CURRENT NOISE IN SOME TRANSITION-METAL COMPOUNDS

TH. G. M. KLEINPENNING*

Fysisch Laboratorium, Rijksuniversiteit Utrecht, Nederland

Synopsis

Measurements are reported on current noise in some single crystals of transition-metal compounds, namely: reduced Al-doped rutile (TiO_2), Li-doped NiO, Li-doped CoO and Ga-doped $CdCr_2Se_4$. Also results obtained with polycrystalline Ga-doped $CdCr_2Se_4$ are reported. The current-noise spectra of the materials mentioned above showed flicker noise with a frequency dependence of $1/f^\beta$, where the value of β is in the range 0.7 to 1.2. The magnitude of the flicker noise is compared with a phenomenological formula for flicker noise in semiconductors and metals. It turned out that the magnitude of the current noise in reduced rutile is smaller by a factor 10^3 than predicted by the phenomenological formula.

1. *Introduction*. We consider current fluctuations in reduced rutile (TiO_2), Li-doped NiO, Li-doped CoO and Ga-doped $CdCr_2Se_4$. These are all transition-metal compounds which have in common the fact that there is some ambiguity as far as electrical conduction is concerned. The free charge-carrier drift mobilities of these materials are found to be very low.

Reduced rutile is an n-type semiconductor. The donors introduced by reduction may be due to oxygen vacancies or titanium interstitials. The electrical properties of reduced rutile have been reported elsewhere[1-12].

For p-type CoO and NiO doped with Li it was found that the resistivity ρ varies with temperature as $\rho = \rho_0 \exp(\varepsilon/kT)$ around room temperature, where T is the absolute temperature and k is Boltzmann's constant. The value of the activation energy ε varies from about 0.2 eV to 0.7 eV[13-17], depending on the Li concentration. It was assumed that the introduction of Li in both CoO and NiO results in an acceptor level above the valency band[13-18]. Both CoO and NiO are antiferromagnetic below their Néel temperature T_N of 290 K and 520 K, respectively.

The compound $CdCr_2Se_4$ is a ferromagnetic semiconductor with a Curie temperature $T_C \approx 130$ K. By substitution of Ga for Cd the material becomes n-type. The electrical properties of n-type $CdCr_2Se_4$ have been studied elsewhere[19, 20]. It was found that the resistivity of n-type $CdCr_2Se_4$ shows a maximum near T_C.

* Present address: Technische Hogeschool, Eindhoven, Nederland.

In this paper the current-noise properties of the above-mentioned materials were studied. The current-noise spectra obtained were all of the $1/f$ type.

Recent investigations[23,24] indicate that the flicker-noise density in the current, $S_{\Delta I}$, of semiconductors and metals can generally be described by the phenomenological expression:

$$S_{\Delta I}/I^2 = \alpha/(Nf) = \alpha q\mu R/(L^2 f),\tag{1}$$

where α is an experimental constant with the estimated value of 2×10^{-3} which does not depend on temperature; I is d.c.-current flow through the sample; N is the total number of free charge carriers equal to $L^2/(q\mu R)$; f is the frequency; $-q$ is the electron charge; μ is the free charge-carrier drift mobility; R is the resistance and L is the contact spacing.

It is suggested that flicker noise is a bulk effect. The flicker-noise data found in the above-mentioned materials will be compared with relation (1).

2. *Experiments.* 2.1. Preparation of the samples. Rutile (TiO_2) single-crystal boules were obtained from the National Lead Company, South Amboy, N. J., U.S.A. and from Nakazumi Crystals Corporation, Osaka, Japan. The crystal obtained from the National Lead Company was grown by the Verneuil method and contained alumina with a concentration of about 0.02 mole % (200 ppm). The Nakazumi crystal was grown by the flame-fusion method and contained about 0.002 mole % Al_2O_3 (20 ppm). For both crystals the crystallographic c axis was parallel to the longitudinal boule axis. The crystal orientation was checked by means of X-ray reflection. Samples with the desired dimensions and crystal orientation were obtained from the boules with the help of a diamond saw. Subsequently the samples were oxidized in open air at about 1000°C for two hours in order to obtain a completely oxidized state[25]. Reduction was performed by heating the samples either in air of about 10^{-2} mm Hg pressure at 780–930°C for one hour, or in a hydrogen atmosphere of about 10^2 mm Hg pressure at 380–420°C for one hour. After polishing the samples with carborundum powder; degreasing in toluene and etching in boiling HCl–H_2O_2, indium contacts were soldered onto the samples. The soldering was done according to a technique described by Belser[26]. Then the samples provided with the contacts were annealed in vacuum of 10^{-2} mm Hg for about one hour at 250°C. In this way low-noise ohmic contacts were obtained.

