recorder tracings of the "before and after" light brushing surface treatment of a Ga crystal are shown in Fig. 3. The upper trace is that obtained with the smooth, untreated surface and shows a complicated superposition of several oscillatory signals. Peaks at $H\sim7.8$ and 5.0 Oe are identified as fundamental $n=1$ to $m=2$ transitions from two different positions on the Fermi surface. We identify peaks at 3.1, 1.9, and 1.2 Oe as $n=1$ to $m=3$, 4, and 5 resonances associated with the 7.8 peak, while the 2.0- and 1.2-Oe peaks belong to the series characterized by the 5.0-Oe fundamental.[8] The lower trace repeats the spectrum for the roughened surface of the otherwise identical sample. Below 1.5 Oe there is no discernible effect, while for peaks at intermediate fields to 3 Oe we find a slight broadening and substantial decrease in relative amplitudes. The high-field fundamentals are no longer identifiable as distinct peaks.

We were concerned that mechanical working of the surface (such as for the brushing treatment) would, in addition to causing diffuse scattering of surface electrons, reduce their bulk relaxation time τ. If this were the case, the observed signals would show precisely the opposite effect. As the reader may readily convince himself by the sample calculation in Ref. 2, as a function of decreasing τ the high-order, low-field peaks would decrease in amplitude relative to the fundamentals. Nevertheless, to allay our fears, we proceeded with a study of the grown rough samples, where such cold-working strains would be of no concern. Figure 4 shows a sequence of three recorder tracings for progressively rougher surfaces. The deliberate choice of a lower experimental frequency—here 15.8 GHz—moves resonance peaks to weaker magnetic fields. The effect is to reduce the importance of surface scattering [see Eq. (3)] and make it appear more gently, as something like the weak perturbation that the theoretical discussion had envisioned. The preferential broadening of the high-field peaks over the low-field structure is apparent. Examining successive (surfaces I–III) traces at fixed field shows the increasing severity of scattering with roughness.

For a given sample, it is possible to examine the scattering effect as a function of field by varying the experimental microwave frequency. The final (surface III) trace of Fig. 4, although showing a marked effect of roughening, still allows easy identification of the high-field fundamental at 3.6 Oe. A repeat of this trace at approximately twice the frequency, as in Fig. 5, shows a relatively stronger scattering effect. The analysis of such frequency-dependent data is complicated by the competing effect of a change in $\omega\tau$; i.e., doubling the frequency is expected to increase the amplitude and decrease the fractional linewidth of the peak in going from Fig. 4 to Fig. 5. Surface scattering

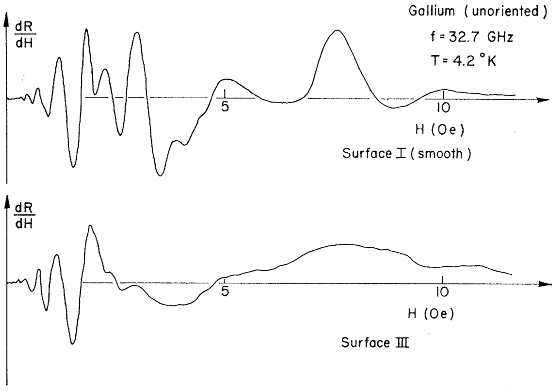

FIG. 5. Comparison of smooth and rough surfaces at a frequency of 32.7 GHz.

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[8] For the series identification and explanation of the resonance spectrum see Refs. 1, 2, or 3.

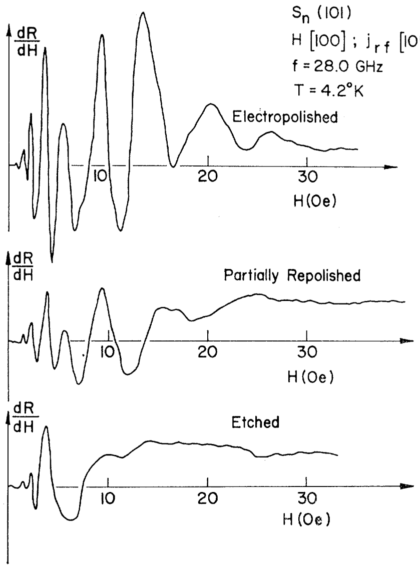

FIG. 6. Sequence of recorder traces for a chemically etched and repolished Sn specimen.

has exactly the opposite effect and, because of its quadratic dependence on field, should predominate. To untangle the relative contributions of $\omega\tau$ and diffuse scattering, Γ_s will require careful fitting of theory to experiment.

Results obtained in a series of experiments with a Sn crystal appear in Fig. 6. The sequence of tracings obtained by first chemically etching and subsequent repolishing of the crystal surface shows the same preferentially high-field scattering effect characteristic of the Ga studies. The lightly etched surface shows only a few surviving low-field peaks. With increasing time of repolishing other peaks of the pattern appear, until with the final best electropolish all the resonance peaks have reappeared in full measure.

V. CONCLUDING DISCUSSION

Our remarks concerning the experimental data of Sec. IV were purposely confined to qualitative observations. The present experiments, we believe, amply demonstrate the predicted magnetic-field dependence—or, if you prefer, the angle-of-incidence dependence—of diffuse surface scattering. Nevertheless, our work represents only a first-order approach to a study of the reflection properties of electrons at a rough surface, and a great deal of careful, considerate theoretical analysis of the data remains to be done to extract a quantitative measure of the scattering, or, for that matter, to substantiate the quadratic dependence of Γ_s on field[9] that appears in Eq. (3). The choice of Ga and Sn samples, although making for easy sample preparation, because of the many superposed oscillations and lack of accurately established Fermi-surface geometry, proves an unfortunate choice for detailed calculation.

