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Microplasmas in Silicon

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At breakdown of reverse-biased silicon junctions one often observes not only discrete current pulses, but also minute luminous spots. It is postulated that these phenomena represent local discharges which are very similar to the gas discharge cathode fall. The mechanism is illustrated for the case of the *n-i-p* structure. Approximate calculations show that the ionizing regions of these microplasmas are about 500 A in extent, have a current density $\approx 2\times 10^6$ amp/cm^2, and a net space charge density $\approx 10^{18}$/cm^3. Two such regions are to be associated with each microplasma, except in such narrow junctions that they cannot properly be separated. The finite duration of the microplasmas, as evidenced by the current pulses, may be explainable on the basis of a statistical fluctuation, in which a fraction of the carriers fail to ionize. If the fluctuation exceeds a critical size, the carrier density rapidly decreases with time, and the microplasma is extinguished. Initiation of the microplasma in linear gradient and step junctions poses a space charge problem that is at present not resolved.

I. INTRODUCTION

CARRIERS injected into reverse-biased silicon (and germanium) *n-p* junctions will, if the applied electric field E is high enough, produce electron-hole pairs by ionization, which themselves produce further ionization, and so on.[1,2] If E is not too high, the consequent charge multiplication M is finite; the situation is closely analogous to the Townsend discharge commonly encountered in gaseous electronics. As E is increased, $M\rightarrow\infty$, which state is called breakdown, and one might expect some new effect to be manifested. In the gas discharge, the manifestation is generally a sudden transition to a (relatively) high-current-density mode, in which the field and current are determined to a large extent by space charge. Such a phenomenon is often referred to as a plasma. Arguing by analogy, one might expect the same thing to happen in the *n-p* junction; and indeed, it appears that this is the case. For want of a better name, the small high-current-density discharges will be referred to as microplasmas.

This paper is concerned with a qualitative description of the transition, and some properties of the microplasma. The analysis is crude. A reasonably exact solution appears virtually impossible; even in gaseous electronics, exact solutions have been obtained for only the simplest plasmas.

Before describing the transition and the microplasma, it will be necessary to review the pertinent data upon which the description will be based.

II. SUMMARY OF DATA

The ionization coefficient α cm^{-1} has been measured[2] for both electrons and holes in silicon, and the rate appeared approximately equal for each. One may write empirically

$$\alpha\sim E^k, \tag{1}$$

where k is itself a function of E. This coefficient $k\gg 1$ at low E, and $k\leq 1$ at very high E. A theoretical calculation of α *vs* E has been made by Wolff.[3] It agrees well with values of α obtained by McKay from observations of charge multiplication in reverse-biased silicon *n-p* junctions. More recently, Miller[4] has concluded that α is larger for electrons than for holes. This fact will affect the subsequent discussion in a minor way, which will be mentioned below.

It is well known from gas discharge technology that a medium in which $k>1$, and in which two electrodes are immersed, will possess, in the absence of other complicating mechanisms, a negative voltage-current characteristic over the range of E approximately defined by the range for which $k>1$. But also to be considered[5] are the spreading resistance of the material surrounding the high-current ionizing region, and heating of the junction, which effects together might be sufficient to give a positive characteristic at the contacts to the silicon. McKay observes, in fact, that at breakdown silicon *n-p* step and linear gradient junctions do show an instability. He notes that the junction breaks down sporadically, giving perfectly constant current pulses all of the same amplitude, about 50 μa at their onset, and increasing with increasing applied current to a maximum value of perhaps 100 μa. This increasing current is accommodated principally through an increase in the on-off time ratio, and time superposition of pulses. It is important to note that all the junction current was carried by these pulses. The check was obtained up to 200 μa, where several sets of pulses were superposed, as if the junction were breaking down at discrete places. The behavior of these current pulses appears to be independent of the breakdown voltage of the junction, i.e., of junction width and built-in space charge.

Confirming evidence of such a mechanism has been provided by the observation of Newman[6] and co-

[1] K. G. McKay and K. B. McAfee, Phys. Rev. **91**, 1079 (1953).
[2] K. G. McKay, Phys. Rev. **94**, 877 (1954).
[3] P. A. Wolff, Phys. Rev. **95**, 1415 (1954).
[4] S. L. Miller, Bell Telephone Laboratories (private communication).
[5] W. T. Read, Bell Telephone Laboratories (private communication).
[6] Newman, Dash, Hall, and Burch, Phys. Rev. **98**, 1176 (1955).

