occurs at a greater energy separation from E_g than the A-TA line is sufficient reason for assigning the H line to an exciton recombination. Whether it is a free exciton or an exciton bound to a N atom with the emission of a higher-energy phonon can not be readily decided on the basis of the present results.

SUMMARY

We have determined E_g as a function of temperature from 0 to 900°K. In the low-temperature range of 6 to 369°K, E_g was determined directly from the A-line absorption. Over the complete temperature range, absorption curves as functions of photon energy were fitted to a theoretical expression with E_g being determined by the best fit. High-temperature diode emission shows an exciton line that parallels the band gap up to 900°K.

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Noise Properties of n-Type Gold-Doped Silicon*

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Measurements are reported of noise in n-type gold-doped silicon at reduced temperatures, both in thermal equilibrium and under optical illumination. The noise level is at least as low as predicted by generation-recombination theory; the shape is complex. Usually, two relaxation times and sometimes three are discernible. The spectrum often has a local maximum, even in thermal equilibrium. Several detailed three- and four-level models are described; their behavior is calculated and compared with experiment. The gross features of the spectra, viz., the temperature and light-intensity dependence of the relaxation times, the occurrence of negative plateau coefficients, and the interrelation between optical and thermal results can be explained if, besides the known gold levels, another level is postulated, situated slightly below the gold-acceptor level. Several features suggest that this level may stem from paired ionized gold-acceptor and shallow-donor impurities.

1. INTRODUCTION

THE properties of gold-doped silicon have been widely investigated, and although the gross features of this material are quite well understood, the details of some experimental results have not been fully explained, as may be seen, e.g., in the review article by Bullis[1] and from the work of Glinchuk *et al.*[2] In the present paper, we give the results of a study of the electrical properties of n-type gold-doped silicon by means of noise measurements. The noise of interest here is generation-recombination (g-r) noise, which stems from fluctuations in the electronic transition rates among the various participating energy levels of the material; in some cases, the nature of the noise spectra may be modified by transport of the charge carriers, i.e., by diffusion or drift.

Detailed studies have been made on the noise properties of germanium with impurities such as nickel, gold, and manganese which give rise to well-defined deep-lying energy levels in the forbidden band gap.[3–6] Similar measurements have been made on gallium arsenide.[7] To our knowledge, no measurements have been reported for silicon with deep-lying energy levels. The measurement of noise in materials with deep energy levels such as gold-doped silicon not only provides information about the specific material under investigation, but, more generally, can be a convenient means of studying g-r processes involving known donor or acceptor states. For crystals which contain as impurities only the common dopants which produce shallow electron-energy states in the band gap, the probability of transitions between these levels and the conduction or valence bands is very small until extremely low temperatures

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[2] K. D. Glinchuk, A. D. Denisova, and N. M. Litovchenko, Fiz. Tverd. Tela 7, 3669 (1965) [English transl.: Soviet Phys.—Solid State 7, 2963 (1966)].
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[7] J. G. Cook, Ph.D. thesis, Free University of Amsterdam, 1966 (unpublished); J. G. Cook *et al.*, Physica 34, 33 (1967); 35, 52 (1967).

are reached. Therefore there are essentially no fluctuations in the occupancy of these levels at room temperature or at moderately reduced temperatures. At the very low temperatures where these fluctuations do occur, the g-r noise is often masked by other noise. The presence of deep-lying energy levels permits the investigation of noise involving donor and acceptor levels ("extrinsic g-r noise") at moderately reduced temperatures.

Since semiconductors with deep levels are extrinsic photoconductors, which are frequently used as infrared detectors, the noise properties are of importance in determining the usefulness of these materials for detection of low-level signals. Also, since the frequency response of the photoconductivity often corresponds to the frequency dependence of the g-r noise, the frequency response of the material can be estimated from the time constants which appear in the noise spectra. As will be apparent from Sec. 4, the noise turned out to be quite low—certainly not exceeding the g-r limit based on suitable models—so that Si:Au is a promising radiation detector. In our measurements, however, our basic aim was to study the material itself.

2. PROPERTIES OF GOLD-DOPED SILICON SAMPLES

The gold-doped silicon used in this study was purchased from Monosilicon, Inc. The approximate dimensions of the samples are 16×3×3 mm, with the noise signal taken from noncurrent-carrying contacts approximately 10 mm apart to reduce the effect of possible contact noise. Electrical contacts were made to the crystals by electroless plating of nickel on the surface.[8]

The silicon samples had gold concentrations in the range of 10^{14} to 10^{15} per cm^3, and were compensated with shallow-donor impurities such that the degree of compensation was approximately 50 to 95%. Thus at reduced temperatures all shallow-acceptor levels and the gold-donor centers 0.35 eV above the valence band are filled by transfer of charges; the acceptor level located 0.54 eV below the bottom of the conduction band is partially filled and the Fermi level is held close to this level over a wide temperature range. With the residual shallow-acceptor concentration negligible compared with the shallow-donor concentration, the concentration of electrons in the conduction band at low temperatures is given by

$$n=\frac{N_d-n}{N_{\mathrm{Au}}-N_d+n}g_A N_C \exp\{-(\mathcal{E}_C-\mathcal{E}_A)/kT\} \quad (2.1)$$

for $n\gg p$. In this expression N_d is the concentration of shallow donors, N_C the effective density of states of the conduction band, $\mathcal{E}_A$ the position of the gold-acceptor level, and g_A the degeneracy factor of this level. For sufficiently low temperatures $N_d\gg n$ and $N_{\mathrm{Au}}-N_d\gg n$, so that log n is proportional to $1/T$.

[8] M. V. Sullivan and J. H. Eigler, J. Electrochem. Soc. **104**, 226 (1957).

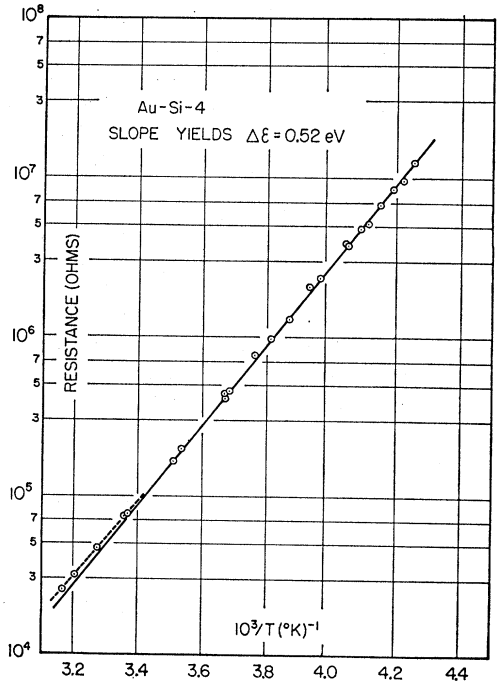

FIG. 1. Resistance versus reciprocal temperature for sample No. 4.

