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Properties of compounds of type Na_xSi_{46} and Na_xSi_{136}

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A qualitative account is given of the electrical and magnetic properties of compounds of the type Na_xSi_{136}. It is suggested that a metal–insulator transition takes place with decreasing x. It is conjectured that in sintered powders the resistance is due to amorphous contacts between grains, leading to a resistivity proportional to $A/T^{\frac{1}{4}}$.

Introduction

Cros, Pouchard, and Hagenmuller (*1*) have described the interesting electrical and magnetic properties of compounds of the type Na_xSi_{136}. In these compounds the alkali atoms occupy sites in polyhedra in a slightly distorted silicon framework. We assume, following Cros et al., that the electrons move in a "sodium band", similar to the impurity band formed by a heavy concentration of donors in silicon [Mott and Twose (*2*), Alexander and Holcomb (*3*)], but differing from it in two ways.

(i) Since the sodium atoms are in "holes" in the lattice, the electron is attracted by the force e^2/r^2 up to the surface of the polyhedron, and only for greater distances by the force $e^2/\kappa r^2$, where κ is the dielectric constant. In substitutionally doped silicon, e.g., Si:P, on the other hand, the bonding orbitals penetrate right into the phosphorus atom, so the field should be taken as $e^2/\kappa r^2$ everywhere. The "band" in these materials therefore lies further below the conduction band of silicon than in say Si:P, and in fact we think that excitation into the conduction band of Si may not play a significant role in determining the electrical properties.

(ii) For the compositions $Na_{24}Si_{136}$, all polyhedron are occupied by Na atoms and the system is ordered. If there are many polyhedra not occupied by Na, the sodium atoms will form clusters (Hagenmuller, private communication).

The system, in our view, provides a means of studying the metal–insulator transition as in doped semiconductors without the need to use very low temperatures, and without complications due to compensation (minority centers). We therefore first summarize what is known about this transition for Si:P and similar systems, as discussed in Ref. (*2*), Mott and Zinamon (*4*), and Mott (*5*). There are four important ranges of composition as follows.

(a) For high concentrations of the donor centers a degenerate gas in the Si conduction band is expected.

(b) For lower concentrations, an impurity band splits off from the conduction band, while conduction still remains metallic (*2*, *3*). As the concentration decreases, the electron gas becomes "highly correlated" in the sense of Brinkman and Rice (*6*). This means that most of the metal atoms carry only one electron, but a proportion c, which may be as small as 0.1, carry two electrons and the same proportion carry none. According to Brinkman and Rice the effective mass m^* at the Fermi surface is enhanced by the factor $1/2c$. This may be seen as follows: If a field F is applied for a time δt and if the Fermi surface is spherical, the current produced is

$$e^2 NF\delta t/m^*, \qquad (1)$$

where N is the number of atoms per unit volume. But the current is due only to the doubly occupied sites, where the extra electron can move from one atom to another, and to the unoccupied sites, and is thus

$$2Nc\delta te^2F/m.$$

Equating the two, we obtain

$$m^*/m = 1/2c.$$

(c) When c drops below about 0.1, we believe that an antiferromagnetic metal will be formed; this is perhaps controversial; for instance, Kohn (*7*) has proposed a more complicated model [see the discussion given by Mott and Davis (*8*, *9*)] and other suggestions are that there is a first-order transition, c jumping from ~0.1 to 0.

(d) Finally the "Mott transition" takes place and the material is then an antiferromagnetic insulator. A "Hubbard gap" opens between the occupied and empty states, as shown in Fig. 1(a).

Interpretation of the Experiments

In Fig. 2 we reproduce from Cros et al. (*1*) the conductivity–temperature curve for these materials, in Fig. 3 the Seebeck coefficient, and in Fig. 4 the magnetic susceptibility. As the authors state, since the results are obtained on powders compressed and sintered at 400°C, care is needed in interpreting them. The two top specimens shown in Fig. 2 are undoubtedly metallic. But a crystalline metal will have a resistance proportional to T and normally a much higher value of the conductivity than 10^2–$10^3 \Omega^{-1}\text{cm}^{-1}$. We assume, therefore, that:

(a) Most of the potential drop is at the electrical contacts between grains, these occupying a small fraction of the total surface area of a grain.

(b) The material there is full of defects or even amorphous, and will have a large residual resistance, so that the resistivity varies little with temperature. If these assumptions are correct, the results in Fig. 2 show the resistance as a function of temperature, in arbitrary units, of the highly defective or amorphous material at the grain joints. We shall assume that this is so for all the conductivity curves, but that the Seebeck coefficient gives results characteristic of the bulk material. Figure 3 then shows the progression from metallic behavior, for which

$$\alpha = \frac{\pi^2}{3}\frac{k^2 T}{e}\left\{\frac{d\ln\sigma}{dE}\right\}_{E=E_F},$$

to insulating behavior, where the high negative value of α is in our view due to a small number of donors of unknown character which have excited electrons into the upper Hubbard band, and are fully ionized at this temperature. We conjecture that the next specimen is a metal with the Brinkman–Rice mass enhancement, which should give a large thermopower and low degeneracy temperature; we think the behavior should be as in Fig. 5.

