

SEMICONDUCTIVITY OF GLASSES*

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Conductivity edges inside the bands are proposed to be responsible for the thermal activation energy of the semiconductivity in glasses. Coulomb-repulsive centers provide the potential barriers, above which carrier drift becomes the predominant charge transport mechanism for narrow gap glasses, yielding a reasonable value for carrier mobility and providing quantitative explanation of the typical behavior of the conductivity. Ambipolar conductivity and highly perturbed band edges due to charged defects are suggested to be responsible for the small observed Hall mobility.

In spite of several recent attempts¹⁻³ to explain the charge transport in semiconducting glasses, the process is little understood. This is so, although for the great majority of the glasses the electrical properties are rather similar: The conductivity is of *p* type, as indicated by a positive Seebeck coefficient,^{3,4} and is given by⁵⁻⁷

$$\sigma = \sigma_0 \exp\left[-\left(\frac{\Delta E}{kT} - \frac{V}{V_0}\right)\right] \quad (1)$$

with $10^3 < \sigma_0 < 10^4 \Omega^{-1} \text{ cm}^{-1}$. The activation energy ΔE is larger⁸⁻¹⁰ by about 0.2 ± 0.1 eV than half the optical band gap,¹¹ $E_g/2$. ΔE is constant over a large temperature range, usually including the softening range of the glass; $\Delta E - E_g/2 = \epsilon$ varies little with the chemical composition (responsible for E_g) but somewhat with the procedure of glass formation.⁵ The voltage dependence given in (1) can be observed at high fields^{6,7} (thin glass layers) and yields empirically $V_0 = cLT$ with L the distance between the electrodes and $c \approx 200 \text{ V/cm deg K}$. Typical curves indicating this behavior obtained for glass samples sputtered from an ingot of composition $\text{Ge}_{12}\text{As}_{30}\text{S}_{25}\text{Se}_1\text{Te}_{22}\text{V}_1$ onto graphite electrodes are given in Fig. 1. (For thick glass samples and higher temperatures, or higher conductivities, deviations from this simple relationship are observed when inhomogeneous Joule heating^{13,14} is estimated to begin; at low temperatures a transition to an exponential branch with a smaller V_0^* is observed with $V_0^*/V_0 \approx 2$; detail will be reported later.)

All these observations could, in fact, have been explained with a relatively simple model (see below), if it were not for the fact that the Hall mobility and the drift mobility of carriers in glasses are very small^{1,2,5} (usually $< 1 \text{ cm}^2/\text{V sec}$), and these mobilities often have been identified with the microscopic carrier mobility. But small carrier mobilities are in contradiction to this simple model. Recently, however, it was pointed out^{15,16} that the Hall mobility in these glasses

can be considerably smaller than the carrier mobility and we will therefore re-examine the car-