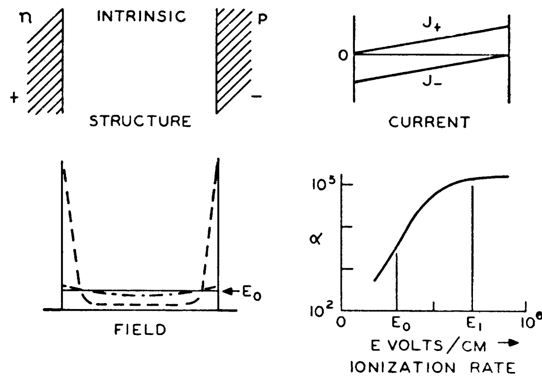

FIG. 1. Diagrams illustrating the mechanism of instability leading to a microplasma, for an n-intrinsic-p silicon structure.

workers that silicon junctions at breakdown emit visible light. Further investigation here by Chynoweth and McKay[7] shows that the light comes from individual regions each of which is too small for microscopic resolution. It appears reasonable to associate these regions with individual microplasmas.

III. INSTABILITY AND THE STEADY-STATE MICROPLASMA

Consider Fig. 1(a), which shows an n-intrinsic-p structure, in which it is assumed that the n and p parts are heavily doped so that they may be considered as metallic boundaries in the subsequent discussion. Figure 1(b) indicates the reverse bias field across the junction. When the field is low, and no ionization occurs, E= constant across it. With increasing E, one begins to get ionization. Eventually, at some field E_0, the multiplication $M \rightarrow \infty$.

This situation is unstable. Consider the current of holes which increases to the right, and of electrons which increases to the left, as in Fig. 1(c). This gives a negative space charge at the left and positive at the right side. The result is to distort the field into a slightly parabolic shape, as shown by the dotted curve of Fig. 1(b). $E>E_0$ at the edges, and $E<E_0$ at the center. But since α, Fig. 1(d), increases more rapidly than linearly with E, the additional ionization near the edges more than offsets the reduction in the center. Thus the net ionization increases still further, increasing the current, distorting the field even more, and so on.

The rapid transition, with increasing current density, will continue until some averaged field near the junction edge becomes so high that α increases only linearly with field [E_1, Fig. 1(d)]. The field distribution corresponds to the dashed curve of Fig. 1(b). At this point, further distortion of E produces no increase in ionization; and at the same time, another stabilizing effect occurs. The ionizing regions are now very narrow, and carriers do not reach an equilibrium velocity distribution. Thus one has an appreciable fraction of the carriers being accelerated in a high field, but ionizing at the end of the region where the field is low. This contribution to the space charge prevents the ionizing regions from becoming narrower. Figure 1 assumes equal values of α for electrons and holes. Qualitatively, the results are the same if α is somewhat different for the two particles. The principal effect will be to introduce some asymmetry between the positive and negative sides.

There is a close analogy here to the dc gas discharge. In the gas, the positive carriers (ions) do not ionize, so there is only one high field region where ionization occurs, at the negative side, called the cathode fall. In the silicon junction there is one at each end, with a high net space charge of holes at the negative side, and of electrons at the positive side. Joining them there is presumably a region of low field and high charge density with, however, low net space charge. This might correspond crudely to the so-called positive column of the gas discharge.

It is possible to estimate the size of these small ionizing regions, which are the most important parts of the microplasma. The field E_1 above which α increases linearly with E is about 700 kv/cm, as determined from McKay's data. Furthermore, these high-field data are obtained with narrow n-p step junctions, about 3000 A wide. In these junctions, it has been estimated that near breakdown, the ionizing region was only about 500 A wide, the rest of the junction being in a field too low to ionize. Since both this n-p step junction at breakdown and the ionizing region of the microplasma are self-sustaining with $E \sim 700$ kv/cm, one concludes that the length of the ionizing regions in the microplasma are also about 500 A. One thus has a voltage drop of about 4 volts across each region, which is a few times the ionization potential.

