PHILOSOPHICAL MAGAZINE B, 1989, VOL. 59, NO. 2, 207–220

Electrical conductivity mechanisms in Au_xSi_{1-x} amorphous alloys

By A. AUDOUARD, A. KAZOUN, N. CHERRADI,
G. MARCHAL and M. GERL

Laboratoire de Physique du Solide, Unité Associée au CNRS 155,
Université de Nancy-I, Campus Victor Grignard, B.P. 239,
54506 Vandoeuvre les Nancy Cedex, France

[*Received 11 March 1988 and accepted 10 June 1988*]

ABSTRACT

Gold–silicon amorphous alloys Au_xSi_{1-x} have been prepared by simultaneous evaporation and condensation of the constituents in a high vacuum. The electrical conductivity was measured in the semiconducting region ($x \leqslant 0{\cdot}13$). For low gold concentration ($x < 0{\cdot}10$), the data can be analysed in the framework of variable-range hopping theories; for gold concentrations $0{\cdot}087 \leqslant x \leqslant 0{\cdot}12$ the conductivity behaviour can be attributed to electron tunnelling between metallic clusters embedded in a semiconducting matrix. The role of electron–electron correlations on variable-range hopping conductivity is also studied.

§ 1. INTRODUCTION

Since the pioneering work of Daver, Massenet and Chakraverty (1972) on amorphous Cr–Ge alloys, many experimental studies have been devoted to the understanding of electrical transport phenomena in amorphous alloys made of a metal and a group-IV semiconductor. In early works the variable-range hopping mechanism was generally invoked to explain the non-activated behaviour of the electrical conductivity (Mott 1969, Massenet, Daver and Geneste 1974, Chopra and Nath 1976, Shimizu, Kumeda, Watanabe and Kamono 1978). These studies were restricted to relatively narrow ranges of temperature and of conductivity. Deviations from Mott's law were sometimes reported (Massenet *et al.* 1974, Kishimoto, Morigaki, Shimizu and Hiraki 1976, Kishimoto and Morigaki 1979). By using phenomenological arguments, Möbius, Vinzelberg, Gladun, Heinrich, Elefant, Schumann and Zies (1985) and Möbius (1985) showed that most of the conductivity data (Massenet *et al.* 1974, Dodson, McMillan, Mochel and Dynes 1981, Kishimoto and Morigaki 1979, Nishida, Yamaguchi, Furubayashi, Morigaki, Ishimoto and Ono 1982) can be represented by the exponential law $\sigma = \sigma_0 \exp[-(T_0/T)^n]$, with the exponent n close to $\frac{1}{2}$. The physical interpretation of this thermal dependence of the conductivity remains unclear.

Among the metal–group-IV semiconductor alloys, the Au_xSi_{1-x} system is of particular interest from the technological point of view. It is also one of the best known, and many conductivity, structural and other measurements have been made on this system (Morigaki 1980, Macneil and Davis 1983). In particular, electron diffraction studies (Marchal, Mangin and Janot 1980, Mangin, Marchal, Mourey and Janot 1980) showed that, in the composition range $0{\cdot}17 \leqslant x \leqslant 0{\cdot}46$, the interference function of amorphous Au_xSi_{1-x} alloys can be interpreted as the superposition of two interference functions attributable to two different amorphous phases. One of these phases is rich in silicon, the other rich in gold. A direct confirmation of the coexistence of two phases

0141-8637/89 $3·00

was made by scanning transmission and high-resolution electron microscopy observations on an amorphous alloy of average composition $Au_{0\cdot17}Si_{0\cdot83}$. This alloy was shown to be composed of domains with an average size of about 50 Å (Audier, Guyot, Simon and Valignat 1985). It is also known that, as the gold content decreases, a semiconductor–metal transition is observed at $x=0{\cdot}14$ (Nishida *et al.* 1982). It was thought interesting to study the thermal behaviour of the electrical conductivity as a function of the average composition in the semiconducting region ($x\leqslant0{\cdot}13$). The underlying idea was that, if the microstructural state of the alloy changes below $x\sim0{\cdot}13$, this must strongly influence the temperature dependence of the conductivity. dependence of the conductivity.

As will be shown in § 3, the conductivity data will be analysed in the framework of:

(1) the variable-range hopping theory for $x\leqslant0{\cdot}13$,

(2) the theory of electron tunnelling between metallic domains for $0{\cdot}087\leqslant x\leqslant0{\cdot}12$.

§ 2. Experimental

Amorphous films of the alloy Au_xSi_{1-x} with composition ranging from $x=0$ to $x=0{\cdot}13$ were prepared by co-evaporation of silicon from an electron gun and of gold from a thermal crucible, in a vacuum better than 5×10^{-8} Torr. The rate of evaporation of each element was controlled by independent piezo-electric quartz balances. The condensation of the elements was carried out on glass substrates held at liquid-nitrogen temperature. Prior to the preparation of alloys, chromium (500 Å thickness) and gold (1500 Å thickness) electric contacts were deposited on the glass plates. The thickness of the samples was about 500 Å and the distance between electrodes was about 10 mm. Simultaneously with resistivity samples, some alloys were prepared on amorphous carbon films deposited on electron microscopy grids.

After preparation, the resistivity samples were heated to 300 K in the preparation chamber. This treatment was made to obtain samples in a standard structural state and to avoid subsequent structural relaxation. Systematic electron microscopy observations were made to check that the films obtained remained amorphous when heated to room temperature.