Nickel oxide (NiO) and cobalt oxide (CoO) single crystals were obtained from Nakazumi Crystals Corporation, Osaka, Japan. The crystals were grown by the flame-fusion method and contained lithium with a concentration of about 1 mole %. The growing axis was ⟨100⟩. Both crystals were p-type. The content of Li may be smaller than 1 mole %, since it is liable to vaporization while being grown. Samples with the desired dimensions were obtained from the boules by cleaving, with the cleavage surface (100).

Before applying electrical contacts the samples were etched in boiling $HCl–H_2O_2$. Contacts were applied to NiO samples using indium amalgam as contact material. CoO samples were provided with electrical contacts using gold paste (Glanz-Gold 42, 15%, Degussa) or silver paste (Poliersilber 281 SE, Degussa). Both metallizing compounds were fired on at 550°C for half an hour in the open air. In this way low-noise ohmic contacts were obtained both for NiO and for CoO.

The n-type $CdCr_2Se_4$ samples were doped with 2% gallium. The measurements were performed on either monocrystalline or polycrystalline samples. The single crystal (s.c.) samples had linear dimensions of about 2 mm, the polycrystalline (p.c.) samples were rectangular blocks with dimensions of about $1 \times 1 \times 10$ mm³. Before applying electrical contacts, the samples were polished with carborundum and etched in boiling $HCl–H_2O_2$. Low-noise ohmic contacts with negligible resistance were made by soldering indium amalgam onto the samples.

2.2. Experimental methods. Noise and resistivity measurements were performed using separate current and voltage probes (four-probe method), as well as common current and voltage probes (two-probe method). By using the four-probe method four contacts were applied side by side to a bar-shaped sample, whereas with the two-probe method two contacts were applied to opposite planar surfaces of the samples. Four-probe measurements are often employed in order to eliminate contributions due to contact resistance. However, our samples were provided with low-noise ohmic contacts, consequently the two- and four-probe measurements yielded the same noise and resistivity data.

In order to obtain temperatures between 77 K and 300 K a liquid-nitrogen cryostat provided with a heater fed from a d.c. power supply was used. Sample temperatures between 250 K and 300 K were also obtained with a Peltier battery (Philips PT 47/5). Temperatures higher than 300 K were obtained by heating a copper block provided with a water-cooled heat sink. The temperatures were measured with the help of copper–constantan thermocouples.

If a d.c. current I flows through the samples noise voltage arises between the voltage probes. This noise voltage was amplified and subsequently analyzed with the help of a Bruell and Kjaer audio-frequency spectrometer analyzer (type 2112). The noise spectra obtained were composed of amplifier noise, Nyquist noise and flicker noise. At zero d.c. current the sum of amplifier noise and Nyquist noise could be measured. Absolute calibration of the spectral noise density $S_{\Delta I}$ was performed with the help of a saturated diode (Philips K81A)[27].

2.3. Results. The results presented here were obtained with a number of samples listed in table I. Fig. 1a shows the resistivity ρ as a function of