A typical plot of the logarithm of the resistance versus reciprocal temperature is shown in Fig. 1. From the straight-line part of the curve at lower temperatures the energy difference $(\mathcal{E}_C-\mathcal{E}_A)$ can be checked and the compensation ratio N_d/N_{Au} can be computed. At higher temperatures (not fully shown in Fig. 1) where the free carrier concentration is no longer negligible compared with N_d and $N_{\mathrm{Au}}-N_d$, estimate of both impurity concentrations can be obtained from the extent to which the curve deviates from a straight line. In n-type gold-doped silicon the transition from the extrinsic region to the near-intrinsic region is not sharply defined, and therefore estimates of the impurity concentrations obtained in this manner may not be very accurate.

3. MODELS POTENTIALLY APPLICABLE TO g-r NOISE IN GOLD-DOPED SILICON

We had expected that noise properties in this material would be rather simple. At the temperatures under consideration the occupancies of all gold levels, except of the 0.54-eV acceptor level, are approximately frozen. This partially filled acceptor level will mainly exchange carriers with the conduction band, and its own occupancy is not strongly temperature-dependent as long as the Fermi level is locked at its position, i.e., as long as $n\ll N_{\mathrm{Au}}-N_d$. One expects that the variance is Poissonian, $\langle\Delta n^2\rangle=n_0$, with the noise given by[9] [Ref. 9,

[9] K. M. van Vliet and J. R. Fassett, in *Fluctuation Phenomena in Solids*, edited by R. E. Burgess (Academic Press Inc., New York, 1965).

Eqs. (131a) and (135)]

$$G_{nn}(\omega)\approx 4n_0\tau_0/(1+\omega^2\tau_0^2),$$
$$\tau_0\approx 1/\sigma_{na}\langle v_n\rangle(N_{\mathrm{Au}}-N_d), \qquad (3.1)$$

where $G_{nn}(\omega)$ is the spectral density of the variance $\langle\Delta n^2\rangle$, σ_{na} is the capture cross section for electrons by the gold-acceptor centers, and $\langle v_n\rangle$ is the average thermal velocity of the electrons. Thus the spectra would exhibit a single relaxation time, which is practically independent of temperature, permitting a direct determination of σ_{na}. Such spectra were observed, for instance, in Ge:Ni (Ref. 3). Our measurements, carried out on several samples, never showed such simple behavior. In fact, the behavior is quite complex (see, e.g., Fig. 6, discussed in Sec. 4). In the light of this surprise, a number of multilevel models was worked out which could potentially explain such complex spectral shapes. Then, new measurements were carried out under conditions which might confirm or discard the applicability of these models, and, finally, attention was given to the chemical and physical justification for these models. Though it is customary first to present the experimental results and then to find a possible model—as was historically also the order of events in this study—it will be more profitable to present and interpret the experimental results together after the formal models have been investigated. In this section, we discuss the possible behavior of the spectra for three such models, presented here in general terms. Particular attention will be given to the occurrence of local maxima in the noise spectra. The relevance of these models for Si:Au and a suggested identification of the main variables will be discussed in the next two sections.

A. General Results

The time rate of change of the electron occupancy of a specific energy level is a semiconductor with s participating levels which can be written as

$$\frac{d\langle n_i\rangle_{\mathrm{cond}}}{dt}=\sum_{j\neq i}^{s}\langle\{p_{ji}(\mathbf{n})-p_{ij}(\mathbf{n})\}\rangle_{\mathrm{cond}}, \qquad (3.2)$$

where p_{ij} is the transition probability per unit time from level $\mathcal{E}_i$ to another level $\mathcal{E}_j$, with the column matrix $\mathbf{n}$ denoting the electron occupancy of all s levels; the subscript cond means that a conditional average is taken with respect to an ensemble with specified conditions at some initial time, say, $t=0$. Writing the instantaneous deviation from equilibrium or steady state as $\mathbf{n}-\mathbf{n}_0=\Delta\mathbf{n}=\boldsymbol{\alpha}$, the time rate of change for all of the levels can be expressed in linearized form as

$$d\langle\Delta\mathbf{n}\rangle_{\mathrm{cond}}/dt=-\mathbf{M}\langle\Delta\mathbf{n}\rangle_{\mathrm{cond}}, \qquad (3.3)$$

where $\mathbf{M}$ is the phenomenological relaxation matrix, describing how the system relaxes to equilibrium after a small disturbance. The characteristic roots of this matrix yield the natural reciprocal time constants τ_i of the g-r processes. The noise spectra can be determined by applying the Wiener-Khintchine theorem to the autocorrelation function expressed in terms of the $\mathbf{M}$ matrix. A convenient form for the elements of the spectral density matrix $\mathbf{G}$ in the general case is [Ref. 9, Eq. (92)]

$$G_{mn}(\omega)=2\sum_{ij}[\langle\alpha_n\alpha_j\rangle c_{mi}^{-1}+\langle\alpha_m\alpha_j\rangle c_{ni}^{-1}]\frac{c_{ij}\tau_i}{1+\omega^2\tau_i^2}, \qquad (3.4)$$

where the c_{ij} are elements of a transformation matrix which diagonalizes $\mathbf{M}$ (for ease in evaluation of the spectra), and the c_{ij}^{-1} are elements of the inverse matrix. The τ_i follow from

$$|\mathbf{M}-\mathbf{I}/\tau|=0, \qquad (3.5)$$

where $\mathbf{I}$ is the unit matrix. The variances and covariances can be evaluated by means of the generalized g-r theorem

$$\mathbf{M}\langle\boldsymbol{\alpha}\boldsymbol{\alpha}^T\rangle+\langle\boldsymbol{\alpha}\boldsymbol{\alpha}^T\rangle\mathbf{M}^T=\mathbf{B} \qquad (3.6)$$

where $\mathbf{B}$ is composed of the second-order Fokker-Planck moments and the superscript T denotes the transposed matrix. For single-electron transitions from single-charge centers the elements of $\mathbf{B}$ are given by

$$B_{ii}=2\sum_{j\neq i}^{s}p_{ij}(\mathbf{n}_0),$$
$$B_{ij}=-p_{ij}(\mathbf{n}_0)-p_{ji}(\mathbf{n}_0), \quad (i\neq j). \qquad (3.7)$$

For a thermal-equilibrium process a more simple expression can be given [Ref. 9, Eq. (85)]:

$$G_{mn}(\omega)=2\sum_{ik}\frac{c_{mi}^{-1}c_{ik}B_{kn}\tau_i^2}{1+\omega^2\tau_i^2}. \qquad (3.8)$$