The increased effectiveness of scattering at high field is very apparent from the experiments, but the local radius of curvature K dependence [Eq. (3)] remains to be verified. Of the many superposed oscillations in the Sn and Ga data, those corresponding to higher K values are expected to first show the effect of surface scattering, other factors being equal. Since we do not know enough of the Sn and Ga Fermi surfaces to establish where the observed signals originate, it is impossible to verify this dependence. Nevertheless, in support of a possible K dependence, we note that the Sn data show the series with peaks at 15 and 6 Oe are more strongly affected than the series with peaks at 10 and 4 Oe. This provides some evidence that the scattering depends not only on field but also on where the electrons are on the Fermi surface. This aspect needs to be explored more fully with metals, such as Cu or Bi, where the Fermi-surface geometry is adequately known.

We have expended considerable effort on techniques for the preparation of rough-surface samples with only partial success in producing the required controlled small-scale roughness. It appears that such approaches as the "etch and repolish" technique that we have used in Sn is not useful in samples of In, where we have found that even the very lightest etches would completely destroy the signal. After considerable repolishing of the In samples,[10] we find that the data indicate an improvement in $\omega\tau$, rather than improved surface specularity. This is expected to be the case when the depth of etch pits (or the root-mean-square amplitude in the theoretical discussion) exceeds or equals the depth of penetration z_n of the surface-state trajectories. In that case, there is simple interruption and scattering of the trajectories, which appears as a reduced mean free path. It seems that for the cases of Ga and Sn, we are dealing with electrons of particularly small K and correspondingly large values of z_n, so that for the relatively large-scale roughness characteristic of the samples, there is no appreciable reduction of mean free path. This suspicion is borne out for the case of our Ga sample, by failure to see any measurable curvature shift[11] using a surface-curvature radius as small as 1 cm. From this we have established that $K \leq 10^5$ cm^{-1} for the signals examined in this experiment.

It also remains for us to work out better schemes to provide a quantitative measure of roughness. Values of $(|a^2|)^{1/2}$ and L quoted in Sec. III are derived from visual observation with a phase-interference microscope

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[9] For the calculation in Ref. 2, a linear variation of Γ_s on H had been assumed. The sharply increased effectiveness of diffuse scattering with field apparent in the present experiment makes an H^2 dependence appear more plausible.

[10] J. R. Maldonado, Ph.D. thesis, University of Maryland, 1968 (unpublished).

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and are at best rough estimates; nor, for that matter, do the experimental surfaces measure up to the smooth statistical distribution assumed in the theory.

In spite of the acknowledged shortcomings, we feel that the experiments provide the first explicit evidence for increasingly diffuse scattering with increasing angle of incidence to the surface for a specific group of electrons at the Fermi surface. The experiments also hold the promise of even more detailed quantitative information on diffuse scattering. Our results substantiate and make appear reasonable theoretical discussions of an angle-dependent specularity parameter as in the work of Greene and O'Donnell[12] and of Soffer.[13]

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Bulk Current Instabilities in Uniaxially Strained Germanium

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Experimental studies of current instabilities in uniaxially compressed n- and p-type germanium are described. The instability reflects the presence of bulk negative differential conductivity due to transfer of carriers between the strain-split high-mobility and low-mobility states of the conduction or valence band. At low temperatures, threshold fields of the order of several hundred volts per centimeter are observed, which is an order of magnitude smaller than the threshold electric field for the Gunn effect in GaAs. In n-type Ge, the effect is observed at room temperature. The dependence of these phenomena on temperature, sample orientation, and stress magnitude is discussed. These results demonstrate the importance of intervalley transfer to the X minima in determining the high-field transport properties of n-type Ge. Unsuccessful attempts to observe similar effects in strained p-type InSb and n-type Si are also described and discussed.

I. INTRODUCTION

In semiconducting materials where the current is carried by electrons or holes in a degenerate conduction or valence band, removal of these degeneracies by the application of uniaxial stress can result in gross changes in the electrical conductivity. The consequent large piezoresistance coefficients have been used to determine the symmetry of conduction and valence bands for a large number of materials. In addition to these effects on the low-field conductivity, the removal of band degeneracies markedly affects the dependance of carrier velocities on applied electric field in the non-ohmic "warm" and "hot" electron regions.

Ridley and Watkins[1] and Hilsum[2] considered the possibility of realizing bulk negative differential conductivity (BNDC) due to intervalley transfer of carriers in semiconductors with multivalley conduction-band structure. Although the primary emphasis in the study of BNDC effects has been on the study of the Gunn effect in n-type GaAs,[3] BNDC and resulting current instabilities have recently been reported in both p-type[4] and n-type[5] Ge under conditions of appropriately oriented uniaxial compression and electric field. The earlier work on p-type Ge was confined to temperatures near 4.2°K, while n-type materials have been studied between 27°K and room temperature. The present paper is a report of an extension of these previous studies. In n-type Ge the phenomenon has been studied in a wide variety of orientations as a function of temperature and magnitude of applied stress. Studies on p-type Ge as a function of stress were carried out at higher temperatures than the original studies, namely, from 27 to 160°K. (The effect has not been observed above 160°K in p-type Ge.) In addition, we report on some unsuccessful attempts to observe similar phenomena in n-type Si and p-type InSb.

In Sec. II, we discuss sample preparation and other experimental details. Section III contains a discussion

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