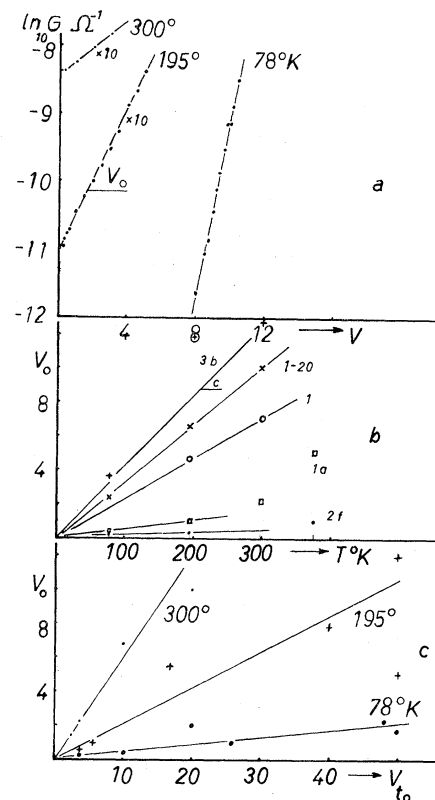


FIG. 1. (a) Current-voltage characteristics of layer 1a [see (b)] of a thickness of about $0.3 \mu\text{m}$ at different temperatures. (b) Slope V_0 of the exponential part of the current-voltage characteristics for samples of different thicknesses as function of temperature. With a slope $c = kL/1.5el$ of these curves and an estimated $l \approx 25 \text{ \AA}$ one obtains a layer thickness of 0.11, 0.22, 1.1, 1.5, and $2 \mu\text{m}$ for layers 2f, 1a, 1, 1-20, 3b, respectively. (c) Slope V_0 as in (b) as function of the minimum threshold voltage V_{t0} for switching (Ovshinsky effect) (Ref. 12) for different temperatures. With $V_{t0}/L = F_c$, one obtains from the slope of these curves a critical field $F_c(300^\circ\text{K}) \approx 1.2 \times 10^5 \text{ V/cm}$, $F_c(195^\circ\text{C}) = 2 \times 10^5 \text{ V/cm}$, and $F_c(78^\circ\text{K}) = 3.4 \times 10^5 \text{ V/cm}$. Such decrease of the critical field with increasing temperature is generally observed (Ref. 6).

rier transport using a simple model of a highly disordered nearly compensated semiconductor.

Charges can be transported in such a semiconductor within the bands or in the gap utilizing the high density of defect levels, as indicated in Fig. 2(a), i.e., via drift^{15,16} (1), percolation^{1,2} (2), or hopping³ (3, 4). For obtaining the activation energy of the measured conductivity, one must determine the predominant contribution of the competing transport processes,

$$\sigma = e \int_{-\infty}^{E_F} \mu(E) N(E) f_p(E) dE = \int_{-\infty}^{E_F} \sigma(E) dE \quad (2)$$

(here given for holes) with $N(E)$ the level density and $f_p(E)$ the Fermi function for holes. Estimations given by Böer¹⁷ show that $\sigma(E)$ has a shape as shown in Fig. 2(b), with a maximum contribution from carrier drift, if such drift occurs not too far from the band edges (<0.3 eV at 300°K).

In contrast to crystalline semiconductors, this drift occurs above potential barriers^{18,19} which can be provided by a statistical distribution of charged defects.² The barriers can be identified as saddles between Coulomb-repulsive centers¹⁵ [A in Fig. 2(c); Fig. 2(c) is similar to Fig. 2(a) but with magnified spatial coordinate]. Assuming that scattering at Coulomb-repulsive centers determines the mobility, one sees that the mobility is steeply increased at energies larger²⁰ than the average saddle energy and at kT (300°K) above the saddle can be estimated to be ≈ 100 cm²/V sec (the scattering cross section of these

defects is drastically reduced). The average saddle energy, ϵ , depends on the density of charged defects¹⁵ and for $N_t \approx 10^{19}$ cm⁻³ is of the order of 0.2 eV.

In contrast to the band edge, E_g , responsible for the steep increase in optical absorption, we will refer to the separation of the predominant conductivity ranges from the Fermi level [Fig. 2(b)] as the conductivity edge,²¹ $\Delta E = E_F - E_v + \epsilon + kT$, and since it can be concluded that the Fermi level lies very close to the middle of the band gap,^{1,2,15} it follows that

$$\Delta E \approx \frac{1}{2} E_g + \epsilon + kT \quad (3)$$

as estimated in Ref. 15 (the precise location of E_g must await a better analysis of the problem at what level density a boundary between localized and nonlocalized states can be drawn).

At the conductivity edge the mean free path is estimated¹⁵ to be of the order of 100 Å, i.e., for noncrystalline solids with a density of charged defects usually $\geq 10^{19}$ cm⁻³, somewhat longer than the mean distance between the potential barriers (ϵ). This allows for a simple approach for the high-field conductivity: Assuming the average distance of a potential saddle from an effective donor to be $1.5l$ [Fig. 2(c), distance A, B], with l the average distance between defects, one estimates a barrier lowering of $\delta\epsilon \approx 1.5eFl$ by the external field (F) and hence an