TABLE I

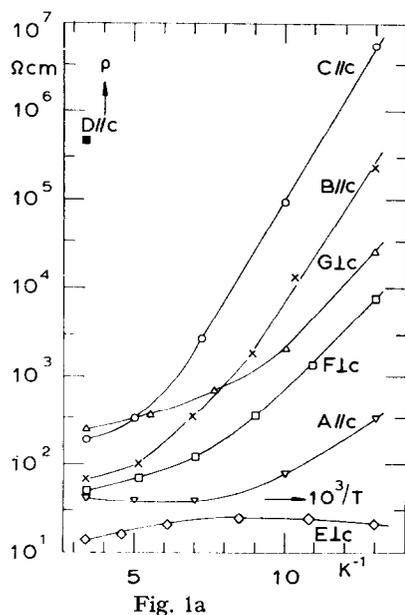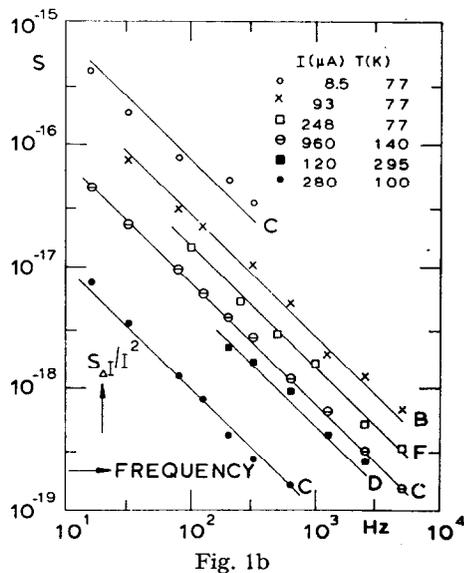| Sample designation	Current // or ⊥ c axis	Reduction temperature and atmosphere	4-probe or 2-probe	Distance between voltage probes (mm)	Cross section (mm²)	Dope
			TiO_2			
A	//	410°C, H_2	2p	1.5	24	200 ppm Al_2O_3
B	//	900°C, air	2p	1.5	24	200 ppm Al_2O_3
C	//	395°C, H_2	2p	1.5	6.0	200 ppm Al_2O_3
D	//	380°C, H_2	2p	1.2	14	200 ppm Al_2O_3
E	⊥	930°C, air	4p	3.5	2.9	20 ppm Al_2O_3
F	⊥	880°C, air	4p	4.0	5.0	20 ppm Al_2O_3
G	⊥	400°C, H_2	2p	4.0	2.6	20 ppm Al_2O_3
			NiO			
—	—	—	4p	3.5	8.5	1% Li
			CoO			
—	—	—	2p	0.8	5.6	1% Li
			$CdCr_2Se_4$			
s.c.	—	—	2p	0.8	3.0	2% Ga
p.c.	—	—	2p	1.0	2.5	2% Ga

Fig. 1a

Fig. 1b

Fig. 1a. Temperature dependence of the resistivity ρ of reduced rutile doped with alumina. Samples A, B, C, D are doped with about 200 ppm Al_2O_3 and samples E, F, G are doped with about 20 ppm Al_2O_3 (cf. table I).

Fig. 1b. Some flicker-noise spectra of reduced rutile as obtained from samples B, C, D and F (cf. table I).

temperature for the rutile samples. Some flicker-noise spectra of the rutile samples corrected for noise contributions at zero d.c. current have been plotted in fig. 1b. The flicker-noise density is found to be proportional to I^2. The rutile samples reduced in vacuum, as well as those reduced in H_2 atmosphere were found to show the same noise and resistivity behaviour, although in the latter case H atoms may diffuse into TiO_2.[9]).

Fig. 2a shows the resistivity ρ for CoO and NiO as a function of temperature, as well as the temperature dependence of the magnitude of the flicker-noise density in terms of $\alpha\mu$ [cf. eq. (1)]. Some flicker-noise spectra as obtained with CoO provided with either Ag or Au contacts and with NiO are shown in fig. 2b. The flicker-noise density was found to be proportional to I^2.

