

Conduction mechanisms and $1/f$ Noise in thick-film resistors with $\text{Pb}_3\text{Rh}_7\text{O}_{15}$ and $\text{Pb}_2\text{Ru}_2\text{O}_7$

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Thick-film resistors with $\text{Pb}_3\text{Rh}_7\text{O}_{15}$ and $\text{Pb}_2\text{Ru}_2\text{O}_7$ as conductors are considered. These compounds are chemically stable during the firing process of the resistors. The variation of sheet resistivity R_{\square} with volume fraction conductor follows a simple power law. This result cannot be explained by percolation theory in its simple form. The conductivity is found to be independent of frequency up to 10 GHz. In both cases a small positive Hall coefficient is observed which is interpreted as being due to mixed electron and hole conduction. Finally the $1/f$ noise is considered, and is found to vary approximately linearly with R_{\square} . A theoretical model for the $1/f$ noise in thick-film resistors is presented that accounts for this linear relationship. The observed deviations from linearity indicate that probably tunneling through barriers at the interfaces between the conducting grains is an important factor in determining the conduction.

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I. INTRODUCTION

The term thick-film resistor (TFR) applies to a variety of resistive materials at present used extensively in hybrid microcircuits and other electronic applications.¹ In this paper we are concerned with metal-glass (cermet) type TFR's, that are normally prepared from an "ink" consisting of sub-micron-size glass and metal or metal oxide particles suspended in a viscous organic fluid. The TFR is obtained by screen printing an ink pattern onto a substrate of ceramic alumina, drying, and firing the printed substrate above the glass transition temperature. The sheet resistivity can be varied over many decades by changing the volume fraction of metal oxide, and may also depend on the conditions of preparation.

In spite of the popularity of TFR's, research on the conduction mechanism is relatively scarce, the most noticeable exceptions being the work of Vest and co-workers,² and of Pike and Seager.³ Reference 3 contains a useful survey of the various models that have been proposed for the conduction in TFR's. The study of the physics of TFR's is hampered by the highly proprietary nature of the resistor inks. Besides the main conductor, commercial inks may contain many additives in small quantities. Moreover, chemical reactions usually occur during the firing process, leading to important uncertainties concerning the composition, which makes the interpretation of physical measurements somewhat ambiguous. In this study we report results for two series of TFR's made in the Philips Laboratory that do not suffer from these problems. To this purpose either $\text{Pb}_3\text{Rh}_7\text{O}_{15}$ or $\text{Pb}_2\text{Ru}_2\text{O}_7$ are used as the conductor. $\text{Pb}_3\text{Rh}_7\text{O}_{15}$ has been reported to be a semiconductor with a band gap of about 0.1 eV, and hence

has a negative temperature coefficient of resistivity [$\text{TCR} = (1/R)(dR/dT)$].⁴ $\text{Pb}_2\text{Ru}_2\text{O}_7$ exhibits metallic conduction with a positive TCR,⁵ and is often formed when other compounds containing Ru are fired in combination with a lead-containing glass.⁶ As discussed by Boonstra and Mutsaers⁴ these compounds are very suitable ingredients for TFR's, because they are stable during the firing process. By an appropriate combination of the two compounds, these authors obtained TFR's with a very small TCR, qualitatively explained by a compensation of the negative TCR of $\text{Pb}_3\text{Rh}_7\text{O}_{15}$ by the positive TCR of $\text{Pb}_2\text{Ru}_2\text{O}_7$.

Measurements are reported for dc and ac conductivity (up to 10 GHz), TCR, Hall coefficient, and $1/f$ noise (current noise). The variation of the sheet resistivity R_{\square} with x_{cond} , the volume fraction of conductor, follows a simple power law, while no frequency dependence of the conductivity is observed. The Hall coefficient is small and positive for both series, indicating mixed conduction with p -type character. The $1/f$ noise varies (to first order) linearly with R_{\square} . A theoretical model for the $1/f$ noise in TFR's is presented that accounts for this linear relationship. Considering possible interparticle contact resistance mechanisms in detail, the experimentally observed deviations from linearity indicate that barriers between the conducting grains are present. In agreement with the results of Biesterbos⁷ and of Pike and Seager,³ we concluded that tunneling is probably an important factor in determining the conduction.

II. EXPERIMENTAL

A. Sample preparation

$\text{Pb}_3\text{Rh}_7\text{O}_{15}$ has been prepared from RhCl_3 , which is first converted into Rh_2O_3 by firing at a temperature of 750 °C for 2 h. Then the Rh_2O_3 is mixed with an excess of PbO and fired at a temperature of 700 °C for 2 h, which results in the desired $\text{Pb}_3\text{Rh}_7\text{O}_{15}$. The remaining PbO is dissolved in dilute HNO_3 . The specific surface area has been determined with Brunauer-Emmett-Teller (B.E.T.) method using krypton at

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78 K. The result is $15.8 \text{ m}^2/\text{g}$, yielding an average particle size of $0.04 \mu\text{m}$.

$\text{Pb}_2\text{Ru}_2\text{O}_7$ is prepared by firing a mixture of KOH , KNO_3 and Ru_2O_3 powders in a mole ratio of 5:1:1 for 1 h at 500°C . The fired mixture is dissolved in an alkaline solution in water; then an excess of $\text{Pb}(\text{NO}_3)_2$ is added. After precipitation the solution is filtered, the dried filtrate consisting of $\text{Pb}_2\text{Ru}_2\text{O}_7$ is fired for 1 h at 800°C and washed with dilute HNO_3 . The specific surface area of the $\text{Pb}_2\text{Ru}_2\text{O}_7$, thus obtained is $13.2 \text{ m}^2/\text{g}$, which yields an average particle size of $0.06 \mu\text{m}$.