In particular, for a process involving one-electron transitions between three levels this result yields [cf. Ref. 9, Eqs. (150)–(153)]

$$G_{11}=4\sum_{1,2}\Phi(\omega;\tau_1,\tau_2)[p_{12}^0(1/\tau_1-M_{22}-M_{12})+p_{13}^0(1/\tau_1-M_{22})], \qquad (3.9a)$$

$$G_{22}=4\sum_{1,2}\Phi(\omega;\tau_1,\tau_2)[p_{12}^0(1/\tau_1-M_{11}-M_{21})+p_{23}^0(1/\tau_1-M_{11})], \qquad (3.9b)$$

$$G_{12}=4\sum_{1,2}\Phi(\omega;\tau_1,\tau_2)[p_{12}^0(-1/\tau_1+M_{22}+M_{12})+p_{23}^0M_{12}]=G_{21}=4\sum_{1,2}\Phi(\omega;\tau_1,\tau_2)[p_{12}^0\times(-1/\tau_1+M_{11}+M_{21})+p_{13}^0M_{21}], \qquad (3.9c)$$

with

$$\Phi(\omega;\tau_1,\tau_2)=\frac{\tau_1\tau_2}{\tau_2-\tau_1}\frac{\tau_1^2}{1+\omega^2\tau_1^2} \qquad (3.9d)$$

and where $\sum_{1,2}$ means that a similar term is to be added in which τ_1 and τ_2 are interchanged. The current fluctuations of the equivalent Norton generator finally have

a spectral density, connected to the spectral densities of the electrons G_{nn} of the holes G_{pp} and of the cross correlation G_{np} by

$$G_i(\omega)=[I/(bn_0+p_0)]^2 \times[b^2G_{nn}(\omega)+2bG_{np}(\omega)+G_{pp}(\omega)], \quad (3.10)$$

where $b=\mu_n/\mu_p$ is the mobility ratio.

In general, as noted from Eq. (3.4) or Eq. (3.8), the spectrum has the form

$$G_i(\omega)=I^2\sum_k \frac{c_k}{1+\omega^2\tau_k^2}. \quad (3.10')$$

Remarks: The above equations will be used in the models considered below. Several assumptions have been made and their validity has been investigated.

First, the assumption of space-charge neutrality, $\sum_{i=1}^{s}\Delta n_i=0$, has been made; this assumption allows us to eliminate one variable, so that an s-level model leads to an $(s-1)$-dimensional Markov process, with $s-1$ nonzero eigenvalues $1/\tau_i$. This condition may not be valid in high-ohmic specimen.[10] We have calculated the dielectric relaxation time for our samples at the reported temperatures, and in all cases deviations from space-charge neutrality were not important in the frequency range under consideration.

Second, modifications in the forms for **B** and **M** occur in the presence of more electron transitions (Auger processes) and of multiple charge centers. For the first we found no indications. The gold impurity does give rise to multiple charge states, but in silicon the energy levels, particularly those of the deep-lying donor and the high-lying acceptor, are far enough apart; in particular, in our study, the deep donor could be ignored. Thus the refinements of the theory encompassing these cases, as reported in Ref. 9, were found to have little bearing on the present results.

Third, in Eq. (3.10), it is assumed that the mobility is a constant. We have wondered whether ionized impurity scattering could affect the g-r noise. This was considered by some Russian workers in connection with fluctuation studies in CdS.[11] The effect on the noise in the presence of several impurities was calculated by Colligan,[12] using standard expressions for the dependence of the mobility on the ionized-impurity concentration. Thus fluctuations in the occupancy of impurity sites give rise to fluctuations in the current *directly* [as via Eq. (3.10)] and indirectly, via a fluctuation in μ_n and μ_p. The results indicate that ionized-impurity scattering has only an effect if μ_n/μ_I is of the order of i_0/n_0,

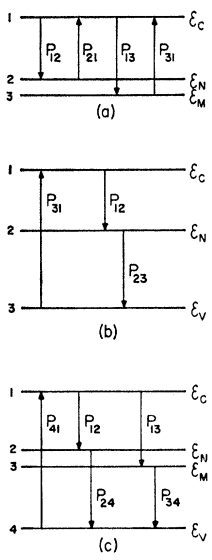

FIG. 2. Transitions in semiconductors with three and four participating energy levels: (a) Thermal-equilibrium model; (b) and (c) optical models.

where i_0 is the average occupancy of the impurity centers in the charged state and n_0 is the free-electron density; $\mu_n^{-1}=\mu_L^{-1}+\mu_I^{-1}$ (ignoring other contributions), where μ_L and μ_I are the lattice and ionized-impurity contribution to the electron mobility, respectively. Since μ_n is less than or equal to μ_I, the free carrier concentration must be approximately equal to or greater than the ionized-impurity concentration, and possibly much greater, depending on the ratio μ_n/μ_I. This condition is difficult to realize in a semiconductor at moderately reduced temperatures.

B. Three-Level Model in Thermal Equilibrium

As a first example, let us consider the three-level system shown in Fig. 2(a). The participating energy levels are the bottom of the conduction band and two types of impurity states which are in thermal communication with the conduction band. It is assumed that the temperature is low enough and the Fermi level high enough above the center of the band gap so that band-to-band transitions and hole conduction are unimportant. With both levels partially compensated, the position of the Fermi level will be determined by the degree of compensation and the temperature; it will be somewhat near the levels $\mathcal{E}_N$ and $\mathcal{E}_M$. Let the concentrations of impurities of levels 2 and 3 be denoted by N and M, respectively, and let the corresponding electron occupancies be i and j. The transition rates are then given by

$$p_{12}=\alpha_{12}n(N-i), \quad p_{21}=\alpha_{21}iN_c, \quad p_{13}=\alpha_{13}n(M-j), \quad p_{31}=\alpha_{31}jN_c, \quad (3.11)$$

where N_c is the effective density of states of the conduction band and α_{kl} is the capture probability for an electron transition from level k to level l. Taking the fluctuations in i and j as the two independent variables and using detailed balance, the elements of the relaxa-

[10] J. R. Fassett and K. M. van Vliet, in *Proceedings of the International Conference of the Physics of Semiconductors, Exeter* (The Institute of Physics and the Physical Society, London, 1962), p. 886.

[11] M. K. Sheinkman and N. B. Lukyanchikova, Fiz. Zh. USSR 8, 1003 (1963) (in Ukranian).

