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Transport Properties of Semiconducting Phosphate Glasses*

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The temperature and frequency dependence of conductivity, dielectric properties, infrared absorption, and electron-paramagnetic-resonance data are presented for semiconducting phosphate glasses based on oxides of Ti, V, Mn, Fe, Co, Ni, Cu, Mo, and W. The vanadate system is examined in a range of compositions, most of the others in the composition 50 mol% oxide. A polaronic model is shown to be generally applicable, and the variation of activation energy for conduction with type of glass and transition-metal-ion (TMI) spacing is found to dominate the magnitude of the conductivity. In particular, a strong preexponential factor containing a term of the form $e^{-2\alpha a}$ arising from electron tunneling is not observed. The results suggest that the theory of small polaron hopping in the adiabatic approximation may be most appropriate for phosphate glasses. Measurements of the static dielectric constant show no effects of disorder at high temperatures. Characteristic differences are noted between the infrared spectra of glasses such as V, Mo, W, and Ti and Ni, Co, Cu, and Mn, respectively, which are attributed to different structures within the glass matrix. These differences are suggested to lead to larger phonon dispersion in the latter glasses. It is found that the dependence of the properties of vanadate glasses upon composition can be described only if effects of polaron interactions are considered leading to a hopping probability of the form $c(1-c)^{n+1}$, where c is the proportion of TMIs in a reduced state and n is the number of sites surrounding the polaron at which strong interactions occur. Reasonable agreement with experiment is obtained on this basis for the change in electrical properties with the value of c.

I. INTRODUCTION

Many transition-metal oxides form glasses when melted with P_2O_5. A review of the compositions investigated up to 1964 has been given by MacKenzie,[1] while more recent reviews of the conduction process are those of Mott,[2] Austin and Mott,[3] and Owen.[4]

The general condition for semiconducting behavior is that the transition-metal ion (TMI) should be capable of existing in more than one valence state, so that conduction can take place by the transfer of electrons from low to high valence states. Possible oxides include those of Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Mo, and W. The vanadium system has been studied most thoroughly,[5–17] and information is also available on glasses containing FeO or Fe_2O_3,[18–22] WO_3 and MoO_3,[23–26] and CuO.[27] Interpretation of the conduction process is difficult since the conductivity is affected by numerous factors including the nature and concentration of the TMI, the concentration of TMIs in a reduced valence state, the preparation conditions, and the existence of microscopic or macroscopic structure within the glass matrix.

Most investigations of the glasses have attempted to define the properties of a single system, that is, one containing a particular TMI. The range of parameters which can be obtained by varying the glass composition and preparation conditions in a single system is limited and it is difficult to distinguish the effects of parameters which may be interrelated. In the present work the properties of glasses prepared from a range of oxides are compared in an attempt to determine common features of the conduction process. Measurements of the temperature dependence of the conductivity, dielectric behavior, infrared properties, and magnetic resonance are reported. It is suggested that the activation energy for conduction has the strongest influence upon the electrical properties but that correlation effects between electrons on neighboring lattice sites are also of importance.

II. THEORY

Mott[2] has discussed the conduction process in terms of hopping between localized states and has proposed an expression for the conductivity of the form

$$\sigma = (\nu_0 N e^2 a^2 / kT)\, c(1-c)\, e^{-2\alpha a}\, e^{-W/kT} \quad , \tag{1}$$

where a is the site spacing, N is the number of sites or TMIs per unit volume, c is the fraction of sites occupied by an electron and therefore in the low valence state, ν_0 is a jump frequency, α is a tunneling probability, T is the absolute temperature, and W is the activation energy for conduction.

Assuming that a strong electron-lattice interaction exists, the activation energy W is the result of polaron formation with binding energy W_H and any energy difference W_D which might exist between the initial and final sites due to variations in the local arrangements of ions. Austin and Mott[3] show that

$$W = W_H + \tfrac{1}{2} W_D \quad \text{for } T > \tfrac{1}{2}\theta_D \tag{2}$$

$$= W_D \quad \text{for } T < \tfrac{1}{4}\theta_D , \qquad (3)$$

where θ_D, defined by $\hbar\omega = k\theta_D$, is a temperature characteristic of the average optical-phonon frequency ω.[28] A detailed theory of this temperature dependence applicable to phosphate glasses has been given by Schnakenberg[29] and applied to the vanadate system by Sayer *et al.*[11] The disorder energy W_D was estimated to be of the order of 0.09 eV for an 80% V_2O_5: 20% P_2O_5 glass.