The conducting powders were mixed with EA1959 glass containing 45.3 mol% SiO_2 , 42.0 mol% PbO , 9.3 mol% B_2O_3 , and 3.4 mol% Al_2O_3 . Two series of TFR's were made with 4, 10, 20, 35, and 60 vol% of $\text{Pb}_3\text{Rh}_7\text{O}_{15}$ and $\text{Pb}_2\text{Ru}_2\text{O}_7$, respectively. By adding an organic binder and a solvent, inks of approximately the same viscosity were prepared. Samples were screen-printed on alumina substrates with a Presco model 330 printing machine equipped with a 51T screen. The samples were fired in a zone oven and kept for 7 min at the maximum temperature at 725°C . The thickness of the TFR thus obtained was, typically, $14 \mu\text{m}$. Most measurements were performed on samples having a geometry like that sketched in Fig. 1(a). The substrates of $2.5 \times 1.25 \text{ cm}^2$ were fitted with solderable electrodes of Ag/Pd prior to the TFR preparation. For the high-frequency measurements alumina substrates of $2.5 \times 2.5 \text{ cm}^2$ were covered almost completely with the TFR. Then gold electrodes were evaporated onto the TFR in the coaxial pattern of Fig. 1(b).

B. Conductivity

The dc conductivity of the TFR's has been measured from 80 to 400 K. The sample is mounted in a sample holder and placed in a Dewar cylinder, which is fluxed with a stream of dry nitrogen gas to control the temperature. A constant current of the order of 1 mA is applied to the outer electrodes of the TFR. The voltage drop across the inner electrodes is measured with a Philips PM 4000 data logger, while the temperature is slowly varied. The temperature is measured by means of a chromel-alumel thermocouple with the same data logger. During a temperature sweep of about 12 K/min every 30 s a measurement is made and its result is punched into paper tape via a teletype. In this way it is possible to obtain both the conductivity and the TCR as a function of temperature by simple numerical calculations.

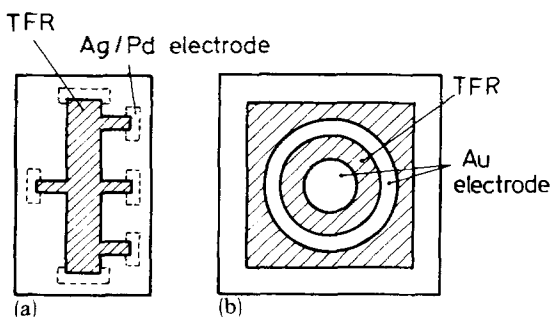


FIG. 1. (a) Geometry of the TFR for the measurement of dc conductivity, Hall effect, and current noise. (b) Geometry of the TFR used for the measurements at high frequencies.

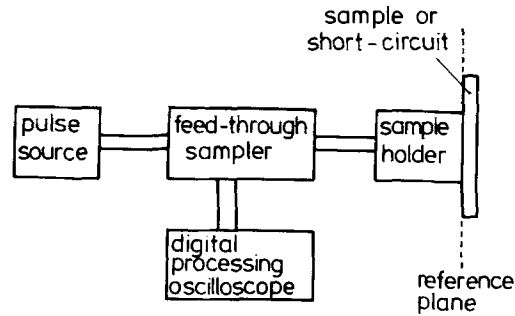


FIG. 2. Setup for the high-frequency measurement.

The impedance of the TFR's has been measured as a function of frequency at room temperature with the setup sketched in Fig. 2. The TFR is placed at the end of a coaxial sample holder [geometry of Figure 1(b)]. A step voltage is applied to the transmission line, and both the incident voltage $V_i(t)$ and the reflected voltage $V_r(t)$ are monitored.⁸ In practice it is advantageous to measure $V_i(t)$ in a separate experiment as the voltage reflected from a short circuit placed in the same position as the TFR. In this way all types of deviations from ideal behavior are accounted for to the best possible extent. Quantitative measurements were performed with a Tektronix digital processing oscilloscope equipped with an S-52 pulse generator and an S-6 sampling unit. The reflection coefficient in the frequency domain can be calculated by Fourier transformation of the incident and the reflected voltage⁹:

$$\rho(\omega) = \mathcal{F}[V_r(t)] / \mathcal{F}[V_i(t)]. \quad (1)$$

The Fourier transforms were performed digitally with the fast Fourier transform algorithm (FFT). In order to prevent any influence of the restricted time-window over which the signals are observed, the FFT is performed on $dV_r(t)/dt$ and $dV_i(t)/dt$. The standard formula $\rho(\omega) = (Z - Z_0)/(Z + Z_0)$, where $Z_0 = 50 \Omega$ is the characteristic impedance of the transmission line, can be used to calculate $Z(\omega)$ of the cermet. The frequency range is limited on the high side by the rise time of the pulse generator, 30 ps, which corresponds to about 30 GHz. Hence reliable results can be obtained up to about 10 GHz.