[12] M. B. Colligan, Ph.D. thesis, University of Minnesota, 1967 (unpublished).

tion matrix are given by

$$M_{11}=\alpha_{12}(N-i_0+n_0N/i_0)\,,\quad M_{12}=\alpha_{12}(N-i_0)\,,$$
$$M_{21}=\alpha_{13}(M-j_0)\,,\quad M_{22}=\alpha_{13}(M-j_0+n_0M/j_0)\,. \tag{3.12}$$

In order to write an explicit expression for the spectrum in terms of densities and capture probabilities, approximations must be made for the relaxation times. For a three-level system the reciprocal relaxation times [Eq. (3.5)] can be written as

$$2\tau_{1,2}^{-1}=(M_{11}+M_{22})\pm|M_{11}-M_{22}| \times\{1+4M_{12}M_{21}/(M_{11}-M_{22})^2\}^{1/2}. \tag{3.13}$$

For $(M_{11}-M_{22})^2\gg 4M_{12}M_{21}$ this can be approximated by

$$\tau_1^{-1}=M_{11}+\epsilon\,,\quad \tau_2^{-1}=M_{22}-\epsilon\,,$$
$$\epsilon=M_{12}M_{21}/|M_{11}-M_{22}|\,. \tag{3.14}$$

With $\alpha_{12}(N-i_0)$ sufficiently larger than $\alpha_{13}(M-j_0)$, $\alpha_{13}n_0M/j_0$, and $\alpha_{12}n_0N/i_0$, we have

$$1/\tau_1=M_{11}+\epsilon\approx\alpha_{12}(N-i_0)\,,$$
$$1/\tau_2=M_{22}-\epsilon\approx\alpha_{13}n_0M/j_0\,. \tag{3.15}$$

According to the assumptions for this model, τ_1 is smaller than τ_2. In the extrinsic temperature range of interest, τ_1 would have a relatively weak temperature dependence (essentially the temperature dependence of α_{12}^{-1}, which is the product of the capture cross section and the average thermal velocity of the charge carrier), while τ_2 is a stronger function of temperature depending on j_0/n_0.

The spectrum is evaluated by means of Eqs. (3.9a)–(3.9d). The subscripts 1 and 2 in these formulas refer to the independent variables i and j. Thus we obtain

$$G_{nn}=G_{ii}+G_{jj}+2G_{ij}\equiv G_{11}+G_{22}+2G_{12} \tag{3.16}$$

or

$$G_{nn}=\frac{4\tau_1\tau_2}{\tau_2-\tau_1}\left(\frac{A\tau_1^2}{1+\omega^2\tau_1^2}+\frac{B\tau_2^2}{1+\omega^2\tau_2^2}\right). \tag{3.17}$$

where

$$A\approx\alpha_{12}n_0(N-i_0)\{\alpha_{12}(N-i_0)+n_0(\alpha_{12}N/i_0-\alpha_{13}M/j_0) +2\alpha_{12}(M-j_0)\}+\alpha_{13}^2n_0(M-j_0)^2 \approx\alpha_{12}^2n_0(N-i_0)^2 \tag{3.18a}$$

and

$$B\approx\alpha_{13}n_0^2(M-j_0)(\alpha_{12}N/i_0-\alpha_{13}M/j_0). \tag{3.18b}$$

The plateau coefficient B corresponding to the longer relaxation time *can be either positive or negative.* A sign change of B in some temperature range depends critically upon the relative temperature dependence of the capture probabilities for the two types of sites and upon the degree of filling and relative change in filling with change in temperature for the two levels. *A negative sign of the plateau coefficient of the longer relaxation time means that a local maximum will be observed in the noise spectrum* if the magnitude of this term is sufficiently large. More will be said of this in Sec. 4.

C. Noise Spectrum for a Three-Level System under Optical Illumination

We shall now evaluate the noise spectrum for the three-level model shown in Fig. 2(b). The three participating energy levels are the conduction and valence bands and a partially compensated intermediate level. The concentration of intermediate centers is designated as N ,with i the concentration of electrons in the centers. The significant transition rates are

$$p_{31}=\eta Z\,,$$
$$p_{12}=\alpha_{12}n(N-i)\,, \tag{3.19}$$
$$p_{32}=\alpha_{23}ip\,,$$

where η is an absorption efficiency and Z is the light intensity. Electronic transitions from the valence band to the N level and from the N level to the conduction band, as well as direct recombination from conduction band to valence band, are taken to be unimportant. In short, then, the system is one of optically induced transitions from valence band to conduction band with recombination through one intermediate level. The variance $\langle\Delta n^2\rangle$ for this three-level cyclic transition model has been treated in detail by one of us.[13]

With the electron concentrations of the conduction and valence bands as the two independent variables, the relaxation matrix is

$$M_{11}=\alpha_{12}(n_0+N-i_0)\,,\quad M_{12}=\alpha_{12}n_0\,,$$
$$M_{21}=\alpha_{23}p_0\,,\quad M_{22}=\alpha_{23}(p_0+i_0)\,. \tag{3.20}$$

In contrast to Ref. 10, we shall treat the case in which the degree of compensation is large enough so that in thermal equilibrium the Fermi level is held close to the N level at reduced temperatures; furthermore, we assume that the light intensity is sufficiently low so that the occupancy of the N level does not change greatly from the thermal-equilibrium situation. For the condition that $N,i_0\gg n_0$, p_0, the approximation (3.14) for the relaxation time yields

$$\tau_1=1/\alpha_{12}(N-i_0)\,,\quad \tau_2=1/\alpha_{23}i_0. \tag{3.21}$$

These can be identified as the capture lifetimes for electrons and holes, respectively, i.e., $\tau_1\equiv\tau_n$, $\tau_2\equiv\tau_p$. In terms of the capture probabilities, we also write $\alpha_{12}=\langle v_n\rangle\sigma_n$ and $\alpha_{23}=\langle v_p\rangle\sigma_p$, where σ_n and σ_p are the capture cross section at the N centers for electrons and holes, respectively, and $\langle v_n\rangle$ and $\langle v_p\rangle$ are the corresponding average thermal velocities of the charge carriers.

The noise spectrum can be evaluated by writing out the spectral components according to (3.4). The general result for a three-level system not in thermal equilibrium in which the two independent variables are the numbers of electrons and holes ($\alpha_1=\Delta n$, $\alpha_2=-\Delta p$) is

$$G_i(\omega)=\left\{\frac{I}{bn_0+p_0}\right\}^2\frac{4\tau_1\tau_2}{\tau_2-\tau_1}\left(\frac{A\tau_1}{1+\omega^2\tau_1^2}+\frac{B\tau_2}{1+\omega^2\tau_2^2}\right), \tag{3.22}$$

[13] K. M. van Vliet, Phys. Rev. **133**, A1182 (1964); **138**, AB3 (1965).

where

$$A=\langle\Delta n^2\rangle b\{b(M_{11}-1/\tau_2)+M_{21}\} -\langle\Delta p^2\rangle\{(M_{11}-1/\tau_1)-bM_{12}\} -\langle\Delta n\Delta p\rangle\{b^2M_{12}+M_{21}+b(1/\tau_1-1/\tau_2)\} \quad (3.23a)$$

and

$$B=-\langle\Delta n^2\rangle b\{b(M_{11}-1/\tau_1)+M_{21}\} +\langle\Delta p^2\rangle\{(M_{11}-1/\tau_2)-bM_{12}\}+\langle\Delta n\Delta p\rangle \times\{b^2M_{12}+M_{21}-b(1/\tau_1-1/\tau_2)\}. \quad (3.23b)$$