Fig. 3a shows the resistivity ρ as a function of temperature for both $CdCr_2Se_4$ samples, as well as the temperature dependence of the flicker-noise density in terms of $\alpha\mu$ [cf. eq. (1)] for the p.c. sample. The maxima for the resistivity were found at $T = 143$ K and $T = 170$ K for the s.c. sample and the p.c. sample, respectively. Some noise spectra are shown in fig. 3b. The flicker-noise density is found to be proportional to I^2 and $I^{1.5\pm0.1}$ for the p.c. sample and the s.c. sample, respectively. We could not determine a
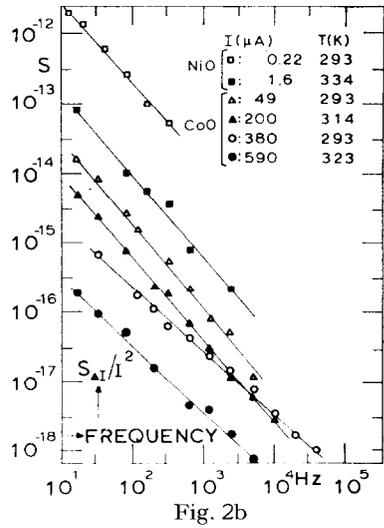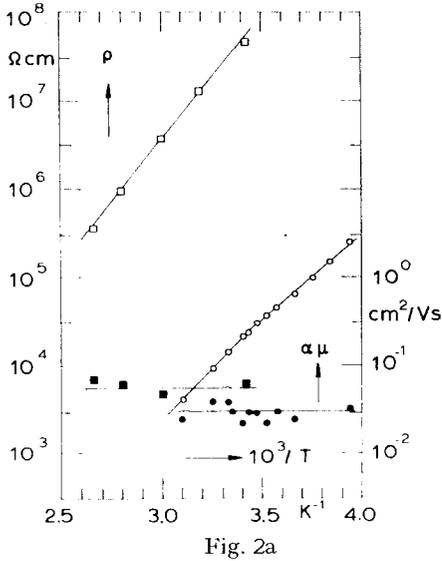

Fig. 2a

Fig. 2b

Fig. 2a. Temperature dependence of the resistivity ρ of CoO–Li (o) and NiO–Li (□), and the magnitude of the flicker-noise density in terms of $\alpha\mu$ as a function of temperature of CoO–Li (●) and NiO–Li (■). α is a dimensionless empirical constant and μ is charge carrier drift mobility.

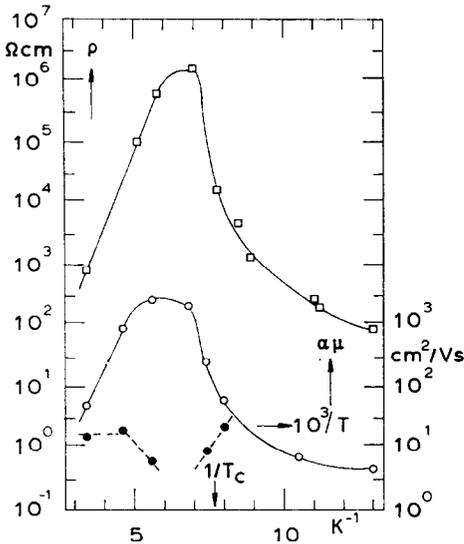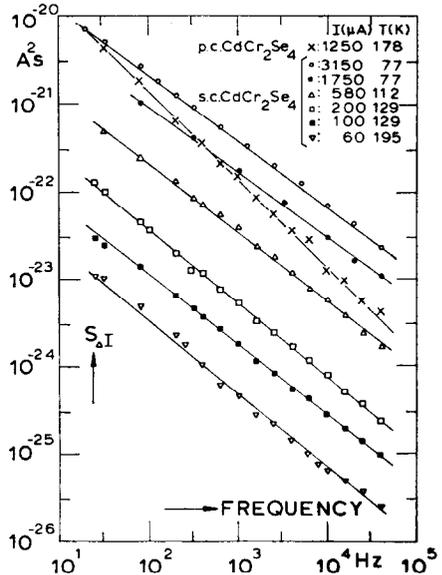Fig. 2b. Some flicker-noise spectra of Li-doped CoO with Au contacts (o, ●) and Ag contacts (△, ▲), and of Li-doped NiO with In–Hg contacts (□, ■).

Fig. 3a. Temperature dependence of the resistivity ρ of polycrystalline (o) and mono-crystalline ($\square$) n-type $CdCr_2Se_4$ doped with 2% Ga, and the magnitude of the flicker-noise density in terms of $\alpha\mu$ as a function of temperature for the polycrystalline sample ($\bullet$). α is a dimensionless empirical constant and μ is the charge-carrier drift mobility.

Fig. 3b. Some flicker-noise spectra of polycrystalline (p.c.) and monocrystalline (s.c.) n-type $CdCr_2Se_4$ doped with 2% Ga.

value for α in the case of the s.c. sample, since the current dependence is not quadratic; in addition, the flicker noise shows a frequency dependence of about $1/f^{0.7}$.