C. Hall voltage and thermopower

The Hall effect is measured using the same samples as described in Sec. II B. The sample holder is constructed such that voltages due to the various thermoelectric effects can be expected to be minimal.¹⁰ The sample plus holder plus Dewar cylinder is positioned between the poles of a magnet, such that the magnetic field (of 1.5 T) is perpendicular to the current and to the substrate. The Hall voltage is measured between the two opposing electrodes with a Keithley model 155 microvoltmeter. The voltage observed in zero magnetic field is compensated with an external battery and potentiometer. The sensitivity of the total set up is limited by the $1/f$ noise generated in the sample itself, which, for a current of 10 mA, amounts to about $5 \mu\text{V}$ (rms).

The sign of the Seebeck coefficient was determined in a rough experiment, in which a pressed pellet of the conductor power is put between two copper electrodes and heated to

some degree, close to one of the electrodes. This creates a temperature gradient of known polarity that leads to a voltage. As the thermopower of the copper electrodes is relatively small, this is sufficient to determine the sign of the Seebeck coefficient S .

D. $1/f$ noise

To measure the $1/f$ noise, a constant current through the TFR under investigation is obtained from a maximum of 10 batteries of 9 V each connected in series, via a large wire-wound resistor (having a resistance appreciably larger than that of the cermet). Because wire-wound resistors are free of $1/f$ noise, a noise-free current is obtained, as can be checked by replacing the cermet by a wire-wound resistor of the same value. The fluctuating noise voltage across the inner electrodes of the cermet [see Fig. 1(a)] is fed into an ultra-low-noise amplifier (Brookdeal 5004). The low R_{eq} ($\approx 100 \Omega$) of this amplifier allows one to disregard the noise from the amplifier for most samples. For the samples with 60 vol% conductor, which have very low resistance, a matching transformer (Philips, PM 9535) was used in addition. The 1000 times amplified voltage is then analyzed in the frequency domain with a Hewlett-Packard 302A wave analyzer, with a bandwidth $\Delta f = 6$ Hz (3 dB points). Using the recorder output of the wave analyzer and a filter with a time constant of 10 s, the average noise voltage can be monitored on an $x-t$ recorder. If no current is applied to the TFR the frequency-independent Johnson noise ($4kTR \Delta f$) is observed. If a dc current I is applied to the cermet, there is an additional $1/f$ noise given by ¹¹:

$$\langle (\Delta V)^2 \rangle \sim I^2 \Delta f / f. \quad (2)$$

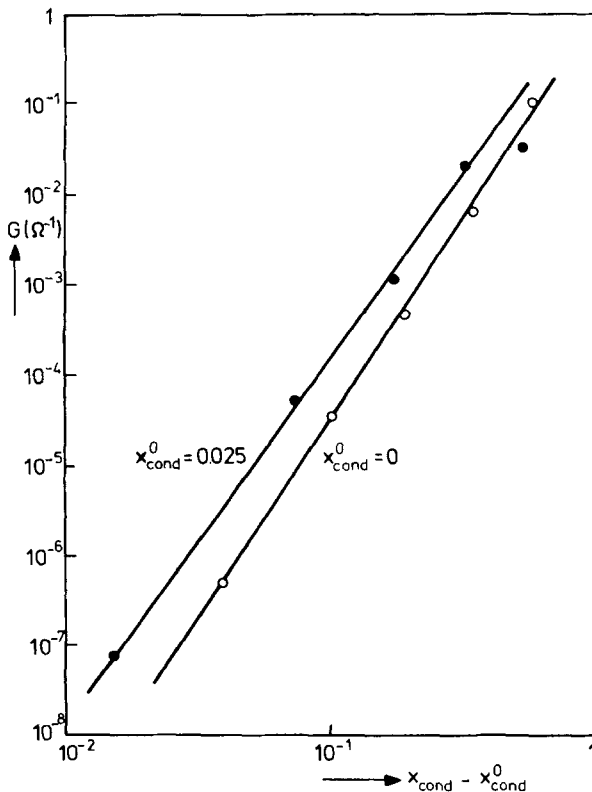


FIG. 3. Logarithmic plot according to Eq. (4); ●Pb₃Rh₇O₁₅, ○Pb₂Ru₂O₇.

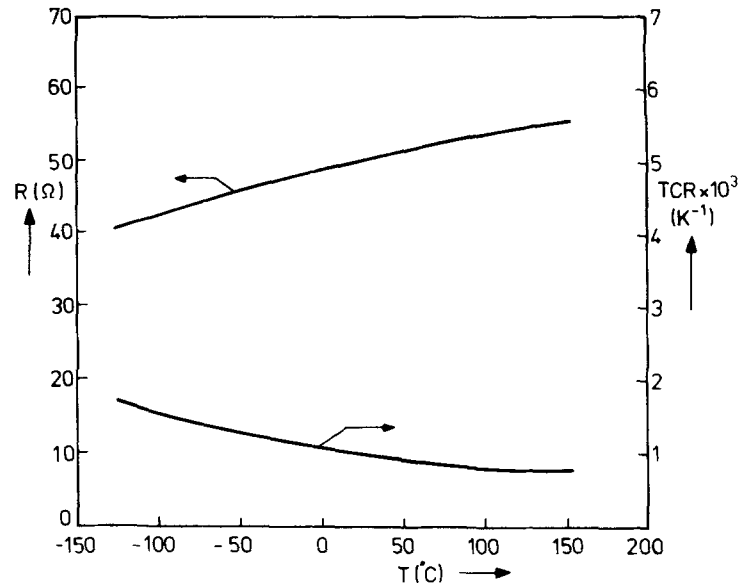


FIG. 4. Resistivity and TCR vs temperature for a typical TFR with Pb₂Ru₂O₇ as conductor ($R_{\square} = 11.65 \Omega$).