In accordance with the assumptions regarding the relative magnitudes for our model, and using the approximation (3.21) for the relaxation times, we have $1/\tau_1=\alpha_{12}(N-i_0)\approx M_{11}$, $1/\tau_2=\alpha_{23}i_0\approx M_{22}$. With τ_2 larger than τ_1, the A and B coefficients of the spectrum are approximately

$$A\approx(1/\tau_1-1/\tau_2)b\langle\Delta n^2\rangle(b-\langle\Delta n\Delta p\rangle/\langle\Delta n^2\rangle), \quad (3.24a)$$

$$B\approx(1/\tau_1-1/\tau_2)\langle\Delta p^2\rangle(1-b\langle\Delta n\Delta p\rangle/\langle\Delta p^2\rangle). \quad (3.24b)$$

With b larger than unity and $\langle\Delta n\Delta p\rangle/\langle\Delta n^2\rangle$, $\langle\Delta n\Delta p\rangle/\langle\Delta p^2\rangle$ less than or equal to unity, the A coefficient is always positive, *while B is negative for $\langle\Delta n\Delta p\rangle/\langle\Delta p^2\rangle$ larger than $1/b$*. For silicon, b is approximately 3 to 4 in the temperature range of 100 to 300°K.

The variances and covariances are determined by means of (3.6). The determinantal solution of this matrix equation is

$$\langle\Delta n^2\rangle=D_2/D_1,\quad \langle\Delta p^2\rangle=D_3/D_1,\quad \langle\Delta n\Delta p\rangle=D_4/D_1, \quad (3.25)$$

where

$$D_1=(N-i_0)^2l(i_0+p_0)+n_0(N-i_0)^2(i_0+p_0)^2/i_0p_0 +n_0i_0(N-i_0)+n_0(i_0+p_0)(N-i_0) +n_0^2(N-i_0)(i_0+p_0)/p_0+n_0^2i_0, \quad (3.26)$$

$$D_2=n_0[(N-i_0)^2(i_0+p_0)+n_0(N-i_0)^2(i_0+p_0)^2/i_0p_0 +n_0i_0(N-i_0)+n_0(i_0+p_0)(N-i_0)+n_0p_0i_0], \quad (3.27)$$

$$D_3=p_0[i_0(N-i_0)^2+n_0(N-i_0)^2(i_0+p_0)/p_0 +2n_0i_0(N-i_0)+n_0^2(N-i_0)(i_0+p_0)/p_0 +n_0(N-i_0)^2+n_0^2i_0+n_0^2(N-i_0)^2/i_0], \quad (3.28)$$

$$D_4=n_0[(N-i_0)^2(i_0+p_0)+n_0(i_0+p_0)(N-i_0) +n_0(N-i_0)^2(i_0+p_0)/i_0 +i_0p_0(N-i_0)+n_0p_0i_0]. \quad (3.29)$$

The solution for $\langle\Delta n^2\rangle$ is in accord with van Vliet.[10] For the present problem we approximate these results using our previous assumptions regarding the relative concentrations of impurities and free carriers (N, $i_0\gg n_0$, p_0). Thus from (3.24)–(3.29) we find

$$\langle\Delta n^2\rangle\approx n_0,\quad \langle\Delta p^2\rangle\approx p_0, \quad (3.30a)$$

$$\langle\Delta n\Delta p\rangle/\langle\Delta n^2\rangle=D_4/D_2\approx p_0/(n_0+p_0), \quad (3.30b)$$

$$\langle\Delta n\Delta p\rangle/\langle\Delta p^2\rangle=D_4/D_3\approx n_0/(n_0+p_0). \quad (3.30c)$$

For the current spectrum we find from (3.22), (3.24a), (3.24b), and Eqs. (3.30) the simple approximate formula

$$G_i(\omega)\approx\frac{4[I/(bn_0+p_0)]^2}{n_0+p_0}\left\{[bn_0+(b-1)p_0]\frac{bn_0\tau_1}{1+\omega^2\tau_1^2} \times[p_0-(b-1)n_0]\frac{p_0\tau_2}{1+\omega^2\tau_2^2}\right\}. \quad (3.31)$$

For $(b-1)n_0$ approximately larger than p_0 it should be possible to observe a local maximum in the spectrum provided that the ratio of the plateau constants $B\tau_2/A\tau_2$ is not too small.

D. Relaxation Times for a Four-Level System under Optical Illumination

As a final example we shall consider the four-level model shown in Fig. 2(c). This model is an extension of the previous case in which we now have cyclic transitions through two intermediate levels instead of one. The two intermediate levels correspond to the two impurity states of the three-level model in thermal equilibrium in Sec. 3 B. The primary recombination level is presumed to be the N level.

The noise spectrum of a four-level system not in thermal equilibrium is extremely complicated to evaluate, but some information can be obtained from the relaxation matrix by determining the dominant time constants. Using the same notation as in Secs. 3 B and 3 C, the transition probabilities in Fig. 2(c) are

$$p_{41}=\eta Z,\quad p_{12}=\alpha_{12}n(N-i),\quad p_{24}=\alpha_{24}ip,\quad p_{13}=\alpha_{13}n(M-j),\quad p_{34}=\alpha_{34}jp. \quad (3.32)$$

Rather than evaluating the relaxation times directly from the 3×3 matrix, an approximation will be made to eliminate one of the variables and isolate one of the time constants. The other two relaxation times will be determined from the resulting matrix of rank two.

We look for conditions where one of the break frequencies in the spectrum will occur approximately a decade or more beyond the others (as found experimentally); this implies that fluctuations in one of the levels occur relatively fast. This level is assumed here to be the valence band. Hence for sufficiently low frequencies we may equate the fluctuation $d\Delta p/dt$ equal to zero. Conditions for the impurity and carrier concentrations and the capture probabilities are N, $i_0\gg n_0$, p_0, N, $i_0>M$, j_0, and $\alpha_{24}>\alpha_{34}$. With these approximations,

$$\frac{d(\Delta p)}{dt}=-\alpha_{24}p_0\Delta i-\alpha_{24}i_0\Delta p-\alpha_{34}p_0\Delta j -\alpha_{34}j_0\Delta p\approx 0. \quad (3.33)$$

From this,

$$\Delta p\approx -C_1\Delta i-C_2\Delta j,$$

where

$$C_1=\frac{\alpha_{24}p_0}{\alpha_{24}i_0+\alpha_{34}j_0}\approx\frac{p_0}{i_0}\ll 1 \tag{3.34a}$$

and

$$C_2=\frac{\alpha_{34}p_0}{\alpha_{24}i_0+\alpha_{34}j_0}\approx\frac{\alpha_{34}p_0}{\alpha_{24}i_0}\ll 1. \tag{3.34b}$$

The dominant time constant in (3.33) is $\tau_1=1/\alpha_{24}i_0$.