One may now derive further properties of these ionizing regions. From Poisson's equation, $E \approx eNd/\epsilon$, where N is the net space charge density, d the width of the region, e the electronic charge, and ϵ the permittivity. The dielectric constant of silicon is about 12. Thus, using $E=0.7\times10^6$ v/cm and $d=5\times10^{-6}$ cm, one obtains $N\approx10^{18}/\text{cm}^3$. Let us assume, analogous to the gas discharge, that in each region the charges are mostly of one sign, so that the carrier density is also about 10^{18}. In order to estimate other gross parameters, one must know the drift velocity of the carriers at these high fields. Wolff[8] suggests the value 1.3×10^7 cm/sec, derived from his solution of the transport equation in silicon. The local current density $J=Nev$ is therefore about 2×10^6 amp/cm^2. The cross-section area A of the region is $A=I/J$, where I is the current, which will be taken as 50 μa. One obtains $A=2.4\times10^{-11}$ cm^2; if the discharge is thought to be cylindrical in shape, one obtains a diameter of 5–600 A. The total number of

[7] A. G. Chynoweth and K. G. McKay, Phys. Rev. **102**, 369 (1956).

[8] P. A. Wolff, Bell Telephone Laboratories (private communication).

charges in one of these regions is therefore about 120. If the carriers in each region are not mostly of one sign, the current density will be increased and the area A reduced accordingly, but the total number of carriers will remain about the same.

These order of magnitude results appear reasonable on two counts. First, the calculated net space charge density is for the most part considerably higher than the space charge built into the junction. Thus one finds justification for the experimental fact that the behavior of the microplasma is substantially independent of the doping of the junction: the microplasma properties are determined in the main by the properties of the silicon itself. To be sure, microplasmas have been observed[9] in a junction with an external breakdown voltage of 6.5 volts. For this case, the builtin space charge density is in some doubt, and might be as high as $10^{18}/\text{cm}^3$. But it appears that no great inconsistency exists at the moment, for junctions with substantially higher doping are observed not to form microplasmas. The second reasonable count is that the diameter of the ionizing region turns out to be comparable to its length. While this is no guarantee that the mechanism is correct, it would be difficult to explain away a calculation showing that the length/diameter ratio was extreme. The result also points out a difficulty in obtaining a very accurate solution: one must solve a nonlinear space charge problem in three dimensions.

The temperature rise and the rate of approach to temperature equilibrium in the ionizing regions may be estimated. If one assumes all the power P to be dissipated uniformly in a sphere of diameter l, one finds that the equilibrium temperature rise at the center is given by

$$T=3\Gamma(\tfrac{3}{2})P/4\pi^{\frac{3}{2}}kl, \qquad (2)$$

where k is the heat conductivity, which for silicon is 0.836 joule/sec cm °C. A calculation of Eq. (2) is given in Appendix I. For one ionizing region with 50 μa current, $P\approx 2\times 10^{-4}$ watt, and $l=500$ A; thus $T\approx 12°$. This number is in fact an absolute lower limit. First, the current may be twice as large; and second, heat diffusion from the other ionizing region and the surrounding resistive medium cannot be ignored. A temperature rise three times as large, i.e., 36°C, may be more realistic.

For either heating or cooling, it is shown in Appendix I that a unique time constant cannot be defined. The approach to equilibrium is at first very rapid, then much slower as equilibrium is approached. The rate is a function of sl^2/k, where $s=1.8$ joules/cm^3 °C for silicon is the heat capacity. The temperature reaches 50% of the final value in a time of about $0.3sl^2/k \approx 1.6\times 10^{-11}$ sec, 75% in a time about 7×10^{-11} sec, and 90% in a time of about 4×10^{-10} sec.

One may suppose that, in common with all such

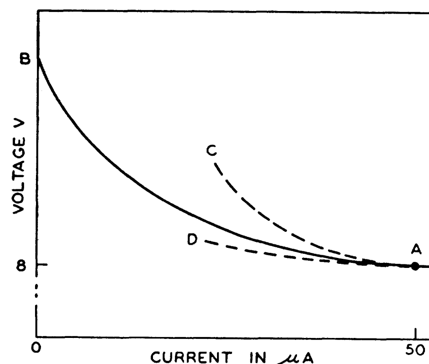

FIG. 2. Voltage-current diagrams of the ionizing region of a microplasma. The equilibrium characteristic is represented by curve AB. Curves AC and AD represent the effect of fluctuations which are respectively stable and unstable.

negative resistance devices, a voltage-current characteristic exists for the ionizing regions which has the general form of Fig. 2. The curve is for the two ionizing regions in series. The breakdown voltage of the junction is at V_B; as the voltage is raised just above it, a rapid transition occurs to a point in the vicinity of A at 50 μa and 8 volts. At that point, the excess voltage is taken up in the resistance drop of the surrounding medium.

