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ELECTRONIC TRANSPORT IN METAL-AMMONIA SOLUTIONS

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1. Introduction

Conductivity measurements are an important tool in the investigation of the charge transport mechanism in disordered materials. The dc transport in solid disordered materials is expected to be of electronic nature involving band conduction or hopping between localized states or both [1]. On the other hand the origin of the ac transport is more controversial [2] involving electronic hopping [3,4] or lattice vibrations [5] or many-body interactions of some charged hopping particles with the surrounding dielectric medium [6]. Both from the theoretical point of view and experimentally the discrimination between dc and ac conduction is hampered due to the fact that the ac transport properties prevail down to the audio or even subaudio frequency range [2]. In these investigations metal-ammonia solutions could play a prominent role since, depending on the metal concentration, the number of charge carriers and, consequently, the transport properties can be varied on a large scale. Furthermore, the structure of these solutions in the concentration range far below the metal-non metal transition is probably better understood than in the case of solid disordered materials. In this communication we report on conductivity measurement of

Li-NH₃ solutions between 0.01 and 1 mole per cent metal (MPM) and in the frequency range $5 \cdot 10^3$ - 10^7 Hz. The conductivity of this system is compared with the conductivity of solid disordered materials in terms of a unified description of the polarization phenomenon which emphasizes the different role of harmonic and relaxational modes of the medium.

2. Experimental

Up to frequencies of 10^7 Hz glass cells with platinum electrodes were used for the conductivity measurements in Li-NH₃ solutions. In order to obtain high enough cell resistances, especially with the more concentrated solutions, the dc path between the electrodes was lengthened by guiding the current in glass tubes which were submerged in the solution. In the experimentally difficult frequency range 10^7 - 10^9 Hz there are no experimental data available. Above 10^9 Hz the conductivities can be obtained from the shift of the resonant frequency and the change of the Q factor due to the insertion of the solution in a microwave resonator [7].

3. Experimental results

In Fig. 1 the solid lines show the results for the conductivity σ at 216K up to 10^7 Hz. The conductivity remains virtually

on the dc level; a slight increase of σ' with increasing frequency of 2 per cent at most is in the order of magnitude of the

Fig. 1. The conductivity of Li-NH₃ solutions versus frequency (solid lines). Dotted lines see text.

accuracy. As the frequency approaches 10^7 Hz the measured resistances of the conductivity cell seem to indicate a rapid increase of conductivity (dotted lines in Fig. 1). However, the specific construction of the glass cell mentioned above leads to apparently enhanced conductivities at high frequencies due to Maxwell-Wagner type losses [8]. For the activation energy of σ' between 200 and 240 K a value of 0.07 eV is obtained.

Results for the complex dielectric constant $\epsilon = \epsilon' + i\epsilon''$ of a 0.1 MPM Li-NH₃ solution at 238 K in the microwave frequency range [7,9] are shown in Fig. 2. The total polarization loss can be separated into the

orientational relaxation of the ammonia molecules, dominating around 10^{11} Hz, and an additional relaxation process around 10^{10} Hz attributed to associations of charged species in the solution [7].

Fig. 2. Real and imaginary parts of the dielectric constant versus frequency for Li-NH₃ solutions. Solid lines, best fitting theory. ϵ'' is separated in NH₃ relaxation ----- and additional relaxation -.-.-.

In Fig. 3 the data are represented in a uniform manner, showing the conductivity in the frequency range up to 10^6 Hz together with the microwave conductivity associated with the additional absorption in Fig. 2 and the dc loss, $\sigma' = \omega\epsilon''/4\pi + \sigma_{dc}$.

4. Discussion

a-As₂Se₃ is one of the few solid disordered materials for which the conductivity has been measured in a comparatively large frequency range. These data are plotted in Fig. 3. In contrast to Li-NH₃ solutions its dc conductivity ($\sigma_{dc} \approx 10^{-13}$ 1/Ωcm) is negligible in comparison with the ac

conductivity above 10^3 Hz. Below 10^9 Hz σ' increases with frequency approximately as [10,11]

$$\sigma' - \sigma_{dc} \sim \omega^n \quad (1)$$

with $n \lesssim 1$. A similar behaviour has been observed in a wide class of solid disor-

Fig. 3. The conductivity of Li-NH₃ and a-As₂Se₃ versus frequency. The data for a-As₂Se₃ are from Ref.10 ($\Delta, \blacktriangle$), Ref. 11 ($\circ$), and Ref. 12 ($\bullet$).