The agreement between the experimental evidence and Eq. (1) is only fair. The variation of conductivity with glass composition is difficult to interpret since the parameters c, W, N, and a vary with the proportion and nature of the TMI. Iron phosphate glasses show a maximum in conductivity for a reduced TMI ratio of $c = \frac{1}{2}$ as predicted by Eq. (1),[18] but the maximum occurs in the vanadate system for a value of c between 0.1 and 0.2.[10,30] The conductivity generally increases for higher concentrations of TMIs, and it is of particular interest for the purpose of elucidating the predominant conduction mechanism to determine whether this observation can be attributed to the effect of the tunneling term $e^{-2\alpha a}$.

Further difficulties arise from the strong influence that short-range order can have on the glass properties. The growth of crystallites in the glassy matrix can lead to long-range order within the crystallites and barrier-layer polarization at the crystallite-glass interfaces.[31] In homogeneous systems, the electrical behavior will be affected if electrons tend to be localized at specific sites in the matrix. Such sites may arise from a particular type of short-range order, and have been postulated to exist in vanadate glasses from magnetic resonance[13,14] and infrared studies.[12] Finally, correlation effects may increase the activation energy for conduction. Friebele *et al.*[22] have recently suggested that Fe^{2+} and Fe^{3+} ions are paired antiferromagnetically in iron phosphate glasses. This would result in an increased energy being required for electron hopping to take place between the pairs.

III. EXPERIMENTAL

All glasses were prepared by heating dry mixtures of the transition-metal oxide and either P_2O_5 or dried H_3PO_4 in a 40-cm^3 platinum or gold crucible. The lower-temperature melts were heated under an atmosphere of oxygen, but air was used for those fired at temperatures in excess of 1000 °C. The compositions, firing temperatures, and atmospheres used are summarized in Table I. All 3*d* TMIs except chromium were incorporated into phosphate glasses. The melt was equilibrated at the melt temperature for 1–3 h and was then cast onto a stainless-steel plate heated to 300 °C if cast from a melt temperature greater than 1100 °C, and onto a copper plate if cast from a lower temperature. This casting procedure served to minimize cracking of the glass due to thermal stress. Since some loss of the components occurred during melting, the concentration of TMIs was determined by atomic-absorption analysis or wet-chemical analysis (W and Ti). The concentration of reduced TMIs was determined by electron paramagnetic resonance[14] for V, Mo, W, and Cu and by Mössbauer-effect measurements for Fe. Wet-chemical analyses of some of the other glasses were attempted

TABLE I. Preparation conditions and analysis.

TMI oxide	Nominal mol % oxide	Nominal wt % oxide	Melt temp. (°C)	Melt atm.	Density (g/cm^3)	Analyzed TMI/cm^3 ($\times 10^{22}$)	TMI spacing (A)	Reduced TMI ratio c	Reduced TMI spacing (A)
V_2O_5	49	55	900	oxy.	2.69	1	4.64	0.40	6.28
	58	64	900	oxy.	2.71	1.16	4.42	0.18	7.86
	65	70	900	oxy.	2.75	1.29	4.26	0.18	7.57
	76	80	900	oxy.	2.79	1.49	4.07	0.08	9.50
	82	85	900	oxy.	2.84	1.62	3.96	0.06	9.84
	88	90	900	oxy.	2.87	1.70	3.88	0.04	11.65
TiO_2	50		1400	air	2.87	1.54	4.02		
Mn_3O_4	50		1200	air	2.96	0.99	4.65		
Fe_2O_3	50		1200	air	3.09	1.16	4.41	0.54	5.42
CoO	50		1250	air	2.91	0.87	4.85		
NiO	50		1250	air	3.11	0.63	5.41		
CuO	50		1340	air	3.10	0.89	4.82	~0.95	
MoO_3	50		1200	air	3.43	1.25	4.31	0.01	19.30
WO_3	80		1200	air	5.71	1.40	4.02		

but the results were not felt to be sufficiently reliable to quote at this time. All compositions are quoted in mol%.