Since these two types of noise are uncorrelated, the $1/f$ noise is simply obtained by subtraction of the two signals.

III. RESULTS

For each volume fraction x_{cond} from five to ten samples were made. The average resistivity of these samples is given in Table I for both Pb₂Ru₂O₇ and Pb₃Rh₇O₁₅ as conductor. In order to check the empirical formula for the conductance G given by Pike¹²:

$$G \sim (x_{cond} - x_{cond}^0)^s, \quad (3)$$

$\log(1/R_{\square})$ is plotted in Fig. 3 against $\log(x_{cond}^0 - x_{cond}^0)$, where the critical volume fraction x_{cond}^0 is adjusted to obtain the best straight line. This results in values $x_{cond}^0 = 0$ and $s = 4.5$ for Pb₂Ru₂O₇, and $x_{cond}^0 = 0.025$ and $s = 4.1$ for Pb₃Rh₇O₁₅. Table I also gives the TCR at room temperature. Figures 4 and 5 show typical plots of resistivity and TCR as a function of temperature. The room-temperature conductivity [real part of the parallel equivalent $Z(\omega)$] was found to be independent of frequency up to the highest frequency possi-

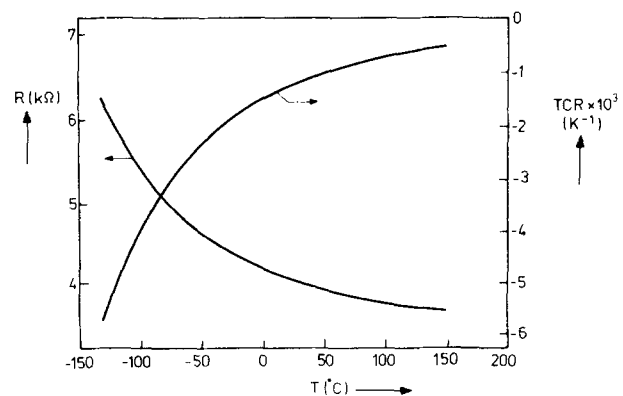


FIG. 5. Resistivity and TCR vs temperature for a typical TFR with Pb₃Rh₇O₁₅ as conductor ($R_{\square} = 1023 \Omega$).

TABLE I. Resistivity and TCR of the samples investigated (1-5: $\text{Pb}_2\text{Ru}_2\text{O}_7$ as conductor, otherwise $\text{Pb}_3\text{Rh}_7\text{O}_{15}$).

No.	Vol % conductor	R_{\square} (Ω)	TCR $\times 10^3$ (K^{-1})
1	60	10.8	1.10
2	35	107	0.65
3	20	1.58×10^3	0.42
4	10	22.9×10^3	0.25
5	4	2.04×10^6	0.20
6	60	37.2	- 0.95
7	35	69.2	- 1.00
8	20	0.91×10^3	- 1.24
9	10	20.0×10^3	- 1.70
10	4	12.8×10^6	...

ble in the present set up (≈ 10 GHz). No reactive part of $Z(\omega)$ was observed other than that associated with the small capacitance of the substrate.

In Table II the Hall voltage is reported for some of the cermets. The Hall voltage being small, measurements were possible only for relatively low R_{\square} . For the other samples the noise from the samples themselves obscured the Hall voltage. Hence no conclusion can be drawn about a possible dependence of the Hall voltage on the volume fraction of conductor. The sign of the Hall coefficient indicates p -type conduction for both $\text{Pb}_3\text{Rh}_7\text{O}_{15}$ and $\text{Pb}_2\text{Ru}_2\text{O}_7$. This is confirmed by the sign of the Seebeck coefficient (Table III).

The $1/f$ noise is conveniently expressed as the noise index (NI), which is defined for a bandwidth of a decade as¹³:

$$\text{NI} = 10[12 + \log \langle (\Delta R/R)^2 \rangle] = 20 \log (v/V), \quad (4)$$

where the rms noise voltage $v = 10^6 \langle (\Delta V)^2 \rangle^{1/2}$ is measured in μV , and the voltage V across the resistor in volts. Measurements for various values of both the current and the frequency indicated that for the cermets under investigation Eq. (2) was well satisfied. Therefore further measurements were restricted to a frequency of 110 Hz only. With the known bandwidth of 6 Hz this is sufficient for the noise index to be calculated through

$$\text{NI} = 20 \log (v/V) - 10 \log \log (f_2/f_1), \quad (5)$$

where f_1 and f_2 are the lower and the upper limit of the frequency band used. Figure 6 indicates the variation of NI with $\log R_{\square}$. For $\text{Pb}_3\text{Rh}_7\text{O}_{15}$ this variation of $\langle (\Delta R/R)^2 \rangle$ with R_{\square} is practically linear; for $\text{Pb}_2\text{Ru}_2\text{O}_7$ this is approximately the case at high values of R_{\square} , but for lower R_{\square} the dependence approaches $R_{\square}^{1/2}$. These results are similar to those of Ringo *et al.*,¹⁴ who find for most of their data a power-law dependence with an exponent of the order of one or less.

TABLE II. Hall voltages for some of the samples ($B = 1.5$ T).