Taking the electron occupancies of the two intermediate levels as the independent variables, the elements of the resulting relaxation matrix are

$$\begin{aligned}
M_{11}&=\alpha_{12}n_0+\alpha_{12}(N-i_0)(C_1+1)+\alpha_{24}p_0-\alpha_{24}i_0C_1,\\
M_{22}&=\alpha_{13}n_0+\alpha_{13}(M-j_0)(C_2+1)+\alpha_{34}p_0-\alpha_{34}j_0C_2,\\
M_{12}&=\alpha_{12}(N-i_0)(C_2+1)-\alpha_{24}i_0C_2,\\
M_{21}&=\alpha_{13}(M-j_0)(C_1+1)-\alpha_{34}j_0C_1.
\end{aligned} \tag{3.35}$$

From (3.14) and the assumptions for this model the eigenvalues of this matrix are

$$\tau_{2,3}^{-1}\approx M_{11}\text{ and }M_{22}-\epsilon. \tag{3.36}$$

The three relaxation times associated with this model are therefore approximately given by

$$\begin{aligned}
\tau_1&=1/\alpha_{24}i_0,\\
\tau_2&=1/\alpha_{12}(N-i_0),\\
\tau_3&=1/\alpha_{12}n_0.
\end{aligned} \tag{3.37}$$

For relatively low light intensities and for significant compensation of the N centers, the first two relaxation times vary slowly with light intensity and temperature, while the third depends strongly on these parameters.

4. EXPERIMENTAL RESULTS AND INTERPRETATION

Results of measurements on three compensated n-type gold-doped silicon samples are presented. The noise spectra were measured both in the dark and with unfiltered light from a tungsten-ribbon lamp. Use of filtered light to eliminate band-to-band transitions did not change the carrier concentrations sufficiently to have any large effect upon the spectra. Dark measurements were generally made from about 230 to 315°K. For lower temperatures the sample resistance was prohibitively high and at higher temperatures the noise level was very low. The crystals were surrounded by a heat shield to prevent background radiation. Measurements under light irradiation were made between 110 and 240°K. Crystal-current levels were kept sufficiently low to insure that Joule heating of the samples would not present a problem.

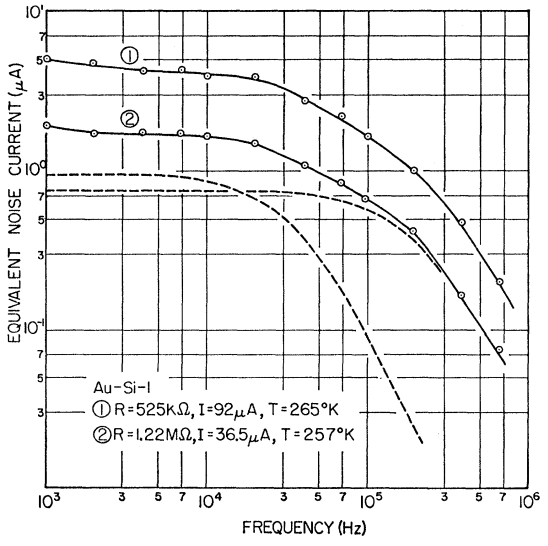

FIG. 3. Noise spectra of sample No. 1 in thermal equilibrium. The dashed lines show a possible resolution of spectrum 2 into two g-r components.

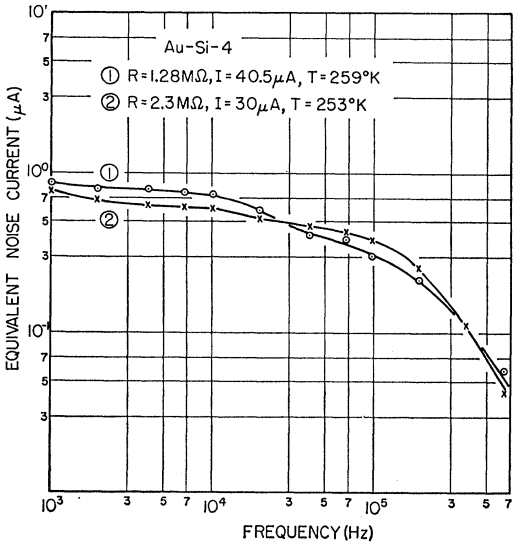

FIG. 4. Noise spectra of sample No. 4 in thermal equilibrium for different temperatures.

A. Noise Spectra in Thermal Equilibrium

Noise spectra measured in the dark for two silicon samples are shown in Figs. 3–6. Sample No. 1 (Fig. 3) has a room-temperature resistivity of 2.65×10^3 ohm cm with a gold concentration of about 10^{15} per cm^3. The spectra of Fig. 3 indicate the presence of two break frequencies, with a resolution of the lower curve into the two g-r components shown by dashed lines.

Figures 4 and 5 show a series of spectra taken at different temperatures for sample No. 4. This sample has a room-temperature resistivity of 5.5×10^3 ohn cm and a gold concentration of about 10^{15} per cm^3. The compensation ratio N_d/N_{Au} computed from Eq. (2.1) is approximately 0.95. The spectra are numbered 1 through 5 according to increasing resistance (decreasing temperature). Figure 4 shows two break frequencies in the spectra in which the magnitude decreases monotonically with frequency. There is little change in the lifetimes between the two spectra, but the ratio of the plateau coefficients has changed noticeably. In spectrum 3 of Fig. 5, the plateau coefficient of the longer relaxation

time appears to have vanished with only one break frequency present. With decreasing temperature for spectra 4 and 5, a local maximum develops, indicating that this plateau coefficient is now negative. There has also been a slight shift of the relaxation times to lower frequencies.

In Fig. 6, we have drawn together a sample of observed spectral shapes for crystal No. 4. This picture offers nothing new over the features of the spectra in Figs. 4 and 5; yet it shows clearly that the situation is quite complex, with a strongly temperature-dependent "evolution" of the regular two time-constant relaxation spectrum of curve 1 to the peaked spectrum of curve 5, over a relatively small temperature range, 236–259°K.

The clear indication of two turnover frequencies requires that the spectra be explained on the basis of a phsycial model with three participating energy levels. In the temperature range of this investigation the free-hole concentration for these samples is sufficiently small so that the valence band plays on part in the g-r processes reflected in the spectra; neither does the donor level 0.35 eV above the valence band play a role, the reason being that the Fermi level is almost locked at the gold-acceptor level, as we explained in the beginning of Sec. 3. Thus the participation of a third energy level is surprising.

