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AC CONDUCTIVITY OF DISORDERED SOLIDS BELOW 10^{11} Hz

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Abstract.- Models for the ac conductivity of disordered solids are reviewed. The difficulty of these models with experimental data particularly at low temperatures is emphasized. An alternate model is outlined which is based on a generalized distribution of low energy configurational two-level systems. Results for the ac conductivity over wide temperature and frequency ranges for the ionic conductor Na β Alumina are presented. The implication of these results to semiconducting glasses is briefly discussed.

Introduction.- At low frequencies ($<10^6$ Hz) the ac conductivity of glasses and many other disordered solids is characterized by a power law dependence such that $\sigma \sim \omega^n$ where $n \leq 1$ (1). We will briefly discuss the models (2,3) that have been proposed to explain this behavior and point out some of their limitations. We conclude that an interpretation which is more consistent with experimental results requires that one take into account ac conductivity measurements at higher frequencies (10^8 - 10^{11} Hz). Such measurements, particularly at low temperatures (<10 K), require the existence in glasses of low energy two-level configurational modes (TLS). We propose that a generalized distribution $N(E)$ of TLS which is nearly constant at "high" energies, corresponding to the experimental temperature range (0.01-10K), and which is proportional to E^{-1} as $E \rightarrow 0$ can account for the essential features of the ac conductivity in the majority of disordered solids. We stress, that in addition to the availability of data over a wide frequency range, it is necessary that measurements are available over a wide temperature range, including very low T (<1 K). On the basis of the limited data that is available we show that two-level configurational modes can make a significant and possibly dominant contribution to the ac conductivity of certain disordered materials. We suggest that the contribution of such modes to the ac conductivity of semiconducting chalcogenide glasses be considered in the manner to be discussed below. This is in contrast to earlier suggestions regarding the involvement of low energy structural modes, specifically via a hopping mechanism (4).

Previous Models.- The ac conductivity of disordered solids can be expressed in a generalized way as $\sigma(\omega, T) = B(T)\omega^{n(T)}$. Austin and Mott (2) have proposed that the ac conductivity is due to thermally assisted quantum-mechanical tunneling (QMT) of charged carriers (not structural modes) between localized states near the Fermi level (1). Although certain qualitative experimental features are predicted by the model, several specific predictions are at variance with experimental data. Difficulties include the predicted temperature and frequency dependences as well as an unusually large predicted density of states $N(E_F)$. The model has further difficulties if it is assumed that electrons (or holes) form diamagnetic paired states in the energy gap of the chalcogenide glasses. The tunneling of pairs of carriers need then be considered in the QMT framework, but Phillips (5) has pointed out that this process is extremely unlikely. As an alternate explanation of ac conductivity data of chalcogenide glasses, Elliott (3) has considered a model in which two electrons are thermally activated over a potential barrier. In terms of the Mott-Street (6) (or Kastner, Adler, Fritzsche (7)) formalism of defect states the electron pair hops from a doubly occupied D^- state to a nearby D^+ center. The coulombic interaction energy between the two neighboring sites is considered to lower the binding energy

W , and the barrier height W will become a random variable due to variations in the distance R separating the two centers: $W = W_0 - 8e^2/\kappa R$, where κ is the bulk dielectric constant. The hopping of the two electrons is described by the pair relaxation time $\tau = \tau_0 \exp(W/kT)$ where τ_0 is of the order of an atomic vibrational period. Assuming a random arrangement of defect sites with concentration N , Elliott arrives at the result (3)

$$\sigma(\omega) = \frac{N^2}{2} \omega \int_{\tau_{\min}}^{\tau_{\max}} \frac{e^2 R^2}{3kT} \frac{\omega \tau}{(1 + \omega^2 \tau^2)} 4\pi R^2 dR \quad (1)$$

Elliott assumes that $\tau_{\min} = \tau_0$ which implicitly assumes that the smallest barrier height W can be exactly equal to zero. This assumption is subject to question. If $W=0$ then the "non-intimate valence alternation pairs" as considered by Elliott would be unstable. Moreover, the intimate valence alternation pairs (7), having an even large coulombic interaction, could not exist as conceived. On the other hand, a non-zero lower bound $W_{\min}$ implies that $\tau_{\min} = \tau_0 \exp(W_{\min}/kT)$ which will lead to a considerable deviation from the $\sigma \sim \omega^n$, $n \approx 1$ behavior at sufficiently low temperatures where $\omega \tau_{\min} \gg 1$. An excellent test of this model then would be a measurement of $\sigma(\omega, T)$ of chalcogenide glasses at very low temperatures ($\ll 1K$). Such measurements are not presently available. There do exist ultra-low temperature measurements of the ac conductivity between 10^2 - 10^4 Hz for the superionic conductor Na β Alumina (8). On the basis of the experimental results we suggest that the model interpretation discussed in the next section should be considered as a viable alternative for the case of ac conductivity in glasses and in particular the semiconducting chalcogenide glasses.