No.	Conductor	I (mA)	V_H (μV)
1	$\text{Pb}_2\text{Rh}_2\text{O}_7$	50	1.4
6	$\text{Pb}_3\text{Rh}_7\text{O}_{15}$	20	4.0
7	$\text{Pb}_3\text{Rh}_7\text{O}_{15}$	20	2.6

Finally we mention that the microstructure of the TFR's as seen with scanning electron microscopy is very similar to that described in the literature for other systems.^{2,3,7}

IV. DISCUSSION

A. Conductivity

The sign of the Seebeck coefficient indicates that both $\text{Pb}_3\text{Rh}_7\text{O}_{15}$ and $\text{Pb}_2\text{Ru}_2\text{O}_7$ are conductors of p -type character. Qualitatively, from the composition of these compounds, p -type conduction can be expected, as the excess of oxygen may lead to acceptor levels. If the Pb is replaced in $\text{Pb}_2\text{Ru}_2\text{O}_7$ by Bi, n -type conduction results (see Table III), in agreement with the observation by Pike and Seager.³ Intuitively this is expected because of the higher valency of Bi as compared with Pb.

When there are equal numbers of electrons and holes of the same mobility, the Hall coefficient of a material is zero. The present case could be close to this limit, in view of the rather small Hall coefficients (see Table II). Alternatively this small coefficient could be attributed to disorder. However, there are reasons to believe that the first interpretation is more correct. Pike and Seager³ tried to measure the Hall effect in cermets with $\text{Bi}_2\text{Ru}_2\text{O}_7$ as the conductor, which is partly converted to $\text{Pb}_2\text{Ru}_2\text{O}_7$, during the firing process in lead-containing glass. In spite of the great sensitivity of their set up they did not succeed in measuring a Hall effect. In combination with the change of sign of the Seebeck coefficient discussed above, and with the fact that in a cermet with pure $\text{Pb}_2\text{Ru}_2\text{O}_7$ we did observe a Hall voltage, this strongly supports the assumption of mixed conduction. This conclusion makes it rather meaningless to convert the Hall coefficient of these systems into an effective number of charge carriers.

As we have seen from Fig. 3 the conductivity of our cermets with a single conductor is described quite well by the power law of Eq. (3). Similar results have been obtained by Pike¹² for cermets with RuO_2 and $\text{Bi}_2\text{Ru}_2\text{O}_7$ as main conducting ingredients. We conclude from these data that the presence of additives or the occurrence of chemical reactions has (apart from the TCR) little influence on the overall conductivity behavior of cermets.

Looking in more detail, the first thing to note is the small value of x_{cond}^0 , which is often as low as zero, and, secondly, the relatively high value of s : $4 < s < 7$ if $x_{\text{cond}}^0 = 0$ (this work and Ref. 12). Equation (3) is reminiscent of the equation for the conduction in a resistor lattice just above the percolation threshold^{15,16}

$$G \sim (p - p_c)^s, \quad (6)$$

TABLE III. Sign of Hall coefficient (measured on cermets) and of the Seebeck coefficient (measured on pressed pellets of the pure conductor).

Compound	Sign R_H	Sign S
$\text{Rb}_3\text{Rh}_7\text{O}_{15}$	+	+
$\text{Pb}_2\text{Ru}_2\text{O}_7$	+	+
$\text{Bi}_2\text{Ru}_2\text{O}_7$?	-

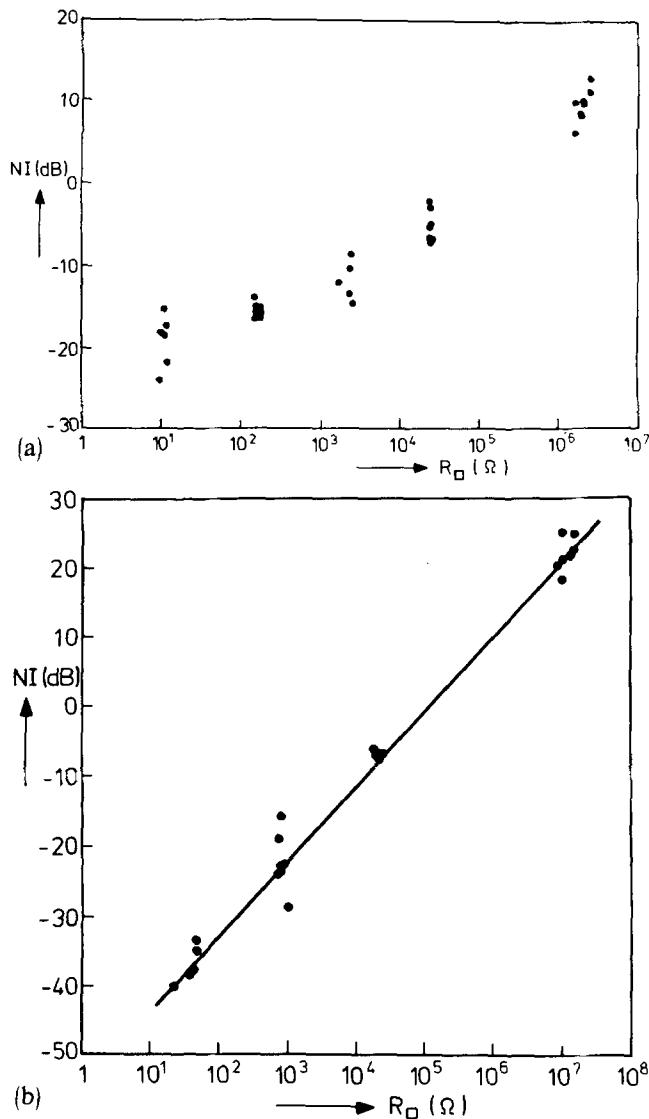


FIG. 6. Noise index for the TFR series with (a) $\text{Pb}_2\text{Ru}_2\text{O}_7$ and (b) $\text{Pb}_3\text{Rh}_3\text{O}_{15}$.