We found that the existence of such a level was also suggested by Glinchuk *et al.*[2] To explain their results of photoconductivity measurements on gold-doped and zinc-doped silicon, they postulated the existence of centers of unexplained origin, called M centers, whose energy level they assume to lay somewhat below the gold-acceptor level. We believe it is quite feasible that this level is associated with the impurities present in the material already, and suggest, in particular, that this level is casued by a pairing of ionized (positively

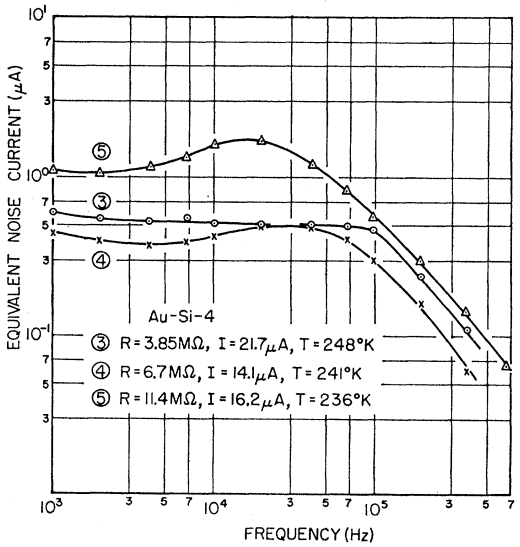

FIG. 5. Noise spectra of sample No. 4 in thermal equilibrium for different temperatures.

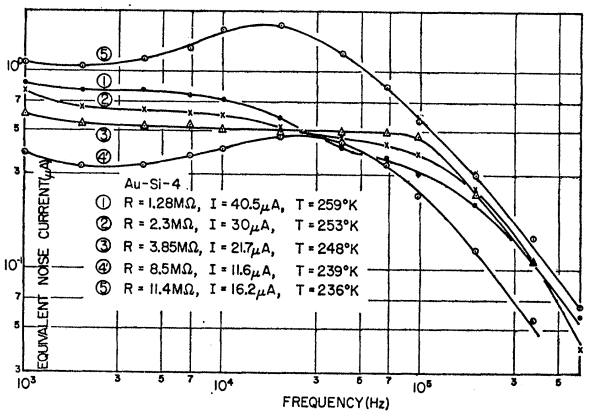

FIG. 6. Compilation of several observed spectral shapes for sample No. 4 in the temperature range 236–259°K.

charged) shallow donors with ionized (negatively charged) gold acceptors. The abundance of such centers will depend on the history of the crystal. With the gold centers quenched in, the probability that a gold atom will be paired with an ionized donor is small. If the crystal is submitted to some heat treatment, however, there will be a greater tendency for migration of impurities, particularly of the gold, with increased probability for pairing. The ionization energy for an electron from such a paired center would be increased over that of unpaired sites.

There are two observations which support this idea for the samples in this study. First, after noise measurements had been completed, resistance and Hall-effect measurements were repeated and extended to higher temperatures. It was found that the slope of the resistance-versus-$1/T$ curve increased slightly upon each heating of the crystals, even though the maximum temperature was only about 450°K. This shows a downward shifting of the Fermi level, indicating an increase in the concentration of a lower energy level. With this explanation, the N level of Sec. 3 B is identified as the 0.54-eV gold-acceptor level and the M level corresponds to the paired sites. The later resistance-versus-temperature measurements indicate that the M level may be about $\frac{1}{10}$ eV below the N level. Secondly, this hypothesis for the origin of the M level is supported by the spectral plateaus and time constants as described in Figs. 3–6. Spectrum 2 of Fig. 4 can be broken up into two g-r components with lifetimes of 6 and 0.7 μsec. From the expressions (3.15) for the lifetimes the capture cross section 253°K for electrons at the N sites is about 10^{-15} cm^2 and for the M sites about 10^{-12} cm^2. The relatively large value for the M centers indicates that they are positively charged when empty, which agrees with the above suggested origin of these centers.

An unusual feature of the noise spectra of sample No. 4, particularly in thermal equilibrium, is the occurrence of a local maximum in a certain temperature range. Similar phenomena have been observed in high-resist-

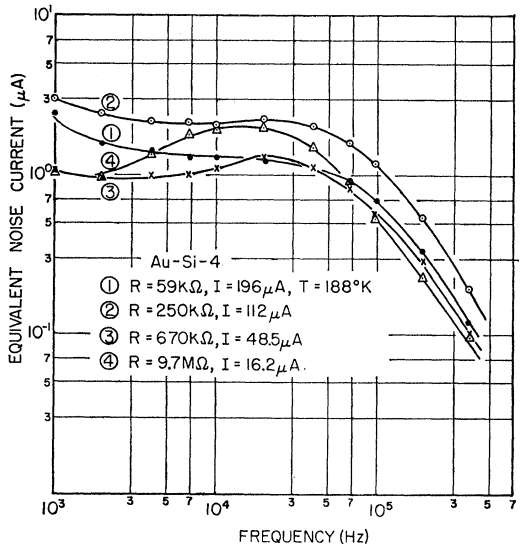

FIG. 7. Noise spectra of sample No. 4 at 188°K for different light intensities.

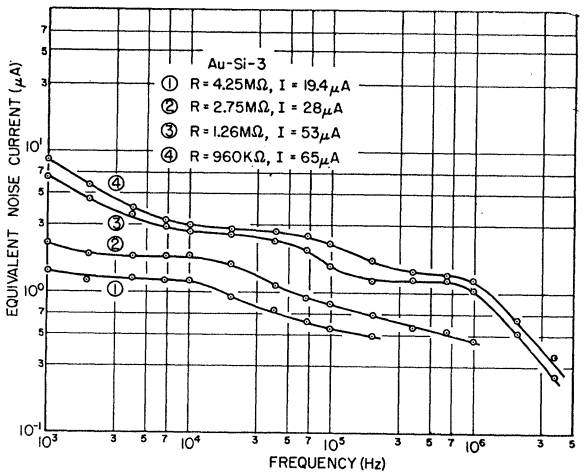

FIG. 8. Noise spectra of sample No. 3 at 162°K for different light intensities.

ance samples of other materials in thermal equilibrium, namely, copper-doped gallium arsenide,[7] manganese-doped germanium,[14] and near-intrinsic silicon,[15] but no detailed investigation and the interpretation of noise has been carried out in any of these cases. A rise in the noise spectrum can occur under certain conditions for frequencies greater than the reciprocal dielectric relaxation time. This was observed by Fassett[3,10] in p-type gold-doped germanium and was shown to result from g-r noise modified by space-charge limited transient fluctuations. It does not appear that this explanation applies here or in the three references cited above.