3. *Discussion of the results.* 3.1. Resistivity. The resistivity of the TiO_2 samples as a function of temperature is shown in fig. 1a. It was found that for lower reduction grades the resistivity shows an activation energy of about 0.10 eV at lower temperatures. At higher temperatures the resistivity depends less strongly on temperature, since the mobility decreases with increasing temperature.[1]) The trapping level, which is responsible for the activation energy of 0.10 eV may be due to aluminium, O vacancies or Ti interstitials[1,3,5]).

It was found that the resistivity ρ of the NiO and CoO samples varies exponentially with temperature, *i.e.* $\rho = \rho_0 \exp(\varepsilon/kT)$. For CoO we found $\varepsilon = 0.40$ eV below the Néel temperature ($T_N = 290$ K) and 0.46 eV above T_N. The NiO sample shows an activation energy ε of 0.58 eV. These values for ε are in agreement with the results of other investigators[13-17]). As to what extent the temperature dependence of ρ is due to the variation of the

drift mobility μ with temperature or to the variation of the charge-carrier density with temperature is not known. However, recent investigations [13,14,16]) indicate that the temperature dependence of ρ is determined chiefly by the variation of the charge-carrier density both for CoO and NiO. Although the conduction mechanism in CoO and NiO is not completely understood, it is known that the drift mobility of charge carriers in the valency band is very low (*i.e.* about 1 cm^2/Vs).

The temperature dependence of the resistivity of the CdCr$_2$Se$_4$ samples is in agreement with the expected behaviour. However, it should be noted that the maximum in resistivity near T_C is steeper for the s.c. sample than for the p.c. sample, which is not surprising since inhomogeneities may smooth such maxima.

3.2. Noise. Comparing the flicker-noise density obtained with rutile samples and the expression given by eq. (1), we find values for α of 3×10^{-6} and larger. In the evaluation of these data we used values for the mobility μ as found from Hall experiments [1]). The very small value for α, *i.e.* 3×10^{-6}, was obtained for sample C both at 77 K and 100 K. As the number of free carriers N strongly varies between 77 K and 100 K it seems that α is here a constant independent of N, temperature and frequency. However, it is difficult to check the independence of α from temperature and the total number of free carriers, since the electrical contacts strongly affect the value of the flicker-noise density in our rutile samples. It should be noted that the lowest value of α found by us is smaller than the value predicted by eq. (1) by a factor 10^3.

For the NiO sample the noise spectra are fairly well described by a $1/f$ dependence. We determined the quantity $\alpha\mu$ from $S_{\Delta I}$ at 100 Hz. The quantity $\alpha\mu$ appears to be nearly independent of temperature (fig. 2a). Other investigators [13,16]) have found temperature-independent drift mobilities for Li-doped NiO in the range 1 to 10 cm^2/Vs at temperatures between 290 K and 375 K, depending on the Li concentration. Hence we conclude that α must lie in the range 6×10^{-3} to 6×10^{-2} and that it must be independent of temperature. This is in agreement with the general findings of Hooge.

By inspection of the flicker-noise data obtained with CoO samples we found that the samples provided with Ag contacts show more flicker noise than the samples provided with Au contacts (see fig. 2b, at $T = 293$ K), and also the frequency dependence is different, namely $1/f^{1.2}$ and $1/f^{1.0}$ for Ag and Au contacts, respectively. The quantity $\alpha\mu$ obtained with the sample provided with Au contacts is shown in fig. 2a, we find that $\alpha\mu$ is nearly independent of temperature. Hence the charge-carrier drift mobility μ is independent of temperature provided that eq. (1) holds, with α being independent of temperature. By taking $\mu = 1$ cm^2/Vs [13,14]) we obtain $\alpha = 3 \times 10^{-2}$.

It should be noted that for the CoO sample the contact material affects the flicker-noise density both in magnitude and in frequency behaviour. Therefore it is questionable whether the flicker noise originates from bulk or contact effects. Note that eq. (1) holds only for bulk effects. We know from experience that the magnitude of the flicker noise is an indication for the quality of an electrical contact. For good ohmic electrical contacts the magnitude of flicker-noise density nearly always corresponds with a value for α in the range 10^{-3} to 10^{-2}, with the exception of the data from rutile.