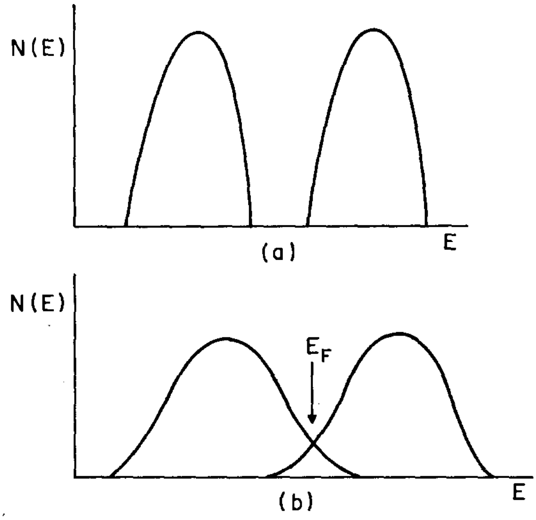

FIG. 1. Hubbard gap in the density of states of an array of one-electron centers: (a) crystalline; (b) amorphous.

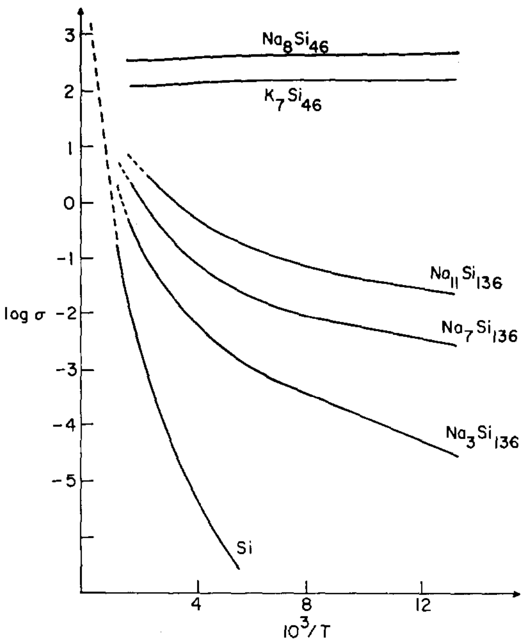

FIG. 2. Conductivity of compounds Na–Si.

We next ask why the variable activation energy in Fig. 2 occurs for the less metallic specimens. We believe that we have here, in the assumed "amorphous" region between the grains, sufficient disorder to cause Anderson localization, so that conduction is by thermally activated hopping. Many examples of this behavior are quoted in Ref. (*9*). If so, the small activation

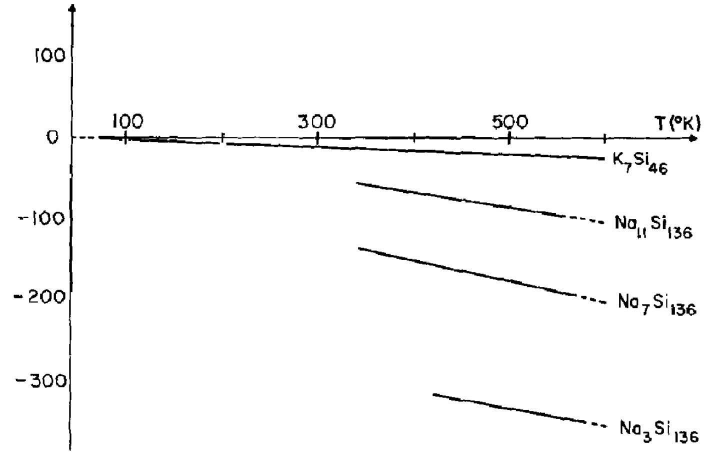

FIG. 3. Seebeck coefficient of compounds Na–Si.

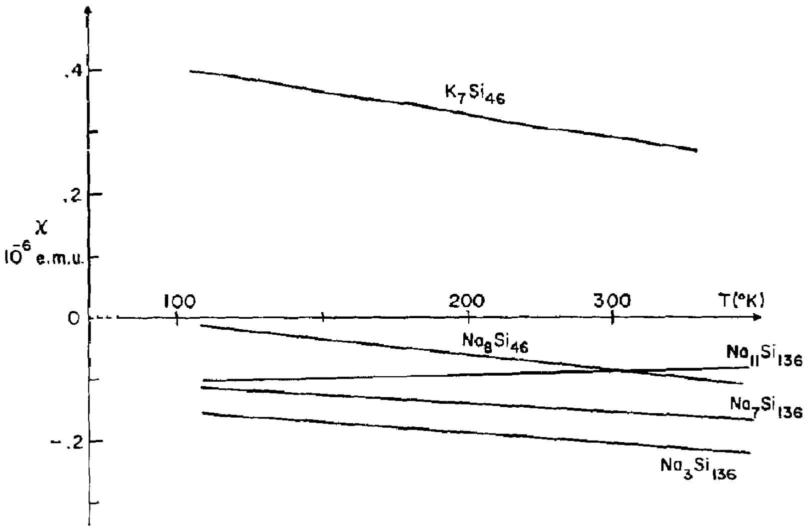

FIG. 4. Magnetic susceptibility of compounds Na–Si.