where p is the fraction of the lattice randomly occupied by resistors. For a three-dimensional cubic lattice p_c ranges from 0.10 to 0.25 while $s = 1.6$.¹² These values are considerably different from those found for Eq. (3) if we identify p with x_{cond} . Moreover, Eq. (6) is only valid close to the percolation threshold, while Eq. (3) is valid over the whole concentration range. Thus from the threshold properties we see that the conductivity of cermets does not look like percolative conduction. This does not necessarily rule out percolative conduction, provided the critical region is small in these cermets. The low values of x_{cond}^0 can in principle be attributed to a difference in size of the glass and the conductor particles. During the formation process of the TFR the small conductor particles can be expected to be confined to channels between the much larger glass particles. As discussed by Pike¹² and Kusy¹⁷ this leads to essentially a modified bond percolation model that gives small values of x_{cond}^0 . Nevertheless it must be said that no explanation exists yet that accounts for the power law that is observed for cermets over the whole concentration range.

The nature of the contacts between the conducting particles has been the subject of considerable discussion. For particles of characteristic dimension w , with ohmic contacts of dimension a , the resistance is concentrated at the contact region for $a \ll w$, and given by

$$r = \rho / \pi a, \quad (7)$$

where ρ is the resistivity. Pike and Seager³ strongly suggest that, apart from contact areas and path tortuosity, tunnel barriers between the conducting particles are also important in cermets. The small particles are then responsible, through electrostatic charging, for a small activation energy which manifests itself in the temperature dependence of the conductance. In spite of their success in explaining the various physical properties of cermets, the question remains whether the assumption of tunneling is necessary to account for the experimental results presently available. First, one might wonder whether the capacitances associated with possible barriers between the conducting grains, might not lead to a measurable reactance of the cermets at high frequencies. Using reasonable estimates of the interparticle distance (1 nm), taking account of the number of particles and chains, one calculates a total capacitance for one sample of the order of from 10^{-1} to 10^{-2} pF. As the capacitance of the substrate is already 0.4 pF, the absence of any detectable reactance of the cermet itself is still compatible with a barrier model of the conduction. Secondly, we note that the results for the TCR, quoted in support of the barrier model, can also be accounted for by the compensation model of Boonstra and Mutsaers,⁴ in which two types of conductors play a role, one with a positive and one with a negative TCR. This leaves only some electric field effects as evidence for barriers.³

B.1/f noise

To discuss the 1/f noise results we shall derive some expression for the intensity of this noise by generally following the treatment of Vandamme.¹⁸ However, a slightly different assumption about the arrangement of conductor particles in the resistor leads us to conclusions quite different from his. We assume that the conductor particles are arranged in chain segments which are widely spaced compared with particle sizes.^{2,3,12} For convenience these chain segments are considered to form a simple cubic array of effective conduction paths as shown in Fig. 7. For a resistor of length l , breadth b , and thickness d , let m be the number of particle contacts per unit length and p be the effective numbers of chains per unit length. (In Ref. 18 the particles were assumed to form a fully packed simple cubic lattice with a single parameter γ to describe the number of contacts per unit length, i.e., $\gamma = m = p$.)

Let r be the resistance of a single contact, assumed to take the same value for all linking branches. Provided that the conduction takes place mainly through chains in the longitudinal direction, one then easily finds

$$R = r(ml)/(pb)(pd) \quad (8a)$$

and

$$R_{\square} = Rb/l = rm/(p^2d). \quad (8b)$$

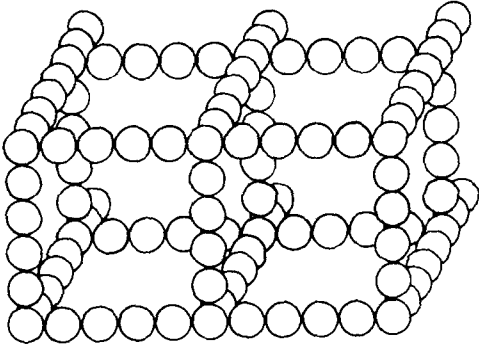


FIG. 7. Effective structure of a TFR as used in the calculation of the $1/f$ noise.