dered materials [1,2]. Above 10^9 Hz σ' increases nearly as [10,12]

$$\sigma' - \sigma_{dc} \sim \omega^2 \quad (2)$$

and above 10^{12} Hz the experimental data seem to indicate a saturation behaviour

$$\sigma' = \text{const.} \quad (3)$$

Any ac conductivity can be described in terms of the following generalized equation of motion for the polarization

$$\gamma \frac{d}{dt} P(t) + \int_0^\infty [D_0 \delta(\tau) - d(\tau)] P(t-\tau) d\tau = E(t), \quad (4)$$

which establishes a causal, linear relationship between the Maxwell field E and the polarization P . In the memory kernel

in Eq.(4) an instantaneous term $D_0 \delta(t)$ is split off, $d(t)$ is the true memory function, and γ and D_0 are constants. Equation (4) gives the following complex dielectric susceptibility, $\chi = \chi' + i\chi'' = (\epsilon - 1)/4\pi$:

$$\chi = [D_0 - d_\omega - i\omega\gamma]^{-1}, \quad (5)$$

where $d_\omega = \int_0^\infty d(t) e^{i\omega t} dt$. The instantaneous term without any memory effects leads to a Debye form for the susceptibility with relaxation time $\tau = \gamma/D_0$. In the pair hopping model [13] this relaxational behaviour is usually ascribed to the interaction between hopping charges and harmonic (phonon) modes of the medium [14]. If, however, relaxational modes of the medium respond slowly with respect to changes of the occupancy of the hopping sites, memory effects occur (Eq.4).

It can be shown [15] that the general conductivity behaviour Eq.1 exhibited by a wide class of solid disordered materials and in particular the ac conductivity of a-As₂Se₃ up to 10^{13} Hz (Eqs. 1-3) is reproduced by

$$d(t) = d_0(t+\alpha)^{n-2}, \quad n \lesssim 1, \quad (6)$$

where $1/\alpha$ is an upper cut-off frequency for the medium response d_ω . The ac conductivity of a-As₂Se₃ is obtained with the following set of parameters [15]: $\tau = 10^{-13}$ sec, $D_0 = 15$, $\alpha = 10^{-11}$ sec, $d_0/D_0 = 1$ and $0.95 < n < 1$. The dotted lines in Fig. 3 show the conductivities according to this phenomenological model for $n=0.95$ and $n=0.999$. It can be seen that with decreasing n the losses at low frequency increase and that then the regime $\sigma' \sim \omega^2$ shrinks in favor of the regime $\sigma' \sim \omega^n$, $n \lesssim 1$. In some disordered systems n may be so small that no region

$\sigma' \sim \omega^2$ can be observed.

The frequency dependency of σ' at high frequencies for both the systems of Fig. 3 can be described on the basis of a Debye relaxation process. Unfortunately the high dc level of the Li-NH₃ solution prevents the experimental investigation of the ac transport at frequencies far below the Debye relaxation frequency. However, on the basis of the following reasons one can not expect memory effects in metal-ammonia solutions which slowly decay in time as in a-As₂Se₃ (Eq.6). Ultrasonic absorption measurements indicate that a-As₂Se₃ responds to mechanical stress with a wide distribution of structural relaxation times [16]. If these modes are coupled with the hopping charges long-tail memory effects as represented by Eq.6 could arise. On the other hand, structural relaxation times in dilute solutions of Li-NH₃ are in the order of about 10⁻¹² sec [17]. The corresponding memory function may be written

$$d(t) = d_0 e^{-t/\theta}, \quad (7)$$

where θ should be in the order of the structural relaxation time.

For a paraelectric static susceptibility $D_0 > d_0$ is required. Since $\theta \approx 10^{-12}$ sec and $\omega\theta \ll 1$ in the investigated frequency range, Eq. 7 inserted in Eq. 5 gives approximately the Debye-type susceptibility

$$\chi = \frac{1}{D_0} [1 - i\omega\tau']^{-1}, \quad (8)$$

where $\tau' = (\tau + \theta d_0/D_0)/(1 - d_0/D_0)$ and $D'_0 = D_0 - d_0$.

The conductivity corresponding to Eq. 8

$$\sigma' - \sigma_{dc} = \omega^2 \tau' / D'_0 (1 + \omega^2 \tau'^2) \quad (9)$$

fits the experimental data (solid line in Fig. 3) for $\tau' = 1.3 \cdot 10^{-11}$ sec and $D'_0 = 1.3$. According to Eq. 9 $\sigma' - \sigma_{dc}$ increases as ω^2 for $\omega\tau' \ll 1$ and saturates for $\omega\tau' \gg 1$. This behaviour is in near coincidence with experimental results for this quantity [9].

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