Since it had been previously found[11] that barrier-layer effects could be easily observed, contacts for electrical measurements were made with great care. Samples were cut and polished to shape and were annealed for 24 h at 200 °C, and gold contacts were prepared by vacuum evaporation. A final anneal at the same temperature for several hours was carried out immediately prior to making measurements. No changes were noted in the electrical properties of samples prepared in this way during subsequent measurements. Crystallite formation of size $> 2\mu$ could only be observed visually, by x rays, or in a scanning electron microscope in vanadium and molybdenum glasses prepared at the limits of the glass-forming range, and these glasses were not used for electrical measurements. All electrical measurements were made under two-terminal conditions under dry nitrogen. The absence of barrier layers at the contacts was checked as far as possible by observation of an accurately linear I-V characteristic and by the observation of no abnormal rise in the magnitude of the measured dielectric constant at low frequencies. Surface conduction was shown to be negligible by the consistency of results between samples having a range of areas and perimeters. Details of the experimental arrangements for dc conductivity, dielectric, and paramagnetic-resonance measurements have been published elsewhere.[11,14] An estimate of the refractive index to within 5% was obtained by a measurement of the Brewster angle, while infrared absorption was carried out by conventional infrared pellet techniques using CsI as the pelletizing medium. The spectrometer used was a Perkin–Elmer model 180. Densities were measured using a displacement method. Most of the glasses were chemically stable and relatively insoluble in water. Copper and molybdenum glasses were the least stable, with white deposits forming on the surface over long periods of time.

IV. RESULTS

A. Temperature Dependence of Conductivity

A semilogarithmic plot of conductivity vs $1000/T$ for the $3d$ transition-metal-oxide glasses of composition 50 mol% oxide is shown in Fig. 1. A similar plot for glasses having various concentrations of oxides of vanadium, tungsten, and molybdenum is shown in Fig. 2. The convention used in the graphs—for example, 50 Mo—represents a molybdenum glass having a nominal concentration of 50 mol% MoO_3. All glasses show a smooth variation of conductivity with $1000/T$, with the temperature dependence of the activation energy being most apparent in the glasses having high conductivity at low temperatures. The limitation in the temperature range utilized was the experimental difficulty of measuring currents of less than 10^{-14} A with the equipment available. At any temperature it was usually possible to reproduce within about 20% the bulk value of the conductivity when using different samples cut from the same melt of glass or samples taken from different melts prepared under the same conditions. The high-temperature activation energy was computed from the slope of the graphs in the highest range of temperatures measured. On the basis of our previous analysis[11] the high- and low-temperature activation energies for the vanadium glasses in Fig. 2 are designated as the polaron hopping and disorder energies, respectively.

A general trend observed in Figs. 1 and 2 is that the magnitude of the conductivity at any temperature tends to be smallest in those glasses having the highest thermal activation energy. This is consistent with Eq. (1), but variations in the preexponential term might be expected to lead to only a very rough correlation between the equation and the experimental data. For example, in the series of vanadium glasses, the number of reduced TMIs decreases as the concentration of V_2O_5 increases (Table I). However, as shown by Fig. 3, a semilogarithmic plot of the conductivity measured at an arbitrarily chosen temperature (500 °K) versus the high-temperature activation energy for all the $3d$ TMI glasses is a straight line with a slope corresponding to a measurement temperature of 530 °K. The general conclusion which may be drawn from Fig. 3 is that the preexponential term of Eq. (1) inclusive of $e^{-2\alpha a}$ is virtually constant not only for the whole series of glasses but also for glasses of different compositions within the same system. The thermal activation energy for conduction therefore appears to dominate the factors which determine the conductivity. In particular, the tunnel factor $e^{-2\alpha a}$ need not be assumed to vary rapidly with site spacing a in order to explain the variation of conductivity with oxide concentration.

Points are also shown which are taken from work reported by other authors, and the agreement with the present results suggests that glasses can be prepared with reproducible characteristics. It may be noted that the two glasses shown from outside the $3d$ series—molybdenum and tungsten—do not show as close an agreement with the general behavior as the $3d$ glasses. This may indicate effects due to the different electronic structure of these ions.

B. ac Conductivity and Dielectric Properties

The total ac conductivity and dielectric constant were measured over a frequency range of 0.1–100