Resistivity measurements were carried out in a helium convection cryostat, using the guard-low technique, with a Hewlett-Packard 4140 B ammeter. This technique allowed us to measure d.c. currents as low as 5×10^{-13} A, which corresponds to a lowest measurable conductivity of about $10^{-9}\,\Omega^{-1}\,\mathrm{cm}^{-1}$.

§ 3. Experimental results and interpretation

Measurements of the conductivity σ were carried out on Au_xSi_{1-x} samples with $x=0$, 0·063, 0·075, 0·087, 0·10, 0·11, 0·12 and 0·13, between room temperature and the lowest temperature for which resistance measurements can be made with our experimental set-up. This temperature varies from about 50 K for $x=0$ to 1·25 K for $x=0{\cdot}13$.

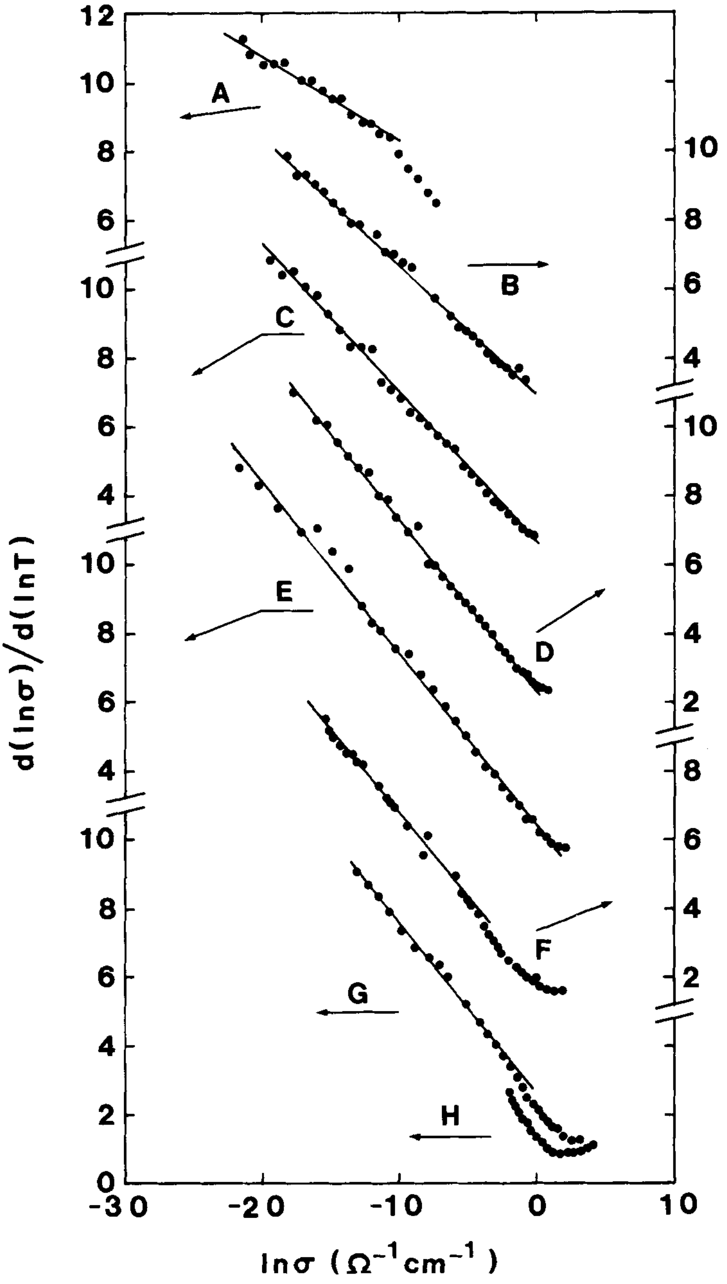
We chose to represent the thermal variation of the conductivity according to

$$\sigma=\sigma_0\exp[-(T_0/T)^n]. \tag{1}$$

Thus the exponent n can be determined from a plot of $\mathrm{d}\ln\sigma/\mathrm{d}\ln T$ as a function of $\ln\sigma$ (Möbius 1985):

$$\frac{\mathrm{d}\ln\sigma}{\mathrm{d}\ln T}=n(\ln\sigma_0-\ln\sigma). \tag{2}$$

Fig. 1



Plot of d ln σ/d ln T against ln σ for amorphous Au_xSi_{1-x} alloys. The linear traces are best fits to eqn. (2). Curve A: $x = 0$; Curve B: $x = 0{\cdot}063$; Curve C: $x = 0{\cdot}075$; Curve D: $x = 0{\cdot}087$; Curve E: $x = 0{\cdot}10$; Curve F: $x = 0{\cdot}11$; Curve G: $x = 0{\cdot}12$; and Curve H: $x = 0{\cdot}13$.