To calculate the relative noise $\langle (\Delta R/R)^2 \rangle$ we consider first a single chain in the length direction with $R_{\text{chain}} = r(ml)$. The fluctuations ΔR_{chain} are obtained as the sum over the fluctuations Δr_i of all grain contacts of the chain in series. The average of the squared fluctuating chain resistance $\langle (\Delta R_{\text{chain}})^2 \rangle$ equals the average of the squared sum of fluctuations Δr_i . We now assume the fluctuations to be uncorrelated, which makes the average values of the cross products $\langle \Delta r_i \Delta r_j \rangle$ equal to zero. Taking, furthermore, the same value for all $\langle \Delta r_i^2 \rangle$ we arrive at the simple result $\langle (\Delta R_{\text{chain}})^2 \rangle = ml \langle (\Delta r)^2 \rangle$. The total resistance fluctuation $\langle (\Delta R)^2 \rangle$ is obtained by summing the contribution of all the chains *in parallel*. Introducing $G = 1/R$, one thus has $\langle (\Delta G)^2 \rangle = (pb)(pd) \langle (\Delta G_{\text{chain}})^2 \rangle$. For small relative fluctuations it is easily seen that $\langle (\Delta G/G)^2 \rangle = \langle (\Delta R/R)^2 \rangle$ and $\langle (\Delta g/g)^2 \rangle = \langle (\Delta r/r)^2 \rangle$. This allows the total relative noise to be calculated as

$$\langle (\Delta R/R)^2 \rangle = \langle (\Delta r/r)^2 \rangle / (ml)(pb)(pd). \quad (9)$$

Macroscopic and microscopic noise coefficients C and C_r , respectively, are defined by $(\Delta f/f)C = \langle (\Delta R_{\square}/R_{\square})^2 \rangle$ and $(\Delta f/f)C_r = \langle (\Delta r/r)^2 \rangle$. Taking $b = l$ for a square resistor, Eq. (9) may be rewritten as

$$C = C_r / (mp^2 l^2 d). \quad (10)$$

Substituting Eq. (8b) into this expression yields

$$C = C_r R_{\square} / (rm^2 l^2). \quad (11)$$

In a thick-film resistor system the value of R_{\square} is a function of the amount of conducting particles present. The primary variation of macroresistivity R_{\square} in Eq. (8b) is through the sharp dependence of p on the volume fraction of conductor. Since all ink compositions are fired under the same conditions, the same degree of particle sintering should result (at least to first order). Thus the interparticle microresistance r is not expected to change much. If r is roughly the same for all volume fractions, then C_r will be roughly the same. Thus Eq. (11) shows that the resistor noise is expected to depend linearly on R_{\square} (to first order) independent of the nature of the interparticle resistance r . This result differs from that given in Ref. 18, where by similar arguments as given above, it is predicted that the resistor noise intensity should vary as R_{\square}^3 independent of the nature of r (to first order). The assumption that the conductor particle geometry could be described by a single parameter γ (which is equivalent to as-

suming the particle and chain spacings are equal) clearly leads to an erroneous result. (In Ref. 18 a relation $C \sim R_{\square}$ is derived for the special case of an "interface dominated contact." However, this is misleading because in that case Vandamme chooses to convert only one of the $1/\gamma$ factors to R_{\square} but to include the remaining $1/\gamma^2$ as part of the interparticle noise C_r (his C_{us}). This is clearly wrong. If the correct substitution is made for $1/\gamma^3$, his treatment yields $C \sim R_{\square}^3$, independent of the nature of the interparticle microresistance.)

Considering Eqs. (8b) and (11) in more detail we note that for various types of contact resistance mechanisms, C_r/r can be explicitly written in terms of contact parameters. Basic to the discussion is Hooge's empirical relation for the current noise (see, for example, Ref. 11)

$$C_r = \alpha / (nV), \quad (12)$$

where α is a constant (that in principle might depend on the nature of the conduction process), n the number density of mobile charge carriers (n_b in the bulk, n_f in a film), V the sample volume. This formula cannot be applied to an inhomogeneous system as a whole, but can be used to estimate the noise generated at the contact between two grains. First, we consider the situation of Fig. 8(a), where the contact resistance r is dominated by the constriction and thus given by Eq. (7). In this situation Eq. (12) still holds,¹⁹ provided V is replaced by an effective volume $V^* = (20/\pi^2)(\pi a)^3$. If $N_p = nV$ is the effective number of mobile carriers per contact, and if spreading resistance is dominant, we find $N_p = 20\pi a^3 n_b$ and $r_b = \rho_b / \pi a$. Thus from Eqs. (11) and (12),

$$C = (\alpha/m^2 l^2 20n_b \rho_b a^2) R_{\square}. \quad (13)$$

The suffix b has been added to make clear that the bulk properties of the conducting particles are involved. If an interparticle film resistance is dominant [Fig. 8(b)], the situation is different. Now we can write $r = 1/(g_f \pi a^2)$, where g_f is a film conductance per unit area, and could be either due to a bulk conduction process or to a tunneling process. For a bulk process $g_f = 1/(\rho_f t)$, where ρ_f is the film resistivity. This

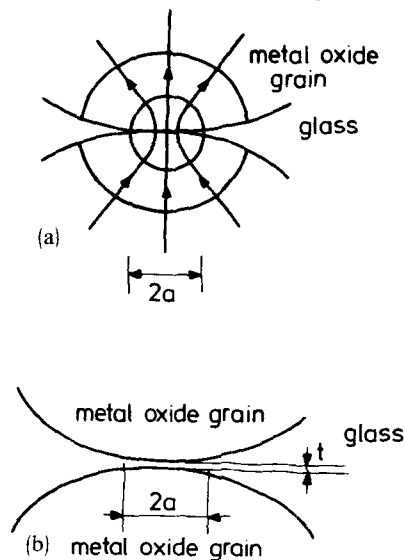


FIG. 8. (a) Constriction dominated and (b) interface dominated contact between two grains.