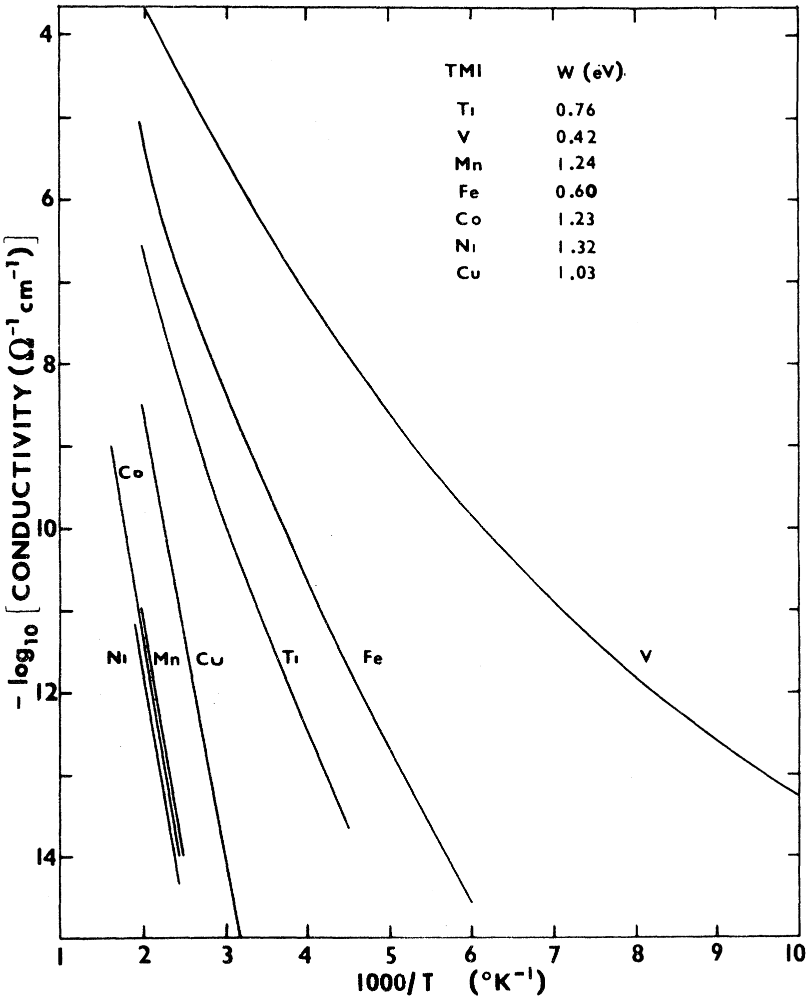

FIG. 1. Semilogarithmic plot of conductivity vs $1000/T$ for a series of phosphate glasses containing ions in the $3d$ series. Glass composition is 50-mol% transition-metal oxide.

kHz and a temperature range of 77–400 °K. A single measurement at 3.6 GHz was made at room temperature. The results for all glasses were similar to those which have been published previously for the vanadate system.[11,32] As an example of the general behavior, the ac conductivity of iron phosphate glasses as a function of $1000/T$ is shown in Fig. 4. At low temperatures the frequency dependence of the ac conductivity is of the form $\sigma_{ac} \sim \omega^n$, where n is about 0.85. This type of behavior is well known in amorphous systems and has been attributed to a distribution of relaxation times arising from local disorder.[11,32] The dielectric loss ϵ'' may be calculated from the ac conductivity using the following expression:

$$\omega\epsilon_0\,\epsilon'' = \sigma(\text{tot}) - \sigma_{dc} , \qquad (4)$$

where ϵ_0 is the free-space permittivity. At any fixed frequency a peak in the dielectric loss is obtained as a function of temperature which moves to higher temperature with increasing frequency. This may be deduced from Fig. 4. This behavior indicates a Debye-type dielectric dispersion characterized by a relaxation frequency f_0, where $f_0 = 1/2\pi\tau$ and τ is the dielectric relaxation time. The loss peak occurs at a temperature at which the measuring frequency equals the relaxation frequency. Using this fact, Fig. 5 shows the temperature variation of the relaxation frequency for vanadium glasses of different compositions and for several other glass systems. Comparison with Figs. 1 and 2 shows that a strong correlation exists between the magnitude and temperature dependence of both the relaxation frequency and the dc conductivity, respectively. In general, it is found that the relaxation frequency has a thermally activated dependence on temperature which is similar to that of the dc conductivity and that the relaxation frequency is small in glasses of low conductivity. It therefore appears likely that the same hopping process determines both the ac and the dc conductivity[32] and that the activation energy for conduction plays a predominant role in both the ac and dc cases. Some authors[20,31] have observed maxima