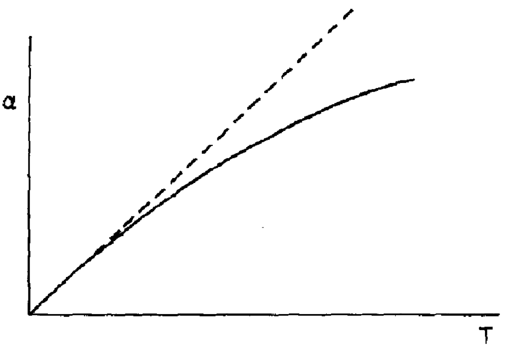

FIG. 5. Conjectured thermopower of a Brinkman–Rice highly correlated gas.

energies are easy to understand and we should expect the conductivity to behave (*8*, *10–12*) at sufficiently low T according to the equation:

$$\ln\sigma = -A/T^{\frac{1}{4}} + \text{constant}.$$

The data of Fig. 2 are plotted against $T^{\frac{1}{4}}$ in Fig. 6. It would be of interest to extend these results to lower temperatures.

Figure 4 shows that the susceptibility of these compounds with one exception decreases with increasing T. A Pauli susceptibility decreasing with T is what we expect for a metal with small values of E_F. For one specimen, $Na_{11}Si_{136}$, however, χ increases with T. As we have stated, one question which remains controversial about

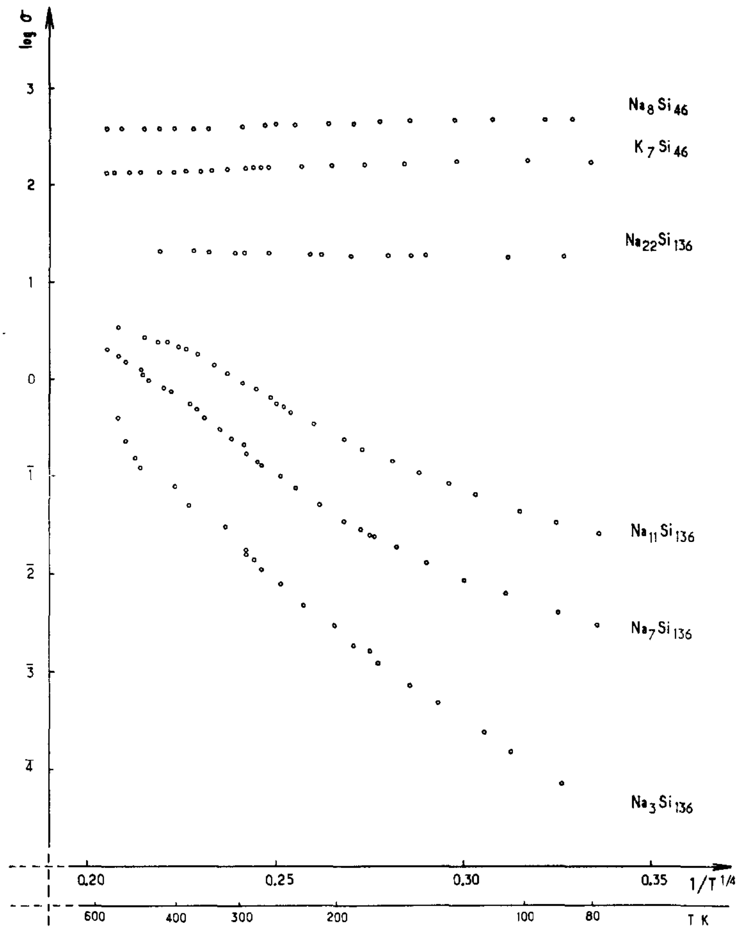

FIG. 6. Plot of lnσ against $1/T^{\frac{1}{4}}$ from measurements of Cros et al.

the "Mott transition" is whether an antiferromagnetic metal should exist for a range of composition between the antiferromagnetic insulator and the non-magnetic highly-correlated metal of Brinkman and Rice. The present author thinks that it should, and we suggest that $Na_{11}Si_{136}$ may be an antiferromagnetic metal with Néel point above 300 K. This would account for a value of χ which increases with T. For Na_3Si_{136}, for which χ decreases with T, we must assume that the Néel temperature lies below 100 K, the lowest temperature of the measurement. Nuclear magnetic resonance or other measurements to find out if the atoms carry fixed moments at low T would be of interest.

Acknowledgment

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