In an n-i-p structure at least, an initiation mechanism appears at hand. With a slight overvoltage, breakdown does not occur immediately, but awaits the entry of a chance carrier into the region. Breakdown in step and linear gradient junctions presents an additional space charge problem which has not yet been resolved. The trouble is that with one side (at least) of the junction possessing finite built-in space charge, a distortion of the field by ionization will act to widen the junction and lower the field in it.[10] One might suppose that the donors (or acceptors) are distributed in such a way that locally intrinsic regions are formed. If they are distributed truly at random, a simple calculation shows that the number of such regions is much too small except for high voltage (lightly doped) junctions. If the donors collect in groups (perhaps at dislocations), the chance of finding essentially intrinsic regions is of course much enhanced. Nothing very definite is known about this point at present.

IV. EXTINCTION OF THE MICROPLASMA

The duration and extinction of the current pulses is of interest. At low average current through the junction, the pulses are infrequent, of amplitude 50 μa, and have a short average life ($\sim$1 μsec, perhaps). Visual observation of the pulses on an oscilloscope indicates that the distribution of pulse lengths is approximately exponential, which would indicate that extinction depends on some random event independent of pulse duration.

[9] A. G. Chynoweth and K. G. McKay, Bell Telephone Laboratories (private communication).

[10] W. T. Read, Bell Telephone Laboratories (private communication).

Further, McKay notes that increasing the average current through the junction results in a relatively small increase in pulse current (maximum current ≈ 100 μa), but a great increase in average duration (as much as 100:1, with sufficient current increase). Again there is an approximately exponential distribution of durations.

A mechanism, albeit speculative, may be proposed to explain these phenomena. It is that by a chance fluctuation, the current decreases through the microplasma. From Fig. 2, the voltage must rise more or less quadratically along or above the stable curve AB with decreasing current if the discharge is not to extinguish. The local capacity and resistance will have this effect of raising the voltage with decreasing current, but the actual voltage-current curve depends on the magnitude of the fluctuation.

For small or sufficiently slow fluctuations, the voltage rises rapidly with current, as in curve AC of Fig. 2, and the discharge is stable. For rapid fluctuations of sufficient magnitude, however, the voltage will be "clamped" by the local capacity and the rise may be represented by curve AD. In this case there is insufficient ionization to maintain the discharge in its reduced circumstances, the current decreases still further, and the discharge is extinguished. The charges are swept out in a time of the order of 10^{-11} sec. At this time the breakdown region is still heated, and the ionization coefficients are reduced by about $5\times10^{-2}\%$ per degree C. Thus if the applied voltage is just above breakdown for the cold junction (as is experimentally the case if the pulses are to be extinguished), the discharge will not immediately reignite, but await another chance carrier.

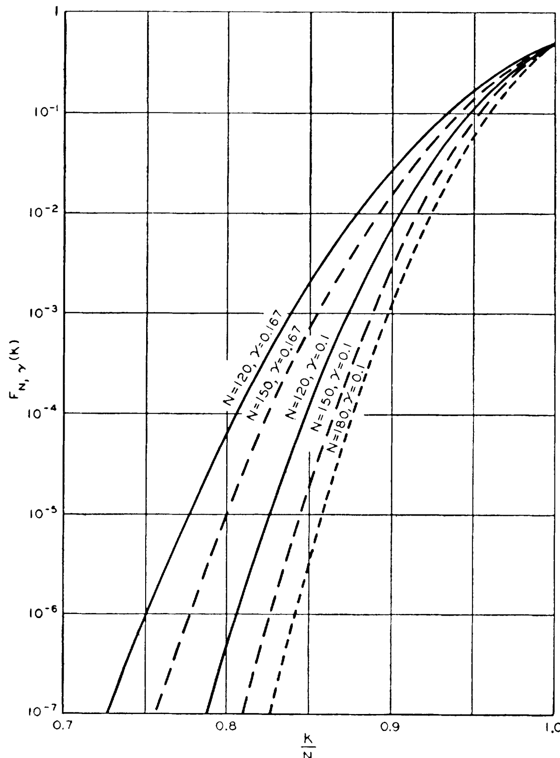

Fig. 3. Probability $F_{N,\gamma}(k)$ that N carriers, each with probability γ of ionizing zero or twice, and probability $1-2\gamma$ of ionizing once, will have k ionizations or less.