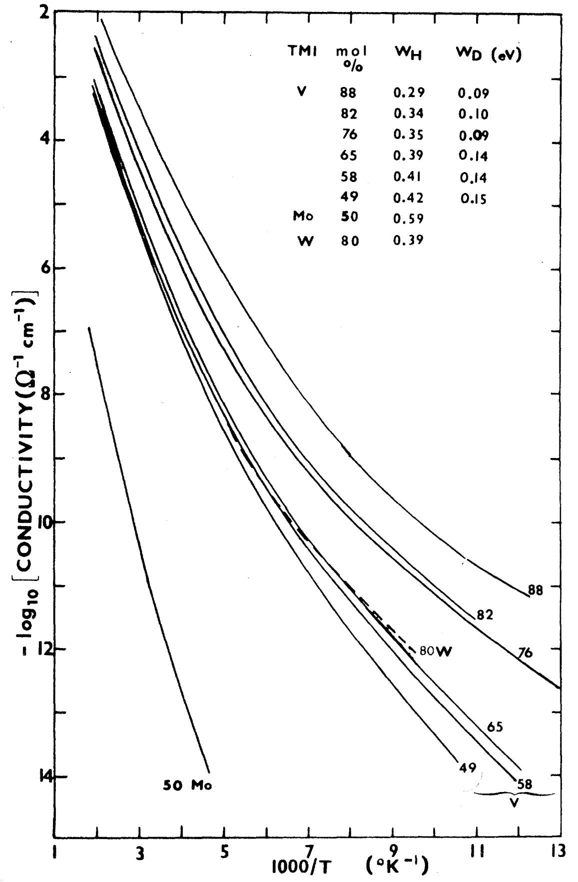

FIG. 2. Semilogarithmic plot of conductivity vs 1000/T for V_2O_5: P_2O_5 glasses of various compositions, 50-mol %-MoO_3 and 80-mol %-WO_3 glasses.

in the ac conductivity of phosphate glasses as a function of temperature without subtracting the dc component and have attributed this to Maxwell–Wagner–Sillars relaxation associated with macroscopic inhomogeneities in the glass. Such effects were not apparent in the present work and were only suspected in the case of the highest vanadium concentration. The low-frequency dielectric properties are consistent with electron hopping in a macroscopically homogeneous matrix.

The variation of dielectric constant with temperature for most of the glasses studied is shown in Fig. 6 for a measurement frequency of 100 Hz. At higher frequencies a similar temperature variation is observed, with the peak in dielectric constant occurring at higher temperatures and lower values of dielectric constant.[11] This is again characteristic of a Debye-type relaxation process.[32] In order to faciliate comparison with theory it is desirable to calculate the low- and high-frequency dielectric constants from the data. The high-frequency dielectric constant may be estimated from the value measured at 3.6 GHz at room temperature or from

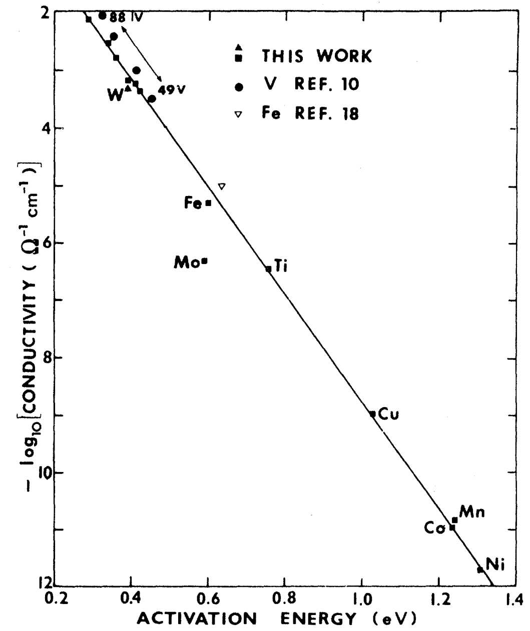

FIG. 3. Semilogarithmic plot of conductivity vs the high-temperature activation energy for conduction W. Conductivity values measured at 500 °K. Vanadate glasses of various compositions, an 80-mol %-WO_3 glass, all other glasses nominally 50 mol % TMI. Data from Refs. 10 and 18 included for comparison.

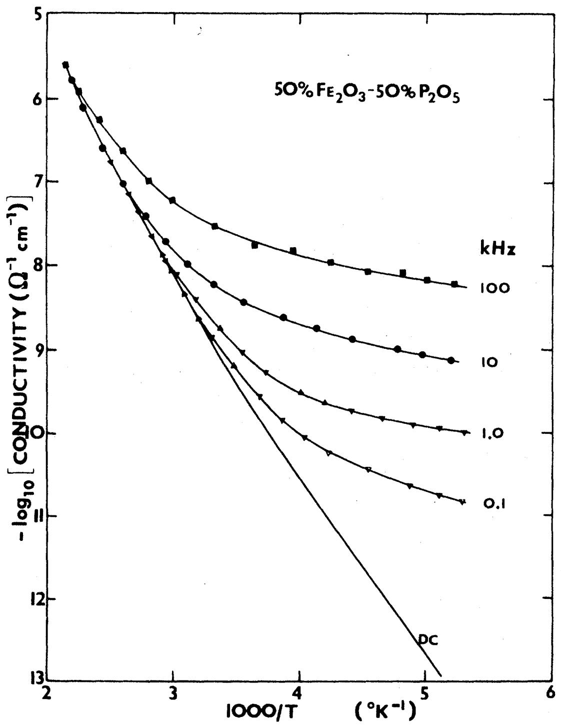

FIG. 4. Total conductivity plotted as a function of 1000/T for various frequencies of measurement for 50-mol %-Fe_2O_3 glasses.