situation has been treated for semiconductors to semiconductor contacts with a native oxide film.²⁰ In that case $r = p_f/\pi a^2$, $N_p = a^2 t n_f$, and $r N_p = t^2 n_f \rho_p$. Thus

$$C = (\alpha/m^2 l^2 t^2 n_f \rho_p) R_{\square}. \quad (14)$$

Alternatively one could consider a tunneling process for which $g_f = n_b \kappa$, where κ is a proportionality factor which includes the tunneling transmission probability per incident electron. The application of Eq. (12) to such a situation has not been considered before. It seems reasonable to take here the effective volume as $\pi a^2 \lambda$, where λ is an electronic mean free path in the conductor. Then

$N_p = \pi a^2 \lambda n_b$, $r = 1/(\pi a^2 \kappa n_b)$, and $r N_p = \lambda/\kappa$. Thus we find tentatively

$$C = (\alpha' \kappa/m^2 l^2 \lambda) R_{\square}, \quad (15)$$

where α' might differ from α in Eqs. (13) and (14).

As discussed above, within a given resistor system the R_{\square} variation is due mainly to the variation of p with volume fraction of conductor in Eq. (8b). To first order r and C_r are constant and from Eq. (11) C is expected to vary linearly with R_{\square} as observed in Fig. 6(b). For corrections to this dependence as shown by the low R_{\square} data in Fig. 6(a), one can examine Eqs. (13), (14), and (15) to look for the most likely sources. In low R_{\square} resistors the conductor particles are more numerous and closer together at the start of the firing process. One could then reasonably expect that more complete sintering might occur during the firing cycle, so that the radius a would be larger and the film thickness t would be smaller. From Eq. (13) this would cause C to decrease faster than R_{\square} as R_{\square} became smaller if spreading resistance were important. This is contrary to the data. From Eq. (14) the variation of t could make C relatively too large at low R_{\square} . However, the data seem to be a factor of from 10 to 100 too large, which is quite a variation for t . However, if tunneling is important, the value of κ depends exponentially on t and thus a small variation of t could easily produce a large "excess" value of C at low R_{\square} from Eq. (15). Thus the existence of interparticle tunneling layers seems to explain the $1/f$ noise data in Fig. 6(a) best.

We conclude that our measurements of the $1/f$ noise of TFR's support the results of Pike and Seager³ in favor of a tunneling mechanism. It should be realized that near room temperature in their tunneling model still approximately 30% of the resistance is due to the conducting particles.

Hence the tunneling model and the compensation effect observed by Boonstra and Mutsaers⁴ are not necessarily mutually exclusive.

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¹See, for example, E. Lüder, *Bau hybrider Mikroschaltungen* (Springer, Berlin, 1977); or P. J. Holmes and R. G. Loasby, *Handbook of Thick Film Technology* (Electrochemical Publishers, Ayr, Scotland, 1976).

²R. W. Vest, Purdue Research Foundation, Final Technical Report, ARPA Order No. 1642 (1975).

³G. E. Pike and C. H. Seager, *J. Appl. Phys.* **48**, 5122 (1977).

⁴A. H. Boonstra and C. A. H. A. Mutsaers, *Thin Solid Films* **51**, 287 (1978).

⁵J. N. Longo, P. M. Raccah, and J. B. Goodenough, *Mater. Res. Bull.* **4**, 191 (1969).

⁶K. R. Bube, Proceedings of the 1972 International Microelectronics Symposium, Washington, Oct. 1972 (ISHM, Park Ridge, Illinois, 1972), p. 2A61; A. H. Boonstra (private communication).

⁷J. W. M. Biesterbos, *J. Appl. Phys.* **45**, 153 (1974).

⁸See, for example, S. Ramo, J. R. Whinnery, and T. van Duzer, *Fields and Waves in Communication Electronics* (Wiley, New York, 1965).

⁹See, for example, A. Papoulis, *The Fourier Integral and its Applications* (McGraw-Hill, New York, 1962).

¹⁰See, for example, E. H. Patley, *The Hall Effect and Related Phenomena* (Butterworths, London, 1960), Chap. 2.

¹¹See, for example, D. Wolf, in *Noise in Physical Systems*, edited by D. Wolf (Springer, Berlin, 1978), p. 122.

¹²G. E. Pike, in *Electrical Transport and Optical Properties of Inhomogeneous Media*, edited by J. C. Garland and D. B. Tanner (AIP Conference Proceedings no. 40 New York, 1978), p. 366.

¹³G. T. Conrad, N. Newman, and A. P. Standbury, *IRE Trans. Component Parts* **7**, 71 (1960).

¹⁴J. A. Ringo, E. H. Stevens, and D. A. Gilbert, *IEEE Trans. Parts-Hybrids-Packag.* **12**, 378 (1976).

¹⁵For percolation theory see, for example, V. K. S. Shante and S. Kirkpatrick, *Adv. Phys.* **20**, 325 (1971).

¹⁶Details about percolative conduction can be found in S. Kirkpatrick, *Rev. Mod. Phys.* **45**, 574 (1973); I. Webman, J. Jortner, and M. Cohen, *Phys. Rev. B* **11**, 2885 (1975); I. Webman, J. Jortner, and M. Cohen, *Phys. Rev. B* **14**, 4737 (1976).

¹⁸L. K. J. Vandamme, *Electrocomp. Sc. Techn.* **4**, 171 (1977).

¹⁹F. N. Hooge and A. M. H. Hoppenbrouwers, *Phys. Lett. A* **29**, 624 (1969).

²⁰L. K. J. Vandamme, *J. Appl. Phys.* **45**, 4563 (1974).