Data and Model Interpretation.— Because of an inherent configurational disorder among the Na cations, the crystalline material Na β Alumina exhibits low temperature thermal, dielectric and acoustic properties which are generally associated with glassy solids (8-10,12). In particular, this material exhibits the ω^n ac conductivity with $n \approx 1$ at low T . Experimental results for $\sigma(\omega, T)$ versus ω and T are displayed in Figs. 1 and 2. The low temperature microwave data ($\sim 10^{10}$ Hz), shown in the upper part of Fig. 1 can be quantitatively interpreted with a model of glass-like two-level structural states (TLS), provided that a nearly constant density of excitations over the accessible energy range (0.01-10K) is assumed (8,9). A characteristic minimum is observed in the ionic conductivity near $T \sim 10K$ at 10^{10} Hz. Very similar, but not as detailed results exist for chalcogenide and oxide glasses which indicate that the microwave conductivity results are very general features of glassy solids (12). The observed minimum is the result of competing dielectric losses due to the resonant excitation of TLS at low T ($< 10K$) and the relaxation via processes of optically excited TLS, which dominates for $T > 10K$. The step-like features in the 10^2 to 10^4 Hz data near 0.1-1K in Fig. 1 can be identified with the inflection due to σ_{rel} near 20K at 10^{10} Hz. The resonant contribution σ_{res} decreases as ω^2 and therefore does not contribute above 0.01K at 10^2 - 10^4 Hz. A single expression for σ_{rel} can be shown to fit the 10^2 - 10^4 Hz as well as the 10^{10} Hz data (13). At the very lowest temperatures, however, a conductivity term $\sigma \sim \omega^n$, $n \approx 1$, needs to be invoked. This term apparently has saturated in magnitude at 10^{10} Hz (see Fig. 2). For low $T < 10K$ the conductivity can be expressed as

$$\sigma(\omega, T) = B\omega^n + \sigma_{\text{res}} + \sigma_{\text{rel}} \quad (2)$$

where $B \cong \text{constant}$ and $n \approx 1$ ($n > 0$ at frequencies $\gtrsim 10^8$ Hz). The quantities σ_{res} and σ_{rel} are given by (8,9)

$$\sigma_{\text{res}} = \frac{4\pi^2}{c} \bar{N} p^2 \tanh \frac{\hbar\omega}{2kT} \quad (3)$$

and

$$\sigma_{\text{rel}} = \frac{2\pi}{c} \bar{N} p^2 \frac{\omega^2}{kT} \int_0^\Delta dE \operatorname{sech}^2 \frac{E}{2kT} \int_{T_{\min}}^\infty dT_1 \frac{(1 - T_{\min}/T_1)^2}{1 + \omega^2 T_1^2} \quad (4)$$

Fig. 1. Conduction plane conductivity of Na- β Alumina. Data at 10^2 - 10^4 Hz: solid lines - Anthony and Anderson (Ref. 8); symbols - Grant et al. (Ref. 11). Data at 10 GHz from Refs. 9 and 10.

Fig. 2. AC conductivity of Na- β Alumina. Dots - Strom et al. (Ref. 10); 77K, 113K data - Grant et al. (Ref. 11); 0.03K data - Anthony and Anderson (Ref. 8).

where $T_1^{-1} = AE^3 \coth(E/2kT)$ is the one-phonon relaxation rate, $T_1^{-1} = T_1^{-1} (\Delta_0/E)^{2\min}$ (Δ_0 is an overlap energy), and where p is the TLS dipole moment and $\bar{N}$ the constant TLS density of states. The nature of the $B\omega^n$ term can be understood within the framework of the dielectric response theory due to Ngai (14). In this theory, the sudden polarization change due to the motion of some polarizable species (such as a subset of TLS) couples to the distribution $N(E)$ of low energy excitations in the solid. The distribution function has the form $N(E) \sim E$ for sufficiently small E , but levels off and turns over at higher energies (14). The linear dependence on E is the result of the mutual repulsion of energy levels. The width and height of the distribution depends on details of the interaction between levels. A schematic drawing of $N(E)$ is shown in Fig. 3. The linear dependence on E defines Region 1 which leads to the $\sigma \sim \omega^n$ ($n=1$) dependence observed at the lowest temperatures. Region 2 contributes to σ_{rel} and σ_{res} as discussed previously. The leveling off of $N(E)$ above 10^8 Hz accounts for the lack of a $B\omega^n$ contribution at 10^{10} Hz at low temperatures (<10 K). The saturation of the ac conductivity at microwave frequencies, which is expected from the $N(E)$ distribution in Region 2, is more apparent in the microwave data at 77K and above (Fig. 2). These results demonstrate the interplay between the two distinct regions of the TLS density of states. In particular, what is interpreted here as contribution due to σ_{rel} at 10^2 - 10^4 Hz between 0.5 and 10K exhibits also a ω^n ($n \sim 1$) (see eq. 4 for large T) dependence which is typical of

Fig. 3. Schematic drawing of density of states $N(E)$ of two-level systems for $\text{Na}\beta$ Alumina. Energy dependence of N in Region 2 is only qualitative.

relaxation effects but which we can associate directly with the states corresponding to Region 2 of Fig. 3. Careful temperature dependent measurements of glasses in the low frequency region are therefore clearly required in order to distinguish between contributions to the ac conductivity which have potentially different physical origins.

Extension of these results to chalcogenide glasses will require consideration of the intrinsic electronic structure of these materials. Configurational TLS are general properties of materials such as As_2S_3 and As_2Se_3 . Therefore the generalized density $N(E)$ in Fig. 3 should also apply. From this follows that the low temperature ac conductivity is very likely dominated by TLS processes. Nevertheless, the proposed bipolarons invoked by Elliott may be intimately tied to the TLS. At elevated temperatures the bipolarons are thermally excited leading to ac loss related to the process proposed by Elliott. This process is expected to reduce the magnitude of the parameter n in the Ngai dielectric response theory from unity to a smaller value. Evidence for the "melting" of the glass-like distribution of TLS and a subsequent temperature dependent $n(T)$ exists for $\text{Na}\beta$ Alumina (13,15). It is not clear whether this concept can be extended to the semiconducting glasses.

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