The noise spectra obtained with $CdCr_2Se_4$ samples showed also flicker noise. Since for the p.c. sample the spectral noise density is proportional to I^2 and inversely proportional to f, we determined the quantity $\alpha\mu$. If α is independent of temperature, we see in fig. 3a that above T_C with decreasing temperature the mobility decreases, whereas below T_C the mobility tends to increase. Hence the temperature dependence of $\alpha\mu$ agrees with the temperature dependence of μ [21,22]). However, we note that this interpretation is questionable since our value for α is much larger than predicted by eq. (1), taking into account a mobility $\mu \approx 1$ cm^2/Vs if $T > T_C$. It is possible that the flicker-noise density in p.c. $CdCr_2Se_4$ is not associated with bulk effects but is due to grain boundaries.

4. *Conclusion.* It has been pointed out that in transition metal compounds electrical conduction occurs mostly be charge carriers moving in narrow conduction bands or by hopping between localized states. In these materials the drift mobility of charge carriers is found to be very low ($\lesssim 1$ cm^2/Vs). On the other hand, the expression given by eq. (1) is found with reference to flicker-noise data obtained with normal broad conduction-band materials, where the drift mobility has normal values of about 10^3 cm^2/Vs. Therefore the unusually low value for α found in rutile may be due to the deviating conduction mechanism.

REFERENCES

1) Acket, G. A., Thesis, Rijksuniversiteit Utrecht (1965).
2) Becker, J. H. and Hosler, W. R., Phys. Rev. **137** (1965) A1872.
3) Acket, G. A. and Volger, J., Physica **32** (1966) 1680.
4) Itakura, M., Niizeki, N., Toyoda, H. and Iwasaki, H., Jap. J. appl. Phys. **6** (1967) 311.
5) Hasiguti, R., Minami, K. and Yonemitsu, H., J. Phys. Soc. Japan **16** (1961) 2223.
6) Haul, R. and Dümbgen, G., J. Phys. Chem. Solids **26** (1965) 1.
7) Kofstad, P., J. Phys. Chem. Solids **23** (1962) 1579.
8) Cronemeyer, D. C., Phys. Rev. **113** (1959) 1222.
9) Kingsbury, P. I., Ohlsen, W. D. and Johnson, O. W., Phys. Rev. **175** (1968) 1091.
10) Frederikse, H. P. R., J. appl. Phys. Suppl. **32** (1961) 2211.
11) Yahia, J., Phys. Rev. **130** (1963) 1711.
12) Barbanel, V. I., Bogomolov, V. N., Borodin, S. A. and Budarina, S. I., Soviet Physics–Solid State **11** (1969) 431.
13) Van Daal, H. J. and Bosman, A. J., Phys. Rev. **158** (1967) 736.
14) Bosman, A. J. and Crevecoeur, C., J. Phys. Chem. Solids **30** (1969) 1151.
15) Morin, F. J., Phys. Rev. **93** (1954) 1199.
16) Austin, I. G., Springthorpe, A. J., Smith, B. A. and Turner, C. E., Proc. Phys. Soc. **90** (1967) 157.
17) Jonker, G. H. and Van Houten, S., Halbleiterprobleme **6** (1961) 118, Verlag Friedrich Vieweg und Sohn, Braunschweig.
18) Feinleib, J. and Adler, D., Phys. Rev. Letters **21** (1968) 1010.
19) Lehmann, H. W., Phys. Rev. **163** (1967) 488.
20) Haas, C., Van Run, A. M. J. G., Bongers, P. F. and Albers, W., Solid State Commun. **5** (1967) 657.
21) Haas, C., Phys. Rev. **168** (1968) 531.
22) Haas, C., Ned. T. Natuurk. **35** (1969) 225.
23) Hooge, F. N., Phys. Letters **29A** (1969) 139.
24) Hoppenbrouwers, A. M. H. and Hooge, F. N., Philips Res. Repts. **25** (1970) 69.
25) Mante, A. J. H., Thesis, Rijksuniversiteit Utrecht (1969).
26) Belser, R. B., Rev. Sci. Instrum. **25** (1954) 180.
27) Van der Ziel, A., Noise, Prentice–Hall, Inc. (Englewood Cliffs, N.J., 1956).