It has been stated,[7,16] and supposedly proved, that in thermal equilibrium the individual plateau coefficients of the spectrum [Eq. (3.10a)] must be positive. According to the model of Sec. 3 B, the plateau coefficient B [Eq. (3.18b)] can become negative under somewhat stringent conditions (see below). We note also that the manner is which the maximum develops in the spectra of sample 4 (Figs. 4 through 6) strongly indicates that a change of sign occurs for the plateau coefficient of the *longer* relaxation time.

In order for the peak to appear in the spectrum in accordance with (3.18b) and the experimental results, the ratio $\alpha_{12}j_0/\alpha_{13}i_0$ must decrease with temperature, i.e., the N level must fill faster than the M level, and the temperature dependence of the capture cross section must comply. With the N level above the M level and the Fermi level between them, the first condition probably is fulfilled. As for the second condition, it has been found in gold-doped silicon[1,17] that the capture cross section at a neutral site is largely temperature-independent and at a charged site has the form C/T^n, where n is in the range of 2.5 to 4. The ratio α_{12}/α_{13} would thus vary as T^n, which qualitatively agrees with the experimental results. Precise calculations cannot be made, since the positions of the energy levels and the impurity concentrations and degrees of filling cannot be determined accurately enough.

B. Noise Spectra under Light Irradiation

Noise spectra of two samples measured under optical illumination are shown in Figs. 7–9. A local maximum was again observed in the spectra of all of the samples, under light irradiation for various light and temperature conditions.

In Fig. 7, several spectra are shown of sample No. 4 at 188°K for different light intensities. Two break frequencies are noticeable. We believe that the spectra can be explained in terms of the three-level nonthermal-equilibrium model of Sec. 3 C, involving optical excitation of electrons from the valence band to the conduction band, with significant recombination via the 0.54 gold-acceptor level only. Recombination by means of the M level presumably is not sufficient to show up in the spectra of this sample.

A series of noise spectra taken at 162°K for different light intensities is shown in Figs. 8 and 9 for sample No. 3. This sample has a room-temperature resistivity of 7.5×10^4 ohm cm and a compensation ratio N_d/N_{Au} of about 0.55. The gold concentration is estimated to be approximately 10^{14} per cm^3. The spectra, numbered 1 through 6 in order of decreasing resistance, show two distinct break frequencies in Fig. 8. The lower turnover frequency shifts to higher frequencies with increasing light intensity, whereas the higher one tends to remain fixed. In Fig. 9, a local maximum is again discernible.

[14] J. R. Fassett, M.S. thesis, University of Minnesota, 1958 (unpublished).
[15] M. B. Colligan, M.S. thesis, University of Minnesota, 1963 (unpublished).
[16] A. C. E. Wessels and S. Kruizinga, Phys. Letters **20**, 243 (1966).
[17] G. Bemski, Phys. Rev. **111**, 1515 (1958).

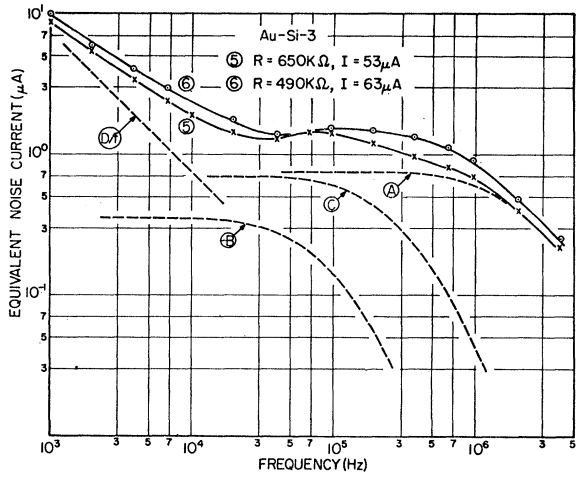

FIG. 9. Noise spectra of sample No. 3 at 162°K for different light intensities. The dashed lines show a possible resolution of spectrum 5 into a $1/f$ component and three g-r components, one of which has a negative plateau coefficient.

The manner in which the maximum develops along with the other features of the spectra requires an explanation in terms of four participating energy levels. The model of Sec. 3 D is employed, with optical excitation from the valence band to the conduction band and recombination by means of two intermediate levels. Obviously, these two kinds of recombination centers are to be identified with the N level (gold acceptor) and the M level. The spectrum for this model was not evaluated, but the three relaxation times can be determined. The dashed lines in Fig. 9 show a decomposition of spectrum 5 into a low-frequency $1/f$ component and three g-r components, one of which has a negative plateau coefficient. From (3.37) the relaxation times are identified as $\tau_A=1/\alpha_{24}i_0=1/\sigma_{pa}\langle v_p\rangle i_0$, $\tau_B=1/\alpha_{12}(N-i_0)=1/\sigma_{na}\times\langle v_n\rangle(N-i_0)$, and $\tau_C=1/\alpha_{13}n_0=1/\sigma_M\langle b_M\rangle n_0$, where subscripts A, B, and C refer to the partial spectra of Fig. 9, curve 5; further, σ_{na} and σ_{pa} are the capture cross sections for electrons and holes, respectively, for the gold-acceptor level, and σ_M is the capture cross section for electrons at the M centers. The values of the first two cross sections computed from the resolution of spectrum 5 are approximately 2×10^{-14} cm^2 for σ_{pa} and 10^{-15} cm^2 for σ_{na}, which agree in order of magnitude with what others have found.[1] The value of σ_M is between about 10^{-11} and 10^{-12} cm^2; the uncertainty is due to the probable inhomogeneous distribution of the free carrier concentration near the surface under light irradiation. However, this value generally agrees with the value of 10^{-12} cm^2 found for sample 4 in thermal equilibrium at 253°K; also, the value of σ_{na} agrees excellently with the value found from thermal measurements for sample 4 (Sec. 4 A). It is finally noted that, as far as can be determined, the light dependence of the relaxation times agrees qualitatively with experimental results: Lifetimes A and B do not depend strongly on the light intensity, while C is inversely proportional to the free electron concentration, as predicted by Eq. (3.37).

5. SUMMARY AND DISCUSSION

The noise properties of the gold-doped silicon samples in this investigation can be explained in terms of physical models with three and four participating energy levels. The models for nonthermal and thermal-equilibrium conditions are consistent with each other. The capture cross sections determined by means of these models for recombination of carriers through the gold-acceptor level agree with what others have found. The magnitude of the noise was consistently found to vary as the square of the current and was somewhat lower than predicted by theory, often by a factor 2 to 5. Since the expressions for the spectra in Sec. 3 are complicated, part of this discrepancy stems from approximations which were necessary to obtain manageable results.

A full explanation of the noise spectra requires the presence of another energy level, designated the M level lying slightly below the gold-acceptor level. This level may arise from pairing of the gold atoms and the ionized shallow-donor impurities.