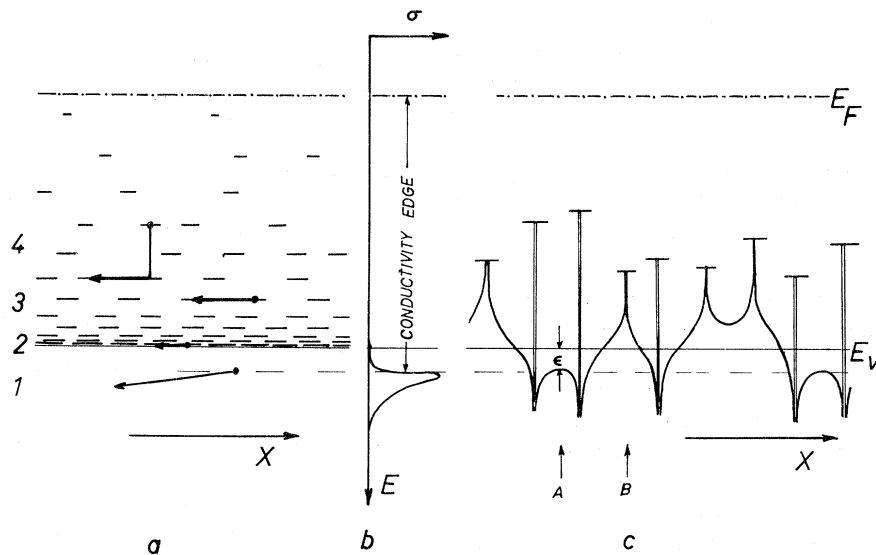


FIG. 2. (a) Level distribution in a semiconducting glass with different conduction mechanisms: 1, carrier drift; 2, percolation; 3, hopping without, and 4, hopping with thermal activation (shown for p -type conductivity). (b) Conductivity distribution and conductivity edge. (c) Potential distribution due to Coulomb-attractive and Coulomb-repulsive defects. E_v indicates the unperturbed edge of the valence band.

increased conductivity

$$\sigma = \sigma_0 \exp[-(\Delta E - \delta\epsilon)/kT]. \quad (1a)$$

By comparison with Eq. (1) one obtains $V_0 = kTL/1.5el$, or $c = k/1.5el$.

From the observed ϵ of 0.25 eV in the chalcogenide glass used,¹⁵ one can estimate l to be of the order of 25 Å and hereby one obtains $c \approx 230$, which is in excellent agreement with the experimental value. The proportionality of V_0 with T and L is also observed. These facts indicate that the proposed model is applicable and indeed the carrier mobility is considerably higher than the Hall mobility²² (the carrier mean free path must surpass l in order to observe this effect, i.e., μ must be at least 50 cm²/V sec for carriers with $m_p \approx m_0$). The Hall mobility can be somewhat reduced below the carrier mobility by the probably ambipolar character of the conductivity¹⁵ (the Fermi-level position close to the middle of the gap is suggested by the observed insensitivity of the conductivity even to moderate doping, and by the history of glasses as being quenched liquids, which have a perfect ability for self-compensation). The Hall mobility is probably drastically reduced due to charged defects, making the glass on a microscopic scale highly inhomogeneous in respect to its potential distribution.¹⁶

Assuming the Fermi level to be in the middle of the gap, one obtains $n/p = N_c/N_v = (m_n/m_p)^{3/2}$. With simple isotropic parabolic (near the gap) bands, as expected for glasses,⁵ one infers $m_n < m_p$ and consequently p -type conductivity.

With scattering at Coulomb-repulsive centers, as referred to above, one estimates¹⁵ a mean free path $\lambda_p \approx \lambda_n \approx 60$ Å at $\epsilon + kT$ inside the bands (at the conductivity edge). Assuming $m_p \approx m_0$ one obtains at room temperature a hole mobility of 100 cm²/V sec. With¹⁵ an effective level density at $E_v - \epsilon - kT$ of $N_v(\epsilon + kT) = 4 N_v[(\epsilon + kT)/\pi kT]^{1/2} = 10^{20}$ cm⁻³ one obtains $\sigma_0 \approx 2 \times 10^3 \Omega^{-1} \text{cm}^{-1}$ again in good agreement with the experiment.

The fact that all known experimental data, as well as the general behavior of semiconducting glasses, can be explained with the proposed simple model makes accidental fitting highly improbable. It is therefore concluded that the conductivity edge of these semiconducting glasses¹² lies a considerable distance inside the bands (~ 0.2 eV), the mobility is of the order of 100 cm²/V sec, the conductivity σ , being of p type, is controlled by barriers caused by Coulomb-repulsive centers, and σ can be markedly increased by lowering these barriers in an external electric

field.

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²⁰The band edge is drawn as boundary between localized and nonlocalized states. This may result in a band gap E_g which is different by $E_g - E_{gc} = \delta E$ from the one for the same material in the crystallite state, E_{gc} . For comparison with the experiment it is assumed that $\delta E \ll \epsilon$.

