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THE MAGNETITE PROBLEM : THE ANOMALOUS SEEBECK COEFFICIENT OF $\text{Fe}_3\text{O}_{4-x}\text{F}_x$

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Résumé. — On a préparé des échantillons polycristallins de $\text{Fe}_3\text{O}_{4-x}\text{F}_x$, avec $0 < x < 0,25$, par frittage sous pression. On donne les résultats des mesures de résistivité et des coefficients de Seebeck en fonction de la température. Les modèles à bande étroite unique ou à petit polaron ne paraissent pas décrire le comportement des coefficients de Seebeck de ce système. On suggère que les résultats peuvent s'expliquer par une *localisation* d'Anderson des porteurs de charge.

Abstract. — Polycrystalline samples of $\text{Fe}_3\text{O}_{4-x}\text{F}_x$ with $0 < x < 0.25$ have been prepared by pressure-sintering. Measurements are reported of the resistivities and Seebeck coefficients as a function of temperature. Simple narrow band or small-polaron models do not appear to describe the behaviour of the Seebeck coefficient of this system. It is suggested that the results can be explained by Anderson *localisation* of the charge carriers.

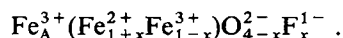
1. Introduction. — It is well known that magnetite can be characterized by the ionic formula $\text{Fe}_A^{3+}(\text{Fe}^{2+}\text{Fe}^{3+})_B\text{O}_4^{2-}$ with the cations being grouped on either A (tetrahedrally coordinated) sites or B (octahedrally coordinated) sites and that the electrical conductivity results from the movement of electrons between B-site cations. However, it is by no means clear whether the electrical properties are to be described in terms of narrow band conduction [1] or small-polaron hopping [2]. Furthermore, the situation is complicated by the possibility that lattice disorder in the solid may have a profound influence on the conduction mechanism [3].

In the present paper an attempt has been made to clarify the situation by reference to measurements on the system of compounds $\text{Fe}_3\text{O}_{4-x}\text{F}_x$, the results for which have been compared with those where cation substitution (e. g. by Ni^{2+} ions for Fe^{2+} ions) rather than anion substitution has been used to modify the properties. In particular, the unusual behaviour of the Seebeck coefficient is discussed in relation to current theories.

2. Experimental. — The feasibility of producing compounds of the formula $\text{Fe}_3\text{O}_{4-x}\text{F}_x$ has been established by Casalot, Claverie and Hagemuller [4]. In the present work, carefully dried powders of Fe, Fe_2O_3 and FeF_2 were ball-milled, sealed in platinum capsules and pressure sintered at 1 000 °C for six hours. Pressures as low as 250 bars were found to be sufficient to produce ceramics having densities greater than

97 % of the theoretical value. However, for values of x greater than 0.25 it was not found possible to produce single phase materials by this method.

From measurements of the saturation magnetization and X-ray analysis it was concluded that all samples were single phase spinel with an ionic distribution given by the formula :



Electrical measurements were made with the specimens in vacuo or in an inert atmosphere. Resistivities were measured in the temperature range 77 K-300 K, using a four-terminal method. The Seebeck coefficient was obtained from measurements of the thermoelectric e. m. f. against spring-loaded platinum or nickel electrodes, investigations being carried out in the temperature range 77 K-1 100 K.

3. Results. — **3.1 RESISTIVITY.** — Typical resistivity curves are shown in figure 1, where $\log \sigma$ is plotted against $1/T$. The resistivity curves for pure Fe_3O_4 produced by the method described above are in agreement with those reported for good quality single crystals [5]. A number of features of the resistivity behaviour of the present system are found to be similar to those observed in nickel, cobalt and zinc substituted magnetite and also magnetite containing differing concentrations of cation vacancies. As in these systems, relatively small quantities of impurities [6] and vacancies [7] are required to suppress the Verwey transition. Thus, in contrast to Casalot *et al.* [4], we find that for concentrations of fluorine $x \lesssim 0.05$ the transition is absent. Moreover, as for several other types of defect [8], deviation from the pure stoichiometric composition Fe_3O_4 lowers the Verwey point.

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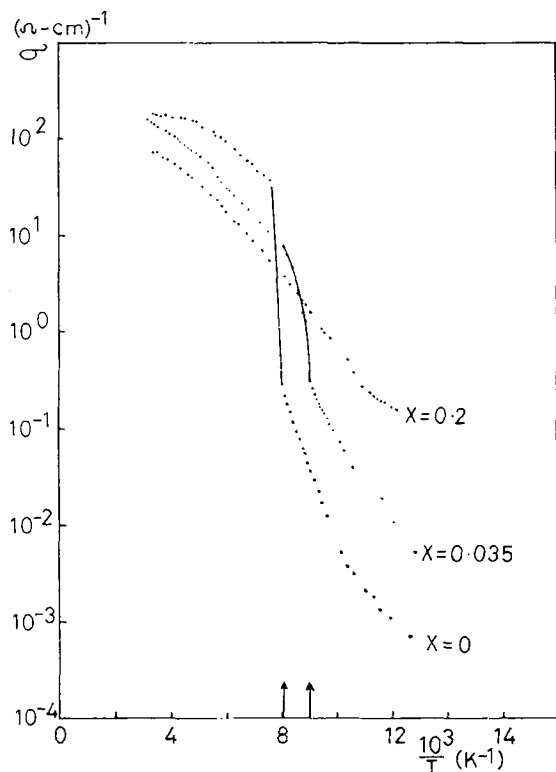


FIG. 1. — Conductivity of $\text{Fe}_3\text{O}_{4-x}\text{F}_x$ as a function of temperature. The arrows indicate the Verwey temperatures of the samples $x = 0$ and $x = 0.035$.

Between the temperature of the Verwey transition (~ 120 K) and about 200 K, it is possible to express the conductivity in the form

$$\sigma = \sigma_{\infty} \exp\left(-\frac{W}{kT}\right) \quad (1)$$

with W equal to approximately 0.06 eV, but above 200 K the conductivity increase is modified by magnetic disorder [9]. The addition of fluorine leads to a decrease in electrical conductivity, but does not appear to change the activation energy W for concentrations $0 < x < 0.25$. Similar behaviour is found in zinc and nickel-substituted magnetite in this concentration region [10].

3.2 SEEBECK EFFECT. — The temperature dependence of the Seebeck coefficient θ , for a range of compositions $\text{Fe}_3\text{O}_{4-x}\text{F}_x$, is shown in figure 2. Although not shown in the figure, a pronounced maximum for the specimen $x = 0$ is seen near the Verwey temperature T_v , in agreement with the single crystal data of Kuipers and Brabers [5].

Below the region of the Néel point, where there is a step which is largely independent of x and which is explicable in terms of magnetic ordering, all specimens show a temperature variation of θ of the form :

$$\theta = -A - BT - C/T \quad (2)$$

where A , B and C are positive coefficients.

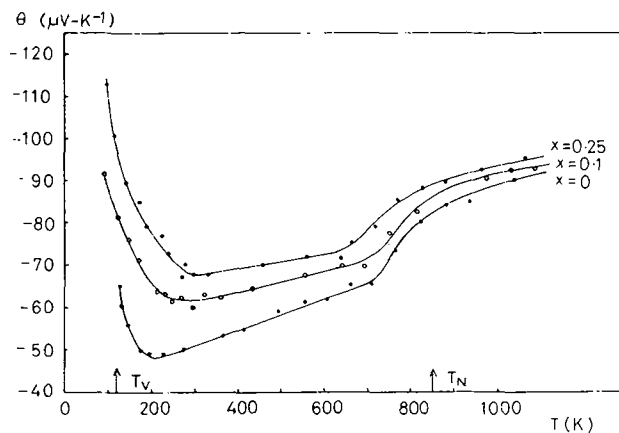


FIG. 2. — Seebeck coefficient of $\text{Fe}_3\text{O}_{4-x}\text{F}_x$ as a function of temperature. The Verwey temperature (T_v) and the Neel temperature (T_N) of the sample $x = 0$ are indicated on the figure.

As discussed below, closer inspection of the data reveals that A increases with x , B decreases with increasing x while C is independent of x . The $1/T$ term is retained below 120 K for concentrations $x > 0.05$, but in the most dilute systems a more complex behaviour occurs near the Verwey temperature.

4. Discussion. — Recent descriptions of conduction in magnetite fall into two major categories, namely the narrow-band [1] or the small polaron hopping models [2]. Neither of the appears able to offer a complete explanation of the present results. For example, the thermopower of magnetite is often discussed in terms of the well-known Heikes formula [11], which is based on a small polaron hopping model, or other similar expressions [12]. Heikes obtains a temperature independent term

$$\theta = \frac{k}{|e|} \ln \frac{c}{1-c} \quad (3)$$

where c is the concentration of carriers, which is equal to the ferrous ion concentration for the systems discussed in this paper (in the case of $\text{Fe}_3\text{O}_{4-x}\text{F}_x$, $c = 1 + x/2$). While this formula gives an approximate description of the thermopower of nickel-substituted magnetite [13, 14] it fails to account for the present observations. For $\text{Fe}_3\text{O}_{4-x}\text{F}_x$ equation [3] predicts that A in equation (2) will be negative and $dA/dc \sim -350 \mu\text{V K}^{-1}$, whereas the observed values of A are positive (for example, $A \approx +20 \mu\text{V K}^{-1}$ at $x = 0.05$) with $dA/dc \sim +300 \mu\text{V K}^{-1}$. We note that all the fluorine substituted samples are n-type and yet A increases as the ferrous-ion concentration is increased. Comparison with results for nickel-substituted magnetite [13, 14] suggests that A is possibly a universal function of the amount for substitution, irrespective of whether the ferrous ion concentration is increasing or decreasing.

Alternatively, it is possible to discard the above description of the carriers and to treat them instead as a degenerate gas, which would require the Seebeck coefficient to be taken as (3) :

$$\theta = -\frac{\pi^2}{3} \frac{k^2 T}{|e|} \left(\frac{d \ln \sigma(E)}{dE} \right)_{E=E_F} \quad (4)$$

where E_F is the Fermi energy and $\sigma(E)$ is the contribution to the conductivity from electrons of energy E . Cullen and Callen [1] discuss the properties of Fe_3O_4 in terms of a band model and find metallic or semi-metallic behaviour above the Verwey temperature, in which case ⁽¹⁾ the Seebeck coefficient should vary as $T/E_F(T)$. While this model can account for the term in θ which is linear in T , it apparently cannot, for example, explain the concentration dependence of θ .

A more promising approach which retains some the features of the above descriptions is to assume, following Mott [3], that disorder in the high temperature *metallic* phase of magnetite produces Anderson *localization* of the carriers. The origin of such *localized* states would be a lattice disorder of the type discussed for Fe_3O_4 by a number of workers [15, 16]. A qualitative density of states curve resulting from such disorder is shown in figure 3, where electrons with

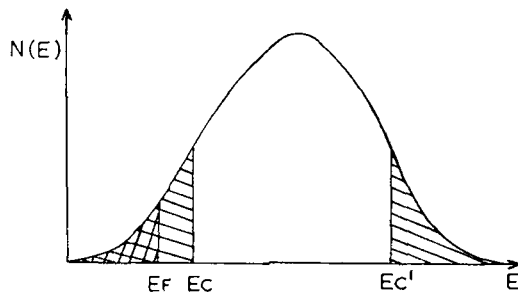


FIG. 3. — Suggested *Anderson Band* description of $\text{Fe}_3\text{O}_{4-x}\text{F}_x$. Cross-hatched area : energy levels occupied at $T = 0$; shaded and cross-hatched areas : energies where hopping transport occurs ; unshaded area : energies where band-like conduction occurs. E_F is the Fermi energy at absolute zero, E_C and E'_C separate the ranges of energy where states are localized and non-localized.

energies below E_C move by hopping between localized states while electrons with energies greater than E_C move by a band-like mechanism in non-localized states. In the present case this situation is likely to be modified by polaron formation.

Cutler and Mott [17] have shown that, if the current is due to carriers near the Fermi energy, equations (1) and (4) should apply, with W and σ_∞ as functions of energy. If then we assume [18] that

$$W(E) \simeq W_H + \frac{1}{2} W_D(E)$$

(1) Cullen, J., private communication.

where W_H , the polaron hopping energy, is considered to be larger than the disorder energy $W_D(E)$, the Seebeck coefficient would be of the form $\theta = -A - BT$ where

$$A = -\frac{\pi^2}{6} \frac{k}{|e|} \left(\frac{dW_D(E)}{dE} \right)_{E=E_F}$$

and

$$B = \frac{\pi^2}{3} \frac{k}{|e|} \left(\frac{d \ln \sigma_\infty(E)}{dE} \right)_{E=E_F}$$

The observed increase in A with x would then be attributed to a variation of dW_D/dE . The composition dependence of B , in which the experimental value decreases from $0.066 \mu\text{V K}^{-2}$ to $0.047 \mu\text{V K}^{-2}$ as x increases from 0 to 0.25, would be consistent with this form of interpretation : it would certainly suggest that the term linear in T is not associated with any magnetic ordering effect since this is expected to be relatively independent of composition.

The term C/T is a general feature of hopping processes [18, 19] ; it represents the contribution of the hopping activation energy to the Seebeck coefficient and arises in cases where the activation energy is unequally divided between the two sites involved in a hop.

The present results are consistent with a situation in which the polaron hopping energy is dominant, for otherwise W in equation (1) should increase with x [3]. In this situation Austin and Mott [18] predict a value $C \simeq 0.05 W_H/|e|$. Both C and W are here found to be independent of concentration in the range $0 < x < 0.52$, with $C \simeq 0.1 W/|e|$.

While the above description appears to be able to account qualitatively for the observed behaviour of the Seebeck coefficient, two points at least are outstanding. First, if the explanation of the increase of the term A with x is correct, then there would be expected to be an increase in activation energy W with increased fluorine concentration ; such an increase is not observed in the composition ranges studied (although it may be masked by a larger polaron hopping energy W_H). Second, the origin of the behaviour of $W_D(E)$ which is necessary to explain the increase of A with x has not been established.

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