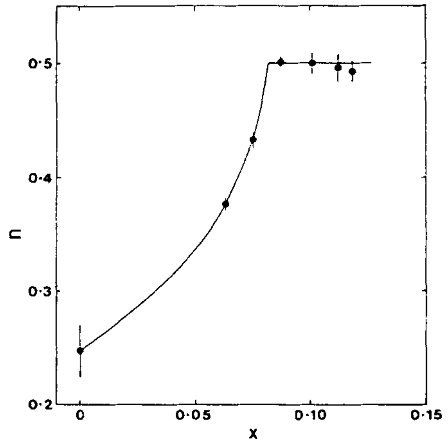
The values of $\mathrm{d}\ln\sigma/\mathrm{d}\ln T$ deduced from the experimental measurements of the conductivity are shown in fig. 1. It can be observed that, for the alloys investigated in the present work, eqn. (1) is fairly well obeyed, at least in the low-conductivity range, for $x \leqslant 0{\cdot}12$. The values of the exponent n, deduced from the slopes of the linear traces obtained by linear regression, shown in fig. 1, change with the composition of the alloy as shown in fig. 2. For pure amorphous silicon ($x=0$), the value of n is close to $\frac{1}{4}$ at low temperature as predicted by the variable-range hopping theory. As the gold content increases, n continuously increases to the value $n=\frac{1}{2}$ for $x=0{\cdot}087$, and remains constant for larger gold concentrations. For $x \geqslant 0{\cdot}13$ our results show that eqn. (1) is no longer valid for representing the thermal variation of the conductivity. Such a value $n=\frac{1}{2}$ has already been observed in metal–group-IV semiconductor alloys as indicated in the Introduction.

Variation of the conductivity according to Mott's formula ($n=\frac{1}{4}$) is only observed for pure amorphous silicon. Deviations from this law may have two different physical origins.

The first is that, in the framework of the variable-range hopping (VRH) theory, it has been shown theoretically (Overhof and Thomas 1976, Ortuno and Pollak 1983) that if the density of states changes with energy in the vicinity of the Fermi level, the conductivity is no longer represented by eqn. (1) with $n=\frac{1}{4}$. This has been experimentally confirmed in amorphous $\mathrm{Si}_x\mathrm{Sn}_{1-x}$ alloys (Maloufi, Audouard, Piecuch and Marchal 1986, Maloufi, Audouard, Piecuch, Vergnat, Marchal and Gerl 1988).

Let us mention that electron–electron correlations lead to an exponential variation of the conductivity with $n=\frac{1}{2}$ (Efros and Shklovskii 1975, Shklovskii and Efros 1984). Such a mechanism is known to operate in doped crystalline semiconductors at very low temperature (Zabrodskii and Zinov'eva 1983, Finlayson and Mason 1986). In elemental amorphous semiconductors the density of states at the Fermi level is too small to allow the observation of electron–electron correlations (Shklovskii and Efros 1984). In amorphous metal–semiconductor alloys however, the density of states in the gap is expected to be rather high and it might be possible to observe the effect of the correlations on the conductivity although such a mechanism has to our knowledge never been reported for such alloys.

Fig. 2



Variation with the gold concentration x of the exponent n (eqn. (1)) deduced from the slope of the linear traces shown in fig. 1.

Electron tunnelling between metallic grains embedded in an insulating matrix also leads to a conductivity that varies with temperature according to eqn. (1) with $n=\frac{1}{2}$ (Ping Sheng, Abeles and Arie 1973, Abeles, Ping Sheng, Coutts and Arie 1975). Although there is experimental evidence that our Au_xSi_{1-x} alloys consist of two phases for $x \geqslant 0{\cdot}17$, the atomic structure of the samples is not known on a small scale for $x < 0{\cdot}17$. It may well be possible that islands or clusters of high conductivity coexist with a low-conductivity matrix, even for $x < 0{\cdot}17$. The continuous variation of n would then result from the transition from variable-range hopping (low gold concentration) to tunnelling between metallic clusters for larger concentrations.

In the following the experimental data obtained for amorphous Au_xSi_{1-x} alloys are interpreted in the framework of VRH theories or of tunnelling between metallic clusters. The influence of electron–electron correlations on VRH conductivity is also discussed.

3.1. *Variable-range hopping*

Since the pioneering theory of Mott (1969) where the hopping rate is obtained through an optimization calculation involving a constant density of states (DOS) in the vicinity of the Fermi level, more sophisticated theoretical treatments have been proposed. Most of them include a percolation calculation (Pollak 1978) and a variable DOS near the Fermi level. A detailed analysis of conductivity data in amorphous Si_xSn_{1-x} (Maloufi *et al.* 1988) showed that the essential ingredient which determines the temperature variation of the conductivity is the shape of the DOS near the Fermi level. In the following we shall then use the optimization treatment of Mott with a variable density of states. The hopping rate w between localized states is given by (Miller and Abrahams 1960):

$$w = w_0 \exp(-\xi), \tag{3}$$

where

$$\xi = \frac{2R}{a} + \frac{\Delta}{kT}. \tag{4}$$

In these expressions R is the hopping distance between two sites whose energy difference is Δ a is the localization length of the one-electron wavefunction and w_0 is a frequency factor. When the temperature is lowered, a given electron can only hop towards sites of low energy difference Δ and has to jump over large distances to find such sites. The optimization of this process leads to the well known relation between R and Δ, namely

$$\frac{4\pi}{3} R^3 \int_0^{\Delta} N(E)\,\mathrm{d}E = 1, \tag{5}$$

where $N(E)$ is the density of states. Using the Einstein relation between the conductivity σ and the hopping frequency, we obtain

$$\sigma = \sigma_0 \exp(-\xi), \tag{6}$$

where

$$\sigma_0 = \frac{ne^2}{6kT} R^2 w_0.$$

The carriers involved in the hopping process are essentially those which are in the energy interval Δ below the Fermi level so that

$$n=\int_{-\Delta}^{0} N(E)\,\mathrm{d}E. \tag{7}$$

When the experimental results are analysed using eqn. (6), unphysically large values of the frequency factor w_0 are generally obtained. This problem has received much attention (Shklovskii and Efros 1976, Pollak 1978), but is not yet completely solved. However, in all theories, σ_0 varies weakly with temperature, with respect to the factor $\exp(-\xi)$, and has a negligible influence on the determination of the physical parameters which characterize the DOS near the Fermi level.