The plausibility of the mechanism depends on a calculation of the frequency of fluctuations large enough to produce a voltage-current curve such as AB of Fig. 2, and a comparison of this frequency with the reciprocal lifetime of the pulses.

Consider first the ionization statistics, and let the probability $P_1(0)$ of one carrier failing to ionize be γ. Now note that $P_1(3)$, the probability of three ionizations across the 4-volt ionizing region, is negligibly small. Since the expectation number of ionizations $n=1$ for a steady state, one must have $P_1(2)=\gamma$ also, and $P_1(1)=1-2\gamma$. The number of practical interest here is $F_{N,\gamma}(k)$, the probability that all N carriers in an ionizing region will actually have k ionizations or less. It is calculated in Appendix II, and is shown in Fig. 3, for $N=120$, 150, and 180, and for $\gamma=\frac{1}{6}$ and $\frac{1}{10}$; these values of γ are shown in the Appendix to be not unreasonable. Note that $[F_N(k)]^2 \gg F_N(2k-N)$ over the range $F<10^{-2}$; in other words, one is much more likely to find a 10% (say) fluctuation simultaneously in each ionizing region than one 20% fluctuation in one region.

The velocity of the carriers in the 500 A ionizing regions is about 1.3×10^7 cm/sec. The ionization frequency per carrier is therefore about 2.5×10^{12} sec^{-1}. The pulse duration is observed to be a few microseconds, so that one must have $F^2\approx10^{-7}$, or $F\approx3\times10^{-4}$. For $N=120$, this corresponds to a fluctuation of about 18% if $\gamma=\frac{1}{6}$, and 14% if $\gamma=\frac{1}{10}$.

One must now estimate the effect of such a fluctuation on the voltage across the ionizing region. Figure 4 is a crude representation of an equivalent circuit. The capacity C must be at least that of a pair of plates 500 A across and 500 A apart, or $C\geq5\times10^{-18}$ farad. The value of R is more in doubt, but it is only required to be large enough that $RC>4\times10^{-13}$ sec, which is the transit time of a carrier across the ionizing region. This means that $R>10^5$ ohms. For high-voltage junctions,

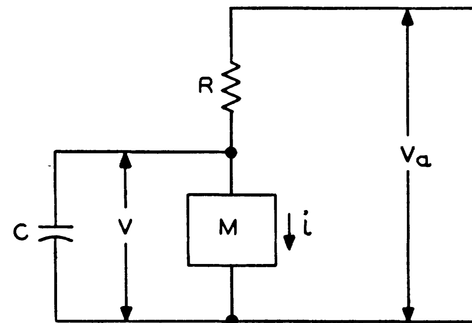

Fig. 4. Equivalent circuit diagram of the microplasma.

the spreading resistance (calculated from the bulk resistivity) and that of the plasma connecting the ionizing regions would probably be sufficient; but for low-voltage junctions, it is not. But one is dealing here with the dynamic resistance, i.e., the rate of change of voltage across the element R with current. Relatively high-field regions exist not only at the microplasma, but also in its vicinity, and at such fields, the drift velocity of carriers varies much less than linearly with field. One might reasonably suppose, then, that R is much greater than that corresponding to the low-field bulk resistivity. Since also the microplasma as a whole changes dimensions with current, it is evident that any representation by equivalent circuit is fraught with difficulty.