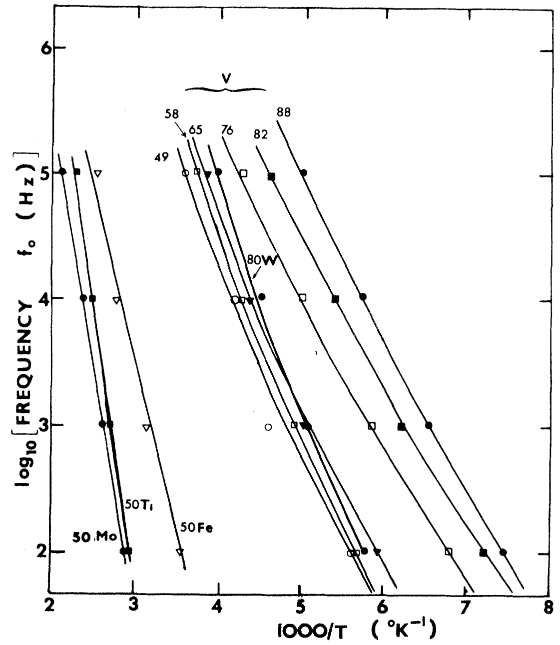

FIG. 5. Temperature dependence of dielectric relaxation frequency for vanadium glasses of various compositions, Fe, Ti, and Mo glasses of 50 mol % composition. W glass of 80 mol % composition.

the low-temperature value of the dielectric constant measured at lower frequencies where $\omega\tau \gg 1$. As was found earlier with the vanadate system,[11] comparison with the square of the refractive index shows that a further dispersive region occurs beyond 3.6 GHz for all glasses. Two methods are available to estimate the low-frequency dielectric constant ϵ_0. The first method applies for a Debye-type process having a symmetrical distribution of relaxation times.[32] In this case the value of the dielectric constant measured at a temperature corresponding to that of the peak of the dielectric-loss curve for the same frequency is given by

$$\epsilon(\text{peak}) = \tfrac{1}{2}(\epsilon_0 + \epsilon_\infty) \; . \qquad (5)$$

Two uncertainties limit the use of this relationship—the difficulty of accurately measuring the temperature corresponding to the relaxation frequency and the possibility that the relaxation-time distribution may be asymmetric. The second method has been utilized by Bosman and van Daal[33] for NiO and is based on the fact that, for a Debye-type system in which the static dielectric constant decreases with temperature, a peak in the dielectric-constant-vs-temperature curve can only occur when $\omega\tau \ll 1$ and the conditions for the measurement of the low-frequency dielectric constant are

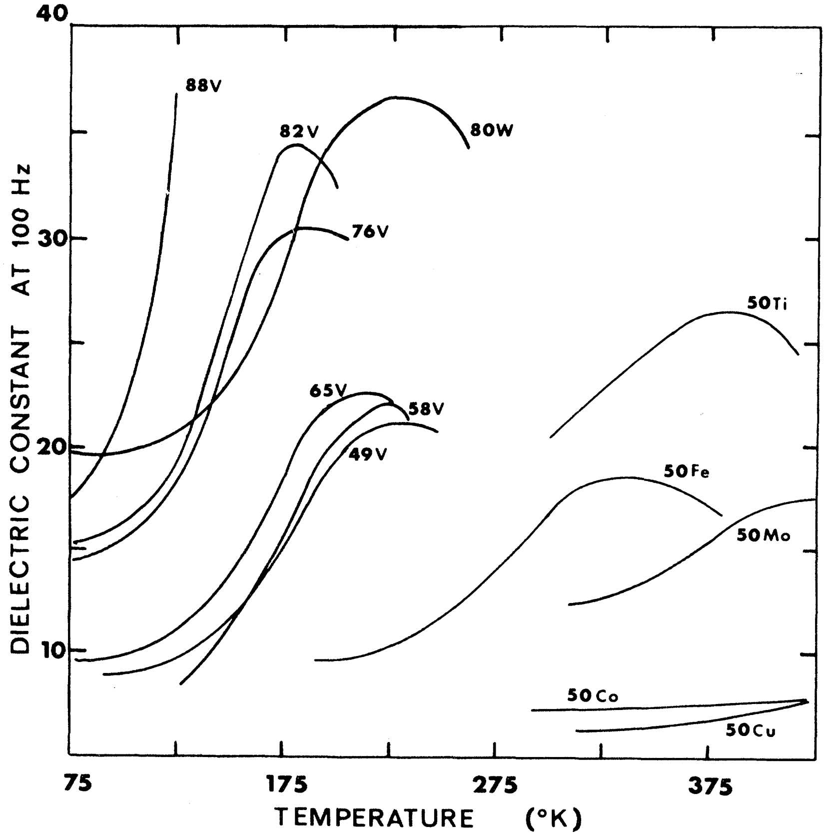

FIG. 6. Temperature dependence of dielectric constant measured at a frequency of 100 Hz for various phosphate glasses.

satisfied. The values calculated using the two methods agree to within 20%, with less scatter in the results for the second method. The results obtained for the dielectric constants and other electrical properties at room temperature are summarized in Table II.

The temperature dependence of the static dielectric constant is of interest. For a system of cN electrons hopping between sites separated by a distance a, and which differ in energy by W_D, the static dielectric constant should be given by[3,34]

$$\epsilon_0 - \epsilon_\infty = \tfrac{4}{3}\pi (Ne^2a^2/kT)\, c(1-c)\, e^{-W_D/kT} . \qquad (6)$$

The temperature dependence can be measured experimentally since the peak value of dielectric constant occurs at different temperatures for different frequencies of measurement. The temperature variation is seen to be of the form $\epsilon_0 \sim 1/T$ in Fig. 7 and there is no evidence for the thermal activation energy W_D. (If $W_D \sim 0.1$ eV, as observed in low-temperature dc measurements, the latter term would cause an increase in $\epsilon_0 - \epsilon_\infty$ over the temperature range of measurement.) The intercept at infinite temperature correlates fairly well with the high-frequency value of the dielectric constant measured at 3.6 GHz. It may be noted that the temperature range considered lies in the region of Fig. 4 where the ac and dc conductivities coincide, and is at a much higher temperature than that used to estimate the disorder energy from the temperature dependence of dc conductivity.

It was not possible to determine the static dielectric constant for Co, Ni, Mn, and Cu glasses owing to the low conductivity of the glasses, and the lowest measuring frequency of 100 Hz is probably much higher than the relaxation frequency at 400 °K. For other glasses, with the possible exception of titanium, a general correlation can be asserted that the dielectric constants are lowest for those glasses with the lowest conductivities. In the vanadate system, the room-temperature static dielectric constant increased from 18 to 50 for glasses containing 49 and 88 mol% V_2O_5, respectively. This behavior is not immediately compatible with Eq. (6) since both the site spacing a and the number of carriers decrease with increasing V_2O_5 concentration.

Finally, a previous discussion of the static dielectric constant[11] suggested that its value increased with temperature. The present more complete analysis shows that this is not the case, at least in the region where the effect of W_D is negligible. Measurements at frequencies lower than 100 Hz at low temperatures may be interesting to determine the variation of the static dielectric constant in the region where disorder effects show up in the dc conductivity.

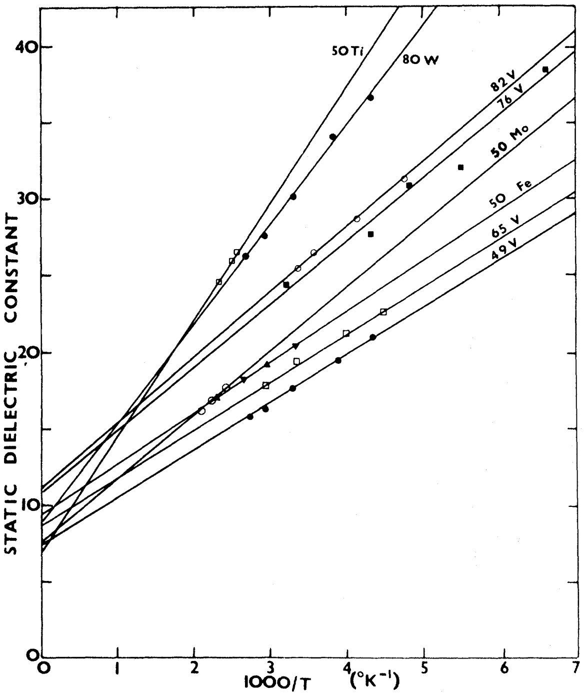

FIG. 7. Static dielectric constant plotted as a function of 1000/T. Most points calculated from peak of curves shown in Fig. 6. 80 mol % V_2O_5 calculated from relaxation-time method.

TABLE II. Measured values of dc activation energy W_H, dc conductivity σ, refractive index κ, ϵ' at 3.6 GHz, and estimated values of static dielectric constant ϵ_0 for different glasses.

Glass	W_H (eV)	σ at 300 °K [(Ω cm)$^{-1}$]	ϵ_0	ϵ' at 3.6 (GHz)	κ^2
88 V_2O_5	0.29	1.0×10^{-4}	50.0	9.0	5.2
81 V_2O_5	0.34	2.0×10^{-5}	25.8	9.3	3.9
76 V_2O_5	0.36	1.0×10^{-5}	24.6	9.0	3.8
64 V_2O_5	0.39	2.5×10^{-6}	19.8	7.4	3.8
58 V_2O_5	0.41	1.6×10^{-6}	19.0	7.4	3.6
49 V_2O_5	0.42	1.3×10^{-6}	18.1	7.0	3.3
50 Fe_2O_3	0.60	1.6×10^{-9}	20.0	8.2	2.8
50 TiO_2	0.76	3.4×10^{-11}	31.5	11.8	3.5
50 CoO	1.23 (400 °K)	3.16×10^{-14}		5.2	2.5
50 NiO	1.32 (400 °K)	1.6×10^{-14}		5.8	2.6
50 Mn_3O_4	1.24 (400 °K)	1.0×10^{-13}		6.2	2.5
50 CuO	1.06 (400 °K)	4.6×10^{-11}		5.5	2.6
80 WO_3	0.39	1.2×10^{-6}	30.2	9.9	3.8
50 MoO_3	0.59	1.0×10^{-11}	21.2	8.4	3.3

C. Electron Paramagnetic Resonance

All the glasses were examined for electron-paramagnetic-resonance behavior. Strong signals were observed from vanadium, molybdenum, and copper glasses, with weaker signals being observed from tungsten and some iron glasses. No signals have been detected as yet in other glasses. It is not possible, at present, to determine whether this is due to spin-ordering effects or to dipolar broadening of the resonance line beyond the detection capability of the spectrometer. The resonance line in copper glass was extremely broad (linewidth of about 500 G) and it was only possible to make a very rough estimate of the spin concentration.

D. Infrared Absorption

Infrared absorption spectra have been used previously in an attempt to ascertain whether any kind of local order characteristic of the constituent oxides is maintained in the glass.[17,25] Previous studies on the vanadate system[12] have shown an absorption band near 380 cm^{-1} whose intensity depends upon the V^{4+} concentration and upon the composition of the glass. An absorption band at 1010 cm^{-1} characteristic of a vanadium-oxygen bond stretching frequency in V_2O_5 was also found to be maintained in high-vanadium-content glasses. Figure 8 shows infrared spectra measured for 50 mol% oxide glasses in the *3d* series compared with spectra for the crystalline oxides and a spectrum for P_2O_5. Figure 9 shows similar results for the tungstate and molybdenum glasses used for the electrical measurements, along with spectra for two additional compositions and those for the two oxides.

Although it is difficult to obtain detailed quantitative information from the spectra, they may be placed into two relatively well-defined groups. The spectra of glasses containing Mn, Co, Ni, and Cu show strong absorption peaks at 760 and 530 cm^{-1}, while Ti, V, Mo, and W show little evidence of peaks at these wave numbers and generally have less pronounced structural features over the entire spectral range. Absorption for wave numbers less than 200 cm^{-1} appears to be more intense in the first group than in the second group.[15] The iron phosphate glasses are somewhat intermediate between the two extremes. Comparison with the infrared spectrum of P_2O_5 shows that a sharp spectral line occurs at 560 cm^{-1} and a broad structure at 760 cm^{-1}. A fundamental frequency (ν_4) of the $(PO_4)^{3-}$ group is known to occur near 500 cm^{-1},[35] and it appears reasonable to assume that the two strong infrared features in the Mn, Co, Ni, Fe, and Cu glasses are characteristic of such phosphate tetrahedra. On the other hand, it has previously been shown that infrared features characteristic of vanadium-oxygen bonds are maintained in vanadate glasses.[12] This may also be said to be true for the molybdenum glasses in Fig. 9, where a strong correlation exists between the infrared spectra of the oxide and the glasses. Qualitatively, the behavior may be summarized by suggesting that phosphate tetrahedra dominate the structure of Mn, Ni, