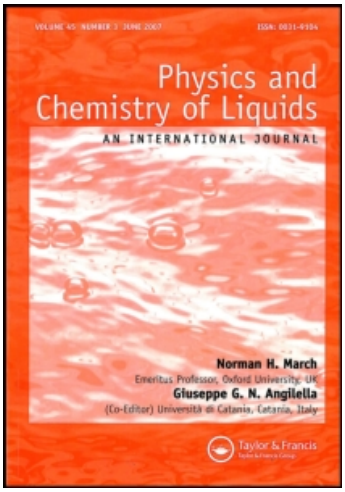

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Toshio Nasu[ab]; Kenzo Kai[a]; Kenji Suzuki[a]
[a] The Research Institute for Iron, Steel and Other Metals, Tohoku University, Sendai, Japan [b] Tohoku Dental University, Kohriyama, Fukushima Pref., Japan

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On the Temperature Dependence of Magnetic Susceptibility of Liquid Tellurium

TOSHIO NASU†, KENZO KAI and KENJI SUZUKI

The Research Institute for Iron, Steel and Other Metals, Tohoku University, Sendai-980, Japan

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The magnetic susceptibility of pure tellurium in the solid and liquid states was measured over the range of temperature from 20 to 1000°C. It was found that the temperature dependence in the magnetic susceptibility of liquid tellurium might be interpreted in terms of Cabane and Friedel's model [*J. de Phys.*, **32**, 73 (1971)] on the chain-network structural transition in liquid tellurium.

1 INTRODUCTION

Liquid tellurium is a semiconductor near the melting point as same as solid tellurium. Electrical conductivity of liquid tellurium increases abruptly near the melting point as temperature rises.[1] Several models[2–5] have so far been proposed to interpret the behaviour of electrical conductivity of liquid tellurium.

Using experimental results of neutron diffraction,[4] Cabane and Friedel[5] have described that the structure of liquid tellurium just above the melting point includes equal amounts of both the chain and network conformations of tellurium atoms. The chain conformation means an atomic arrangement in which a tellurium atom is coordinated to two nearest neighbours existing in the chain (hereafter called a tellurium atom occupying the binary site). On the other hand the three dimensional network conformation consisting of tellurium atoms connected with three nearest neighbours becomes predominant in liquid tellurium with increasing temperature (hereafter called a tellurium atom occupying the ternary site).

† Present address: Tohoku Dental University, Kohriyama, Fukushima Pref. Japan 963.

Assuming that a tellurium atom in the network conformation releases a few electrons into the conduction band, Cabane and Friedel have considered that the semiconductor to metal transition in liquid tellurium is caused by the increase of conduction electron densities due to the chain to network structure change.

This work is aimed at verifying whether the Cabane and Friedel model may be applicable to the temperature dependence in the magnetic susceptibility of liquid tellurium or not.

2 EXPERIMENT AND RESULT

The magnetic susceptibility of solid and liquid tellurium was measured as a function of temperature from 20 to 1000°C by means of a torsion balance magnetometer[6] using Faraday method. The tellurium sample of a 99.9999% was sealed in vacua in a silica capsule. Figure 1 shows that solid tellurium has a diamagnetic susceptibility of $-39.6 \pm 0.8 \times 10^{-6}$ emu/mol almost independent of temperature up to the melting point. However the diamagnetic susceptibility of tellurium varies discontinuously to $-10.9 \pm 0.2 \times 10^{-6}$ emu/mol upon melting. The absolute value of the diamagnetic susceptibility of liquid tellurium decreases gradually with increasing temperature and then a paramagnetic susceptibility appears near above 780°C. These

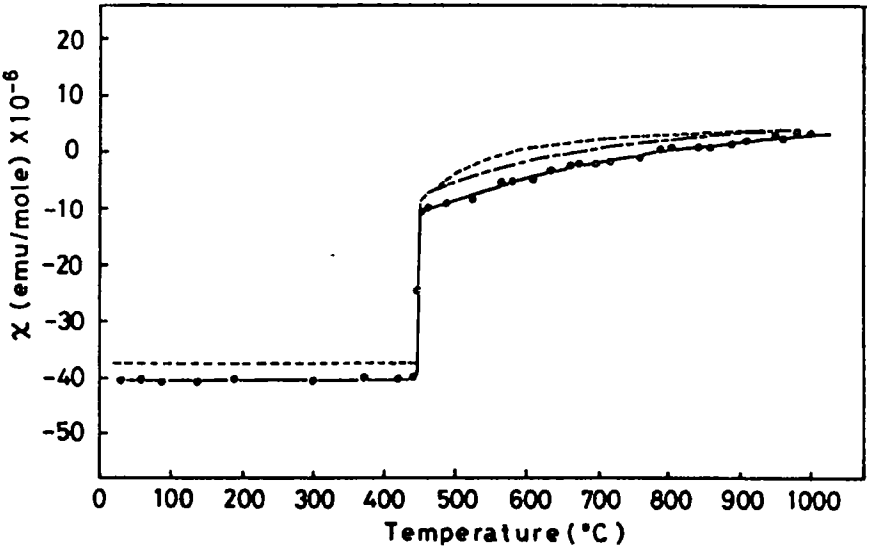

FIGURE 1 Magnetic susceptibility of solid and liquid tellurium (—O—; this work, ----; Urbain and Übelacker[7] and – – – – –; Tsuchiya *et al.*[8]).

behaviours of temperature dependence of the magnetic susceptibility of pure tellurium are in a qualitative agreement with experimental observations by Urbain and Übelacker[7] and Tsuchiya *et al.*[8]

3 DISCUSSION

The observed magnetic susceptibility χ of liquid tellurium may be regarded to consist approximately of three contributions,

$$\chi = \chi_i + \chi_p + \chi_d, \tag{1}$$

where χ_i is the ion core diamagnetic susceptibility, χ_p the Pauli spin paramagnetic susceptibility of conduction electrons and χ_d the Landau–Peierls diamagnetic susceptibility of conduction electrons.

When the diamagnetic susceptibilities due to ion cores of tellurium occupying the binary and ternary sites in liquid tellurium are assigned to χ_i^b and χ_i^t respectively, the total ion core diamagnetic susceptibility χ_i is written as the sum of the both terms

$$\chi_i = (1 - c)\chi_i^b + c\chi_i^t, \tag{2}$$

where c is the concentration fraction of the ternary site in liquid tellurium at the temperature T that has been obtained by Cabane and Friedel[5] as shown in Figure 2.

If the electronic structure of ion cores in liquid tellurium is assumed to be almost identical to that of free ions, we can find several sets of values of the ion core diamagnetic susceptibility calculated so far by several methods in the literature. Therefore proper choice of these values is critical and crucial so as to have a reasonable explanation on the magnetic behavior of liquid tellurium. Figure 3 shows the values of the ion core diamagnetic susceptibility of tellurium calculated as a function of the valence number by means of both the modified Slater's semiempirical method[9] and self-consistent Hartree–Fock method.[10,11]

On the other hand the average number of conduction electrons per tellurium atom in liquid tellurium at the temperature T is given as

$$n = (1 - c)z_b + cz_t, \tag{3}$$

where z_b and z_t are the valence numbers of tellurium ions occupying the binary and ternary sites respectively, if all the electrons released from tellurium atoms become conduction electrons. Hence the Pauli spin paramagnetic susceptibility χ_p can be calculated as

$$\chi_p = \alpha\chi_{p0}, \tag{4}$$

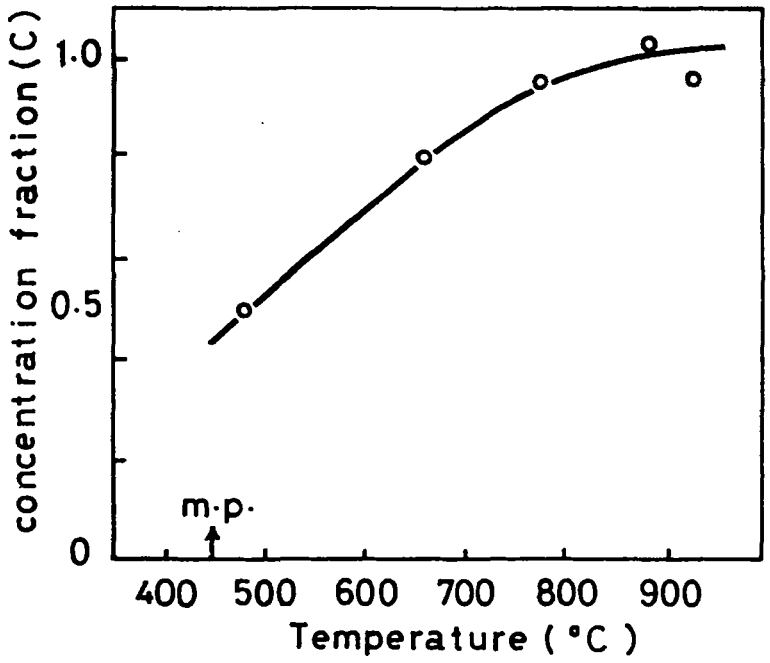

FIGURE 2 Concentration fraction of the ternary site in liquid tellurium.[5]

where $\chi_{p0} = (3/2)\{(1-c)z_b + cz_t\}\mu_B^2/(k_B T_F)$ is the Pauli spin paramagnetic susceptibility of free electrons, α is the enhancement factor due to electron–electron interactions and the temperature dependence of the Fermi distribution function is simply neglected.

The Landau–Peierls diamagnetic susceptibility χ_d is given as

$$\chi_d = \beta\chi_{d0}, \tag{5}$$

where $\chi_{d0} = -\chi_{p0}/3$ is the Landau diamagnetic susceptibility of free electrons and $\beta = 1 + \gamma r_s\{\ln r_s + 4 + \ln(\gamma/2\pi)\}/6\pi$ is the correction due to electron–electron interactions[12] where r_s is the radius of the sphere of which volume is available to each conduction electron and $\gamma = \{4/(9\pi)\}^{1/3}$.

Values of z_b and z_t are self-consistently determined under the restraint that the value of $\chi_i + \chi_p + \chi_d$ calculated from Eqs. (2), (4) and (5) using trial values of z_b and z_t becomes equal with the value of the observed magnetic susceptibility χ. In this calculation a boundary condition $z_b = 0$ was originally accepted, because the character of the chemical bond between tellurium atoms occupying the binary site in the chain conformation in the liquid state could be regarded to be very close to that in crystalline trigonal tellurium. In fact the value of the observed magnetic susceptibility of crystalline trigonal

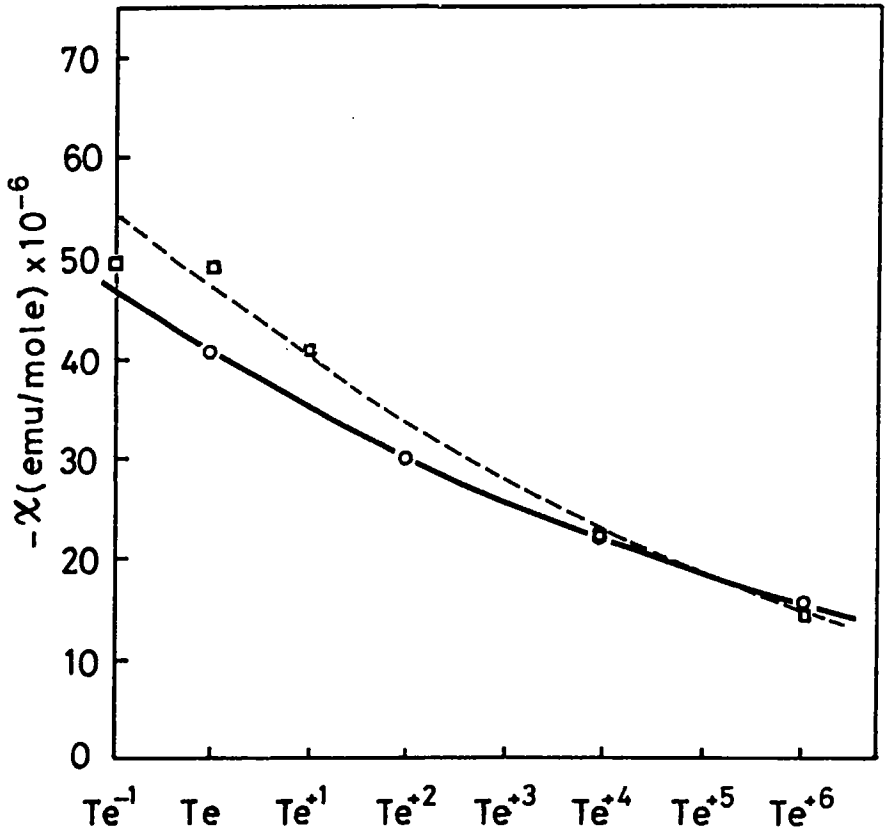

FIGURE 3 Ion core diamagnetic susceptibility of tellurium ions (—○—; modified Slater's semiempirical method and --□---; self-consistent Hartree–Fock method[10,11]).

tellurium is $-39.6 \pm 0.8 \times 10^{-6}$ emu/mol which is in an excellent agreement with the value of the ion core diamagnetic susceptibility of neutral tellurium atom calculated by Angus[9] as shown in Figure 3. Furthermore we accepted $\alpha = 1.5$ and 2.0 in this calculation according to the suggestion by Cabane and Friedel.[5] The experimental value of the atomic number density of liquid tellurium observed by Nisel'son and Glazov[13] was used in this calculation.

When the modified Slater's semiempirical method by Angus[9] is chosen for the evaluation of χ_i^b and χ_i^f, $z_t = 3.7$ is obtained for $\alpha = 1.5$ and $z_t = 2.2$ for $\alpha = 2.0$. On the other hand $z_t = 4.0$ for $\alpha = 1.5$ and $z_t = 2.5$ for $\alpha = 2.0$ are resulted from the use of the self-consistent Hartree–Fock method.[10,11]

The average number of conduction electrons per atom in liquid tellurium can be calculated from Eq. (3) using the values of c as shown in Figure 2 and z_t described above. Results are shown in Figure 4 together with the

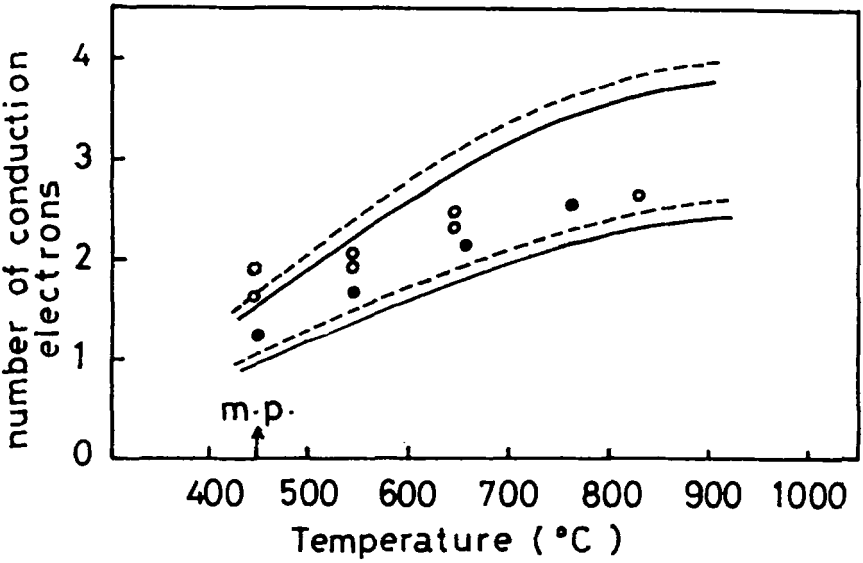

FIGURE 4 Number of conduction electrons in liquid tellurium [——— calculated using modified Slater's semiempirical method for ion core diamagnetic susceptibility (the upper line is a set of $\alpha = 1.5$ and $z_t = 3.7$, and the lower $\alpha = 2.0$ and $z_t = 2.2$); —— calculated using self-consistent Hartree–Fock method for ion core diamagnetic susceptibility (the upper $\alpha = 1.5$ and $z_t = 4.0$ and the lower $\alpha = 2.0$ and $z_t = 2.5$); ○ obtained from Hall coefficient data[2,14,15] and ● obtained from Knight shift data[16]].

numbers of conduction electrons deduced from the experimental observations of Hall coefficients[2,14,15] and Knight shift[16] by Cabane and Friedel.[5]

Dupree and Seymour[17] have described that the choice of Angus's values for the ion core diamagnetic susceptibility is best to deduce quantitatively reasonable values of the Pauli spin paramagnetic susceptibility of conduction electrons in 18 liquid metals. This trend also is verified in the present observation that the ion core diamagnetic susceptibility can reproduce a better agreement between the calculation and experiment of the temperature dependence in the magnetic susceptibility of liquid tellurium near the melting point than the self-consistent Hartree–Fock method, whatever values of the set of α and z_t are chosen.

Figure 4 shows that a combination of $\alpha = 2.0$ and $z_t = 2.5$ with the value of the ion core diamagnetic susceptibility by the self-consistent Hartree–Fock method happens to give a best agreement about the average number of conduction electrons between the present and Cabane and Friedel's results. The value of z_t is quite sensitive to the choice of the value of α rather than the ion core diamagnetic susceptibility. Furthermore Dupree and Seymour have obtained a relationship between α and r_s for 18 liquid metals, from which the

values of $\alpha = 1.5 - 1.8$ may be expected for liquid tellurium in the temperature range from the melting point to 800°C. The values of $\alpha = 1.5$ and 2.0 adopted this work are interestingly consistent with those expected from Dupree and Seymour's work.[17]

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