²¹It is misleading to speak about a mobility edge, since there exist several mobility edges for competing transport processes, and without evaluating Eq. (2) it is not transparent which one of these edges contributes

most to the conductivity. Moreover, the mobility edge has little connection to the optical absorption as suggested in Ref. 1.

²²A model recently proposed by M. Cohen yielding a similar result (Ref. 2) poses difficulties since he assumes carrier percolation with a "mean free path" short compared to the distance between barriers, and

that the barriers are produced by space-charge fluctuations, causing potential valleys of ~ 0.1 eV. These difficulties force the assumption (Ref. 2) of a long equilibrium distance between hole and electron quasi-Fermi levels of ≈ 1 μm , and deal with the fact that localization in shallow potential valleys (0.1 eV) cannot be achieved (uncertainty relation).

MAGNON SPECTRUM OF ALPHA OXYGEN*

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The far-infrared absorption in solid alpha oxygen at 27 cm^{-1} is shown to be definitively associated with the magnetic rather than orientational ordering in the crystal. A second magnetic excitation has been found at 6.5 cm^{-1} . The properties of both absorptions are described using the excitation-wave formalism.

It has been well established that structural phase transitions occurring at low temperatures in simple diatomic molecular solids are associated with the rotational degrees of freedom of the molecule.¹ In particular, the α - β transition in oxygen is coincident with the onset of precession of the molecules.² It is also coincident with the Néel point of the electronic spin system, clearly emphasizing the possibility of interdependence of the orientational and magnetic ordering in the crystal. With these considerations in mind, we have experimentally and theoretically re-examined the magnon spectrum of α oxygen. The excitation-wave method has been applied to a biaxially anisotropic magnetic structure to explain satisfactorily the energies, relative intensities, and magnetic-field dependence of magnons observed in our own and earlier work.

Molecular crystals such as α - N_2 are known to exhibit phonon absorptions in the far infrared with temperature-dependent frequencies and intensities near the transition from the α to the β phase.³ Therefore, for α - O_2 , observation of temperature-dependent behavior for the 27-cm^{-1} absorption⁴ is not sufficient evidence to associate it with magnetic excitation. Absence of an isotopic mass shift would be sufficient. Thus a sample of 99.2% isotopically pure α - $^{18}\text{O}_2$, 3.1 mm thick, was grown, and its far-infrared spectrum measured at 1.6°K. The frequency shift of $\sim 1.5\text{ cm}^{-1}$ expected for the 27.5-cm^{-1} line, had it been a phonon, was not observed.⁵

It should now be possible to construct a phenomenological spin Hamiltonian which would predict the 27.5-cm^{-1} magnon. On the basis of the monoclinic symmetry (C_{2h}^3) of the crystal lat-

tice⁶ and the assumption of isotropic exchange, we write

$$H = \sum_i (AS_{ix}{}^2 + BS_{iy}{}^2) + \sum_{i>j} J\vec{S}_i \cdot \vec{S}_j.$$

J is the isotropic antiferromagnetic exchange constant, and $\pm z'$ is taken to be the direction of the moments. The subscript i indexes all molecules and the subscript j indexes the eight near neighbors of the i th molecule. A and B characterize the "single-molecule" anisotropy for which there are at least two sources. The magnetic dipole-dipole interaction between the two unpaired electronic spins in the free oxygen molecule produces an anisotropy energy of the form $AS_{x'}^2$.⁷ $S_{x'}$ is the projection of the total molecular electronic-spin angular momentum ($S=1$) on the internuclear axis. Since A has been shown to be positive,⁷ the spin S in the ground state is confined to a plane perpendicular to the internuclear axis. An assumption of this note is that the planar localization is not significantly disturbed when the molecule is placed in the α crystal lattice.⁸ A second, in-plane, anisotropy is needed to stabilize the antiferromagnetic ordering of the α solid. Since the site symmetry of the oxygen molecule is C_{2h} , the twofold directional degeneracy of Π electronic states is removed. The nonzero off-diagonal elements of the total electronic orbital angular momentum between the Σ ground state and the excited Π states will reflect this anisotropy, which in turn will affect the spin orientation via the spin-orbit coupling. Because of the smallness of the spin-orbit coupling constant,⁷ such a term is expected to be small, but nevertheless, important.

According to this picture, the sublattice mag-