It is also well known that localized defects introduce a band of energy states in the gap of an amorphous semiconducting alloy. In the alloys investigated in the present paper, these defects may arise from topological disorder (such as dangling bonds) and from the impurity band associated with gold impurities. In crystalline silicon, acceptor levels close to the top of the valence band are associated with gold impurities. In amorphous alloys the situation is less clear, but it has been shown by photoemission from sputtered alloys (Macneil and Davis 1983) that the density of states near the top of the valence band is reinforced by the introduction of gold atoms.

In what follows we use three possible analytical functions for $N(E)$ in order to interpret the data:

(1) A defect band with a Lorentzian shape, centred at the Fermi level:

$$N(E)=\frac{N(E_\mathrm{F})}{1+(E/E_0)^2}, \tag{8}$$

(2) A defect band lying below E_F. In this case we describe the density of states by the decreasing exponential function:

$$N(E)=N(E_\mathrm{F})\exp(-E/E_0), \tag{9}$$

(3) A defect band lying at an energy larger than E_F, and described by an increasing exponential function:

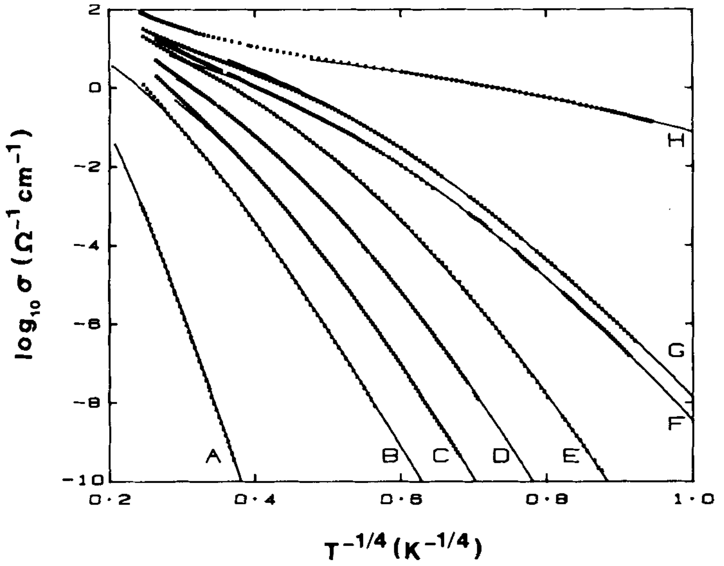
$$N(E)=N(E_\mathrm{F})\exp(+E/E_0). \tag{10}$$

To interpret the experimental data we used these expressions of $N(E)$ in eqn. (5) which, with eqns. (3) and (6), lead to an expression of the conductivity involving three parameters only: σ_0, $a^3N(E_\mathrm{F})$ and E_0 (Maloufi *et al.* 1986, 1988).

The best fits to the experimental data are shown in figs. 3, 4 and 5, where $\log_{10}\sigma$ is plotted as a function of $T^{-1/4}$. Irrespective of the expression chosen for $N(E)$, good agreement between theory and experiment is observed at low temperature. It can be observed, however, that, as the gold concentration increases, this agreement becomes rather poor at high temperature. The temperature for which deviation of the theoretical curves from the experimental data occurs decreases as x increases. This feature is not unexpected because, as the gold concentration grows, the optical band-gap shrinks (Morigaki 1980), so that conduction through activated processes may operate at increasingly lower temperature.

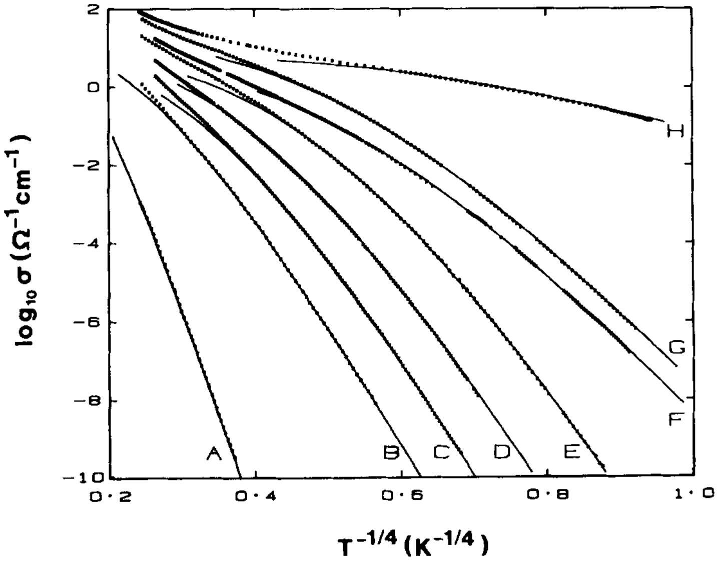
The variation of E_0 and $a^3N(E_\mathrm{F})$ with gold concentration is depicted in figs. 6 and 7 respectively. Whatever the analytical expression of the DOS, E_0 is shown to continuously decrease with x. This shrinking of the shape of the density of states near

Fig. 3



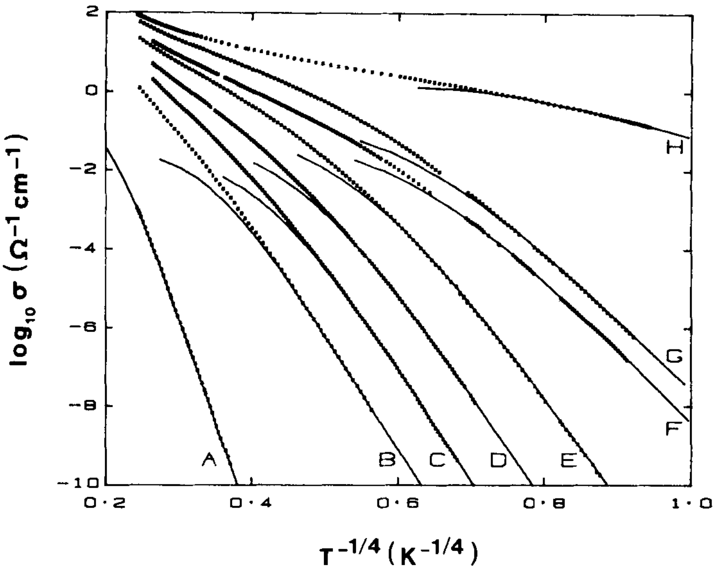
Variation of $\log_{10}\sigma$ with $T^{-1/4}$ in amorphous Au_xSi_{1-x} alloys. The solid lines represent the best fits of experimental data to the VRH model with a DOS given by eqn. (8). The labels on the curves have the same meaning as in fig. 1.

Fig. 4



Same as fig. 3, with a DOS given by eqn. (9).

Fig. 5



Same as fig. 3, with a DOS given by eqn. (10).

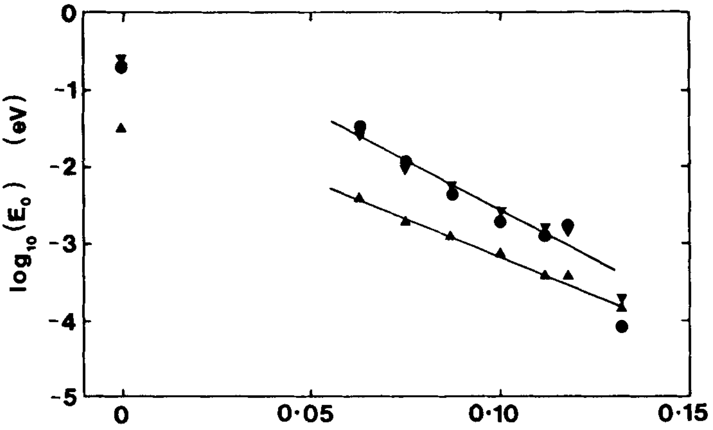
E_F can be attributed to the fact that localized levels, associated with gold impurities, contribute a narrow energy band in the pseudo-gap of the alloy. It is very likely that the Fermi level is pinned in this region of large density of states.

As shown in fig. 7, the product $a^3N(E_F)$ is, for a given analytical expression of the DOS, higher by an order of magnitude for $x=0{\cdot}063$ than for pure amorphous Si. The overall variation with x of $a^3N(E_F)$ is, within an order of magnitude, independent of the model used to describe the density of states. This product remains approximately constant for $0{\cdot}063 \leqslant x \leqslant 0{\cdot}10$, and grows quickly for $x > 0{\cdot}10$. For $x > 0{\cdot}10$, unrealistic values of the density of states near E_F are obtained, so that the model is clearly not valid for x larger than 0·10. This observation, and the fact that the exponent n becomes equal to $\frac{1}{2}$ for $x \geqslant 0{\cdot}087$, seem to indicate that another mechanism takes place for $x \gtrsim 0{\cdot}10$. It is possible that the alloys develop a two-phase structure when the gold concentration becomes of the order of 0·09. Electron microscopy observations have shown that, for $x=0{\cdot}17$, the alloys consist of two different phases (Audier *et al.* 1985), but no direct observations have been made at lower gold concentration. Our contention is that the change in the exponent n from $\frac{1}{4}$ to $\frac{1}{2}$ could be an indication of the evolution of the morphology of the alloys when the gold concentration increases. This hypothesis is investigated further in § 3.2.

The exponent $n=\frac{1}{2}$ is also observed for hopping conduction in systems where electron–electron Coulomb interactions are important (Efros and Shklovskii 1975). In fig. 8, we plot $\log_{10}\sigma$ as a function of $T^{-1/2}$ and notice that eqn. (1) with $n=\frac{1}{2}$ fits rather well to the experimental data at low temperatures for $0{\cdot}087 \leqslant x \leqslant 0{\cdot}12$. The values obtained for T_0 should be related to the dielectric constant ε of the material and to the localization length a by the equation (Shklovskii and Efros 1984):

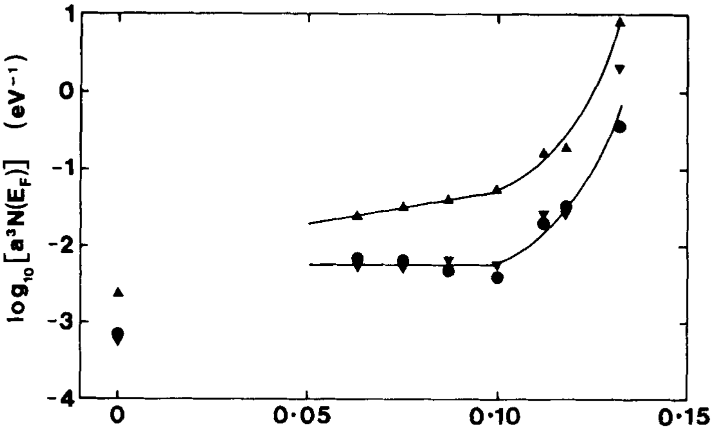
$$kT_0 = 2{\cdot}8e^2/\varepsilon a. \tag{11}$$

Fig. 6



Variation with x of the energy parameter E_0, when the DOS is given by eqn. (8), (●); eqn. (9), (▼) or eqn. (10), (▲).

Fig. 7



Variation with x of the product $a^3N(E_F)$ for different choices of the DOS: eqn. (8), (●); eqn. (9), (▼); eqn. (10), (▲).

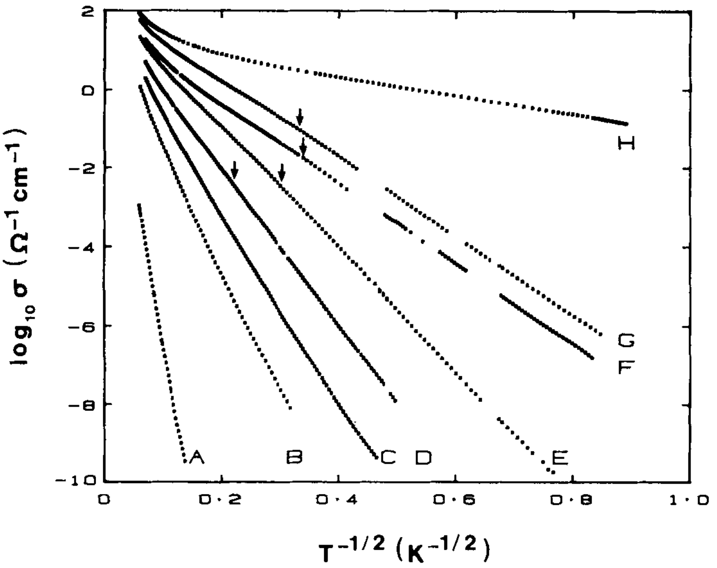
According to Shklovskii and Efros (1984), a and ε diverge near the metal–semiconductor transition:

$$a = a_0\left(\frac{x_c}{x_c - x}\right)^{\nu}, \tag{12}$$

$$\varepsilon = \varepsilon_0\left(\frac{x_c}{x_c - x}\right)^{\zeta}, \tag{13}$$

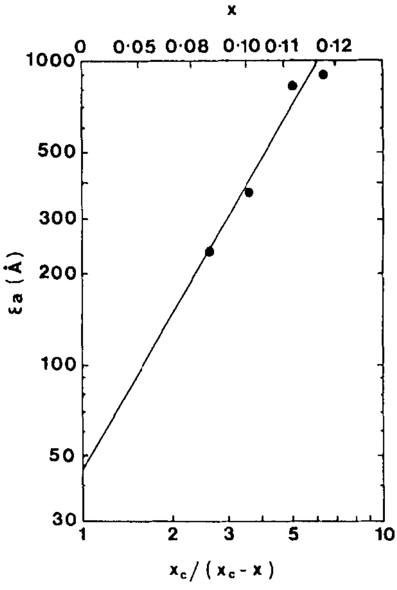
where a_0 and ε_0 refer to pure amorphous silicon.

Fig. 8



Variation of $\log_{10}\sigma$ with $T^{-1/2}$. The arrows correspond to the maximal temperature T_c for which the $T^{-1/2}$ law is observed (see text). The labels on the curves have the same meaning as in fig. 1.

Fig. 9



Variation with x of the product εa (see text). The black dots are obtained from the experimental data for T_0 (fig. 8) using eqn. (11).

From these expressions, we obtain for T_0:

$$kT_0 = 2{\cdot}8\frac{e^2}{\varepsilon_0 a_0}\left(\frac{x_c - x}{x_c}\right)^{\nu+\zeta}.$$

In order to check this theory, we plotted (fig. 9) the values of $\log_{10}(\varepsilon a)$ derived from the experimental value of kT_0 (eqn. (11)), as a function of $\log_{10}[x_c/(x_c - x)]$. The slope of the straight line in fig. 9 is 1·7, and from the intercept we obtain $a_0 = 3{\cdot}7$ Å by using $\varepsilon_0 = 12$. These results are not unreasonable: for uncompensated silicon, Hess, De Conde, Rosenbaum and Thomas (1972) obtained $\zeta = 1{\cdot}15$ and $\nu = 0{\cdot}55$, and thus $\zeta + \nu = 1{\cdot}7$. As for the value obtained for a_0, it compares fairly well with the value $a_0 = 3$ Å quoted by Knotek (1975). Finally the maximal temperature T_c for which the $T^{-1/2}$ law is experimentally observed varies from 20 K for $x = 0{\cdot}087$ to 9 K for $x = 0{\cdot}12$ (fig. 8). According to Efros and Shklovskii (1975), this temperature T_c is given by

$$kT_c = \frac{e^4 a^3 N(\Delta_c)}{(\varepsilon a)^2}, \tag{14}$$

where Δ_c is the half-width of the Coulomb gap. From the values we obtained for T_c, we deduce values of $N(\Delta_c)$ of the order of 10^{21} eV^{-1} cm^{-3}, which are compatible with the density of states at the Fermi level obtained in VRH calculations.

The conclusion of this paragraph is that VRH theories account fairly well for the variation of the conductivity of semiconducting Au_xSi_{1-x} amorphous alloys. A density of states that varies with energy in the vicinity of the Fermi level is needed to account for the high- and low-temperature behaviour. Finally electron–electron correlations might explain the variation of the conductivity at low temperatures in the composition range $0{\cdot}087 \leqslant x \leqslant 0{\cdot}12$.

3.2. *Tunnelling between isolated metallic grains*

As discussed in the introduction, it is known that for $x = 0{\cdot}17$ the alloys are made of a gold-rich phase which percolates through a silicon-rich phase (Audier *et al.* 1985). Thus it is not unrealistic to assume that when x decreases, the alloy is composed of metallic (gold-rich) grains embedded in a silicon-rich matrix. This amounts to assuming that, below the insulator–metal transition, there exists a concentration range for which the conduction proceeds by electron tunnelling between metallic grains.

The model of conduction used in granular systems is based on several assumptions (Ping Sheng *et al.* 1973, Abeles, Ping Sheng, Coutts and Arie 1975):

(1) The electronic transport results from tunnelling between grains of diameter d and of separation S;
(2) a broad distribution is assumed for d and S;
(3) when an electron hops from one grain to another the charging energy $E_c(S, d)$ is a function of the path S between grains and of their diameter d.

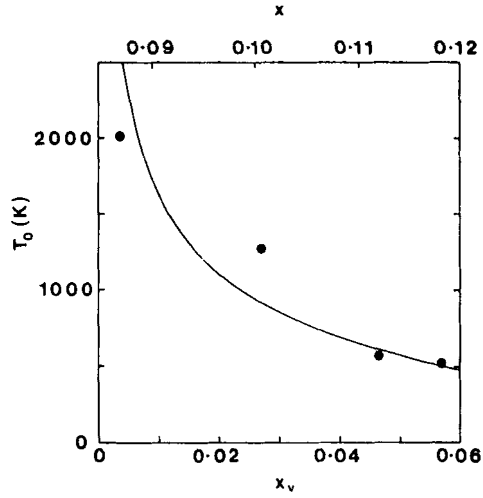
At each temperature the optimal path is determined by an optimization calculation, which leads to the following expression for the conductivity:

$$\sigma = \sigma_0 \exp[-(T_0/T)^{1/2}]$$

with

$$kT_0 = 4\frac{\eta(\alpha^{1/3} - 1)^2}{\alpha^{1/3} - \frac{1}{2}}, \tag{15}$$

Fig. 10



Variation of T_0 (obtained from fig. 8) with the volume fraction x_v of the metallic phase. The solid line is obtained from eqn. (15) with $\eta = 0{\cdot}015$.

with $\alpha = (\pi/6)x_v$, x_v being the volume fraction of the metallic phase and

$$\eta = \left(\frac{2m\phi}{\hbar^2}\right)^{1/2} \frac{2e^2}{\varepsilon}, \tag{16}$$

where ϕ is the potential barrier for tunnelling and ε is the dielectric constant of the insulating phase.

In order to determine x_v, the metallic phase was assumed to have the composition $Au_{0{\cdot}75}Si_{0{\cdot}25}$ (Mangin *et al.* 1980) and the silicon-rich phase was taken as $Au_{0{\cdot}085}Si_{0{\cdot}915}$. The values of T_0 obtained through best fits to experimental data (fig. 8) are plotted in fig. 10 as a function of the volume concentration x_v. The full curve represents the variation of T_0 against x_v, as given by eqn. (15) with $\eta = 0{\cdot}015$ eV.

In classical granular systems the parameter η is found of the order of 1 eV (Abeles *et al.* 1975) so the value obtained here is about 70 times smaller. This is not unexpected because ε is large in Au_xSi_{1-x} alloys ($\varepsilon \gg 12$, as reported by Sano, Iwami, Hiraki and Morigaki (1977)), and the potential barrier is probably much smaller than in metal–oxide granular structures.

In conclusion, the analysis presented here seems consistent so that we might expect that, at least for $x \geqslant 0{\cdot}087$, tunnelling between metallic grains could play an important role in the electrical conductivity of Au_xSi_{1-x} amorphous alloys. It is to be noticed, however, that, in the model we have used, a broad distribution of sizes and distances has been assumed. This assumption has not been checked experimentally. Electron microscopy observations in the concentration range $x = 0{\cdot}07$ to $x = 0{\cdot}17$ would be very valuable in this respect.

§4. CONCLUSION

The work presented in this paper is devoted to the analysis of electrical conductivity processes in Au_xSi_{1-x} amorphous alloys prepared by simultaneous condensation of the constituents.

At low gold concentration ($x<0{\cdot}1$) the conductivity data can be analysed in the framework of the variable-range hopping theory, with a density of states that varies with energy near the Fermi level. The density of states at the Fermi level is large ($\sim 10^{20}\,\mathrm{eV}^{-1}\,\mathrm{cm}^{-3}$) and varies rapidly with energy near E_F. This indicates the presence of a region of high density of states in the pseudo-gap of the material, which can be attributed to topological defects and to deep levels associated with gold impurities.

As the density of states is large, electron–electron correlations can also be invoked to explain the low-temperature data in the concentration range $0{\cdot}087 \leqslant x \leqslant 0{\cdot}12$. In the framework of this interpretation, the highest temperature for which correlations would play a role in the conductivity can be as high as 20 K. This point needs further experimental confirmation.

For gold concentrations $0{\cdot}087 \leqslant x \leqslant 0{\cdot}12$, the conductivity behaviour can be attributed to electron tunnelling between metallic grains embedded in a semiconducting matrix.

An important piece of information brought about by this work is that a change in the conductivity mechanism occurs for a gold concentration close to $x = 0{\cdot}10$. Further structural observations are needed to determine whether this phenomenon can be attributed to the morphological evolution of the alloys with concentration or to a change of the conductivity mechanism in homogeneous alloys.

ACKNOWLEDGMENTS

The authors wish to acknowledge Dr N. Maloufi for her help during the experiments.

REFERENCES

ABELES, B., PING SHENG, COUTTS, M. D., and ARIE, Y., 1975, *Adv. Phys.*, **24,** 407.

AUDIER, M., GUYOT, P., SIMON, J. P., and VALIGNAT, N., 1985, *J. Phys., Paris*, **46,** C8–433.

CHOPRA, K. L., and NATH, P., 1976, *Phys. Stat. sol.* a, **33,** 333.

DAVER, H., MASSENET, O., and CHAKRAVERTY, B. K., 1972, *Solid St. Commun.*, **11,** 131.

DODSON, B. W., MCMILLAN, W. L., MOCHEL, J. M., and DYNES, R. C., 1981, *Phys. Rev. Lett.*, **46,** 46.

EFROS, A. L., and SHKLOVSKII, B. I., 1975, *J. Phys. C*, **8,** L49.

FINLAYSON, D. M., and MASON, P. J., 1986, *J. Phys. C*, **19,** L299.

HESS, H. F., DE CONDE, K., ROSENBAUM, T. F., and THOMAS, G. A., 1982, *Phys. Rev.* B, **25,** 5578.

KISHIMOTO, N., and MORIGAKI, K., 1979, *J. phys. Soc. Japan*, **46,** 846.

KISHIMOTO, N., MORIGAKI, K., SHIMIZU, A., and HIRAKI, A., 1976, *Solid St. Commun.*, **20,** 31.

KNOTEK, M. L., 1975, *Solid St. Commun.*, **17,** 1431.

MACNEIL, J., and DAVIS, E. A., 1983, *J. non-crystalline Solids*, **59–60,** 145.

MALOUFI, N., AUDOUARD, A., PIECUCH, M., and MARCHAL, G., 1986, *Phys. Rev. Lett.*, **56,** 2307.

MALOUFI, N., AUDOUARD, A., PIECUCH, M., VERGNAT, M., MARCHAL, G., and GERL, M., 1988, *Phys. Rev.* B, **37,** 8867.

MANGIN, P., MARCHAL, G., MOUREY, C., and JANOT, C., 1980, *Phys. Rev.* B, **21,** 3047.

MARCHAL, G., MANGIN, P., and JANOT, C., 1980, *Phil. Mag.*, **42,** 81.

MASSENET, O., DAVER, H., and GENESTE, J., 1974, *J. Phys., Paris*, **35,** C4–279.

MILLER, A., and ABRAHAMS, E., 1960, *Phys. Rev.*, **120,** 745.

MÖBIUS, A., 1985, *J. Phys. C*, **18,** 4639.

MÖBIUS, A., VINZELBERG, H., GLADUN, C., HEINRICH, A., ELEFANT, D., SCHUMANN, J., and ZIES, G., 1985, *J. Phys. C*, **18,** 3337.

MORIGAKI, K., 1980, *Phil. Mag.* B, **42,** 979.

MOTT, N. F., 1969, *Phil. Mag.*, **19,** 835.

NISHIDA, N., YAMAGUCHI, M., FURUBAYASHI, T., MORIGAKI, K., ISHIMOTO, H., and ONO, K., 1982, *Solid St. Commun.*, **44,** 305.

ORTUNO, M., and POLLAK, M., 1983, *Phil. Mag.* B, **47,** L93.

OVERHOF, H., and THOMAS, P., 1976, *Proceedings of the Sixth International Conference on Amorphous and Liquid Semiconductors*, edited by B. T. Kolomiets (Leningrad: Nauka), p. 107.

PING SHENG, ABELES, B., and ARIE, Y., 1973, *Phys. Rev. Lett.*, **31**, 44.

POLLAK, M., 1978, *The Metal–Non Metal Transition in Disordered Systems*, edited by L. Friedman and D. P. Tunstall (Edinburgh: Scottish Universities Summer School Publications), p. 95.

SANO, T., IWAMI, M., HIRAKI, A., and MORIGAKI, K., 1977, *Solid St. Commun.*, **23**, 971.

SHIMIZU, T., KUMEDA, M., WATANABE, I., and KAMONO, K., 1978, *Solid St. Commun.*, **26**, 445.

SHKLOVSKII, B. I., and EFROS, A. L., 1976, *Soviet Phys. Usp.*, **18**, 845; 1984, *Electronic Properties of Doped Semiconductors, Solid State Sciences 45* (Berlin: Springer-Verlag).

ZABRODSKII, A. G., and ZINOV'EVA, K. N., 1983, *Soviet Phys. JETP Lett.*, **37**, 436.