If one admits the qualitative picture of Fig. 4, one may calculate the voltage change resulting from a fluctuation of the sort described, which has occurred over one transit time. The voltage rise is approximately

$$\Delta V = -\Delta q/C, \tag{3}$$

substantially independent of R, where Δq is the fluctuation in charge. For a 15% decrease of the 50 μa current over a time of 4×10^{-13} sec, one obtains $\Delta V=0.6$ volt. One cannot say whether such a point, plotted on Fig. 4, will lie above or below the stable curve; but one can say that it is of the right order of magnitude, and that therefore the mechanism proposed does not appear totally unreasonable.

The mechanism also explains the strong dependence of pulse duration on pulse current. According to this picture, one supposes that some fixed value of γ exists, and that some fixed percent fluctuation will extinguish the microplasma. Although neither quantity can be experimentally determined with much accuracy, one can investigate the dependence of extinction probability on N. Consider the curves $\gamma=0.1$ of Fig. 3 for a 15% fluctuation. The ratio $(F_{120}/F_{150})^2=36$, and $(F_{120}/F_{180})^2 \approx 1300$. This would imply that the average duration increases by such factors as the pulse current increases by 25% and 50%, respectively.

The writer takes pleasure in thanking K. G. McKay, A. G. Chynoweth, P. A. Wolff, and W. T. Read for many helpful and pleasant discussions in regard to the problem.

APPENDIX I. TEMPERATURE RISE IN THE MICROPLASMA

Consider the power Q/cm³, and an elementary volume dV in which the energy $QdVdt'$ is generated in a time dt' at t'. Then at a later time t, this energy is distributed throughout the surrounding volume. The contribution d^2T to the temperature at a distance r from dV is

$$d^2T = \frac{QdVdt'}{s[4\pi D(t-t')]^{\frac{3}{2}}} \exp[-r^2/4D(t-t')], \tag{4}$$

where $D=k/s$ is the heat diffusion coefficient. Let the microplasma be initiated at time $t=0$, and let $t-t'=\tau$. Then at the later time t, the total contribution dT of this volume element dV to the temperature is

$$dT = \int_0^t \frac{QdVd\tau}{s[4\pi D\tau]^{\frac{3}{2}}} \exp\left(-\frac{r^2}{4D\tau}\right) = \frac{QdV}{4\pi^{\frac{3}{2}}kr} \int_{r^2/4Dt}^{\infty} z^{-\frac{1}{2}} e^{-z} dz. \tag{5}$$

The observed current pulses have durations of the order 10^{-6} sec. For typical distances of the order 500 A, the lower limit of the incomplete gamma function in Eq. (5) is $\approx 10^{-6}$, and may be set equal to zero. Physically, this means that temperature equilibrium is approached very closely in this time. Equation (5) then becomes

$$dT = \Gamma(\tfrac{3}{2}) QdV/4\pi^{\frac{3}{2}}kr. \tag{5a}$$

Consider now the temperature T at the center of a sphere of diameter l heated in this way. From Eq. (5a) one obtains, using the fact that the total power $P=\pi Ql^3/6$,

$$T = \frac{\Gamma(\frac{3}{2})Q}{4\pi^{\frac{3}{2}}k} \int_0^{l/2} 4\pi r dr = 3\Gamma(\tfrac{3}{2})P/4\pi^{\frac{3}{2}}kl. \tag{6}$$

The approach to equilibrium, or conversely the cooling after cessation of the current, involves integration of incomplete gamma functions. A simple approximate answer is obtained if one considers all the heat to be generated at one point, and calculates the conditions at a distance r: the integral of Eq. (5) gives the time dependence. The assumption $r=l/2=250$ A then leads to the results stated in the text.

APPENDIX II. CALCULATION OF PROBABILITY $F_{N,\gamma}(k)$

Consider first the probability γ. An approximate value is obtained from the following argument. At breakdown, a carrier traveling across the whole region has an expectation $n=e-1\approx 1.7$, and let us for the moment assume this to be true in the microplasma also. But the carriers are not produced right at the end of the ionizing region; in fact, about half of them must be produced in places where $1<n<1.7$. Thus for these favored carriers, one has some average $\langle n\rangle \approx (1.7+1)/2 \approx 1.35$, and for the whole ensemble, $\gamma \approx (1.35-1)/2 \approx \frac{1}{6}$. It is likely that $\gamma < \frac{1}{6}$ in the microplasma, because the electrons are not in equilibrium with the field, and tend to ionize nearer to the ends of the ionizing regions than would otherwise be the case.

If $\gamma=\frac{1}{4}$, the quantity $F_{N,1/4}(k)$ can be simply ex-

pressed.[11] It is

$$F_{N,1/4}(k)=\binom{2N}{k}\Big/4^N. \quad (7)$$

Unfortunately, F is not simple for $\gamma\neq\frac{1}{4}$, but one may check that Eq. (7) is very close to a normal distribution for $F>10^{-12}$. For other values of γ, one may therefore write with some confidence

$$F_{N,\gamma}(k)=\int_{-\infty}^{(N-k)/\sigma}\exp(-y^2/2)dy/(2\pi)^{\frac{1}{2}}, \quad (8)$$

where

$$\sigma=(2\gamma N)^{\frac{1}{2}}. \quad (9)$$

For small F, the expansion

$$F_{N,\gamma}(k)=\frac{\sigma}{(N-k)(2\pi)^{\frac{1}{2}}}\left[1-\left(\frac{\sigma}{N-k}\right)^2+\cdots\right]\times\exp\left[-\frac{(N-k)^2}{2\sigma^2}\right] \quad (10)$$

is convenient.

[11] E. N. Gilbert, Bell Telephone Laboratories (private communication).

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Thermal Expansion of Rare Earth Metals*

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Thermal expansion measurements at temperatures ranging up to 900°C for polycrystalline samples of La, Ce, Pr, Nd, Gd, Tb, Dy, Er, and Yb metals are reported. La, Ce, Pr, and Nd exhibit plastic flow properties at temperatures well below their melting points. High-temperature phase transformations are reported for Pr, Nd, and Yb. The coefficient of expansion for Yb is found to be three times as large as the coefficients for the other metals reported. Negative coefficients are observed near the Curie points of Gd, Tb, and Dy.

I. INTRODUCTION

In recent years rare earth metals have become available in good purity and in sufficient quantity to make possible fairly reliable measurements of their intrinsic properties. The present dilatometric study of several of these metals was undertaken in an attempt to detect possible unknown phase transitions in these elements and to clarify certain transitions previously indicated by studies of other physical properties.

Of particular interest were regions of the high-temperature thermal arrests found by Spedding and Daane[1] in their thermal analyses of lanthanum, cerium, praseodymium, neodymium, samarium, and ytterbium. Herrmann, Daane, and Spedding[2] showed that large changes in the electrical resistivities of several of these metals occurred at corresponding temperatures; they were unable to determine the crystal structures of the high-temperature forms, however, since x-ray diffraction patterns became extremely diffuse above these transitions.

In the cases of gadolinium, terbium, and dysprosium, magnetic transitions are known to occur not far below room temperature. An extension of dilatometric measurements into this region was thus also of interest and was included in the present study.

II. SAMPLES TESTED

Dilatometric measurements were made on polycrystalline samples of lanthanum, cerium, praseodymium, neodymium, gadolinium, terbium, dysprosium, erbium, and ytterbium. The salts from which these metals were produced were separated and purified by an ion-exchange process described by Spedding and others.[3,4] The metals, with the exception of ytterbium, were prepared by a reduction of the rare-earth fluorides with calcium metal.[5,6] Excess calcium was removed by distillation in a subsequent vacuum casting. In the case of ytterbium, however, a reduction of the oxide with lanthanum metal was necessary.[7] The ytterbium metal, with its high vapor pressure, was then distilled off from the remaining lanthanum and lanthanum oxide.

The actual samples used were cast to the approximate size required, finished by turning to shape, and annealed by a preliminary heating in the apparatus. In all cases

* Contribution No. 483. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

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[1] F. H. Spedding and A. H. Daane, J. Metals 6, 504 (1954).

[2] Herrmann, Daane, and Spedding, J. Metals (to be published).

[3] F. H. Spedding and others, J. Am. Chem. Soc. 73, 4840 (1951).

[4] F. H. Spedding and others, Ind. Eng. Chem. 44, 553 (1952).

[5] F. H. Spedding and A. H. Daane, J. Am. Chem. Soc. 74, 2783 (1952).

[6] A. H. Daane and F. H. Spedding, J. Electrochem. Soc. 100, 442 (1953).

[7] Daane, Dennison, and Spedding, J. Am. Chem. Soc. 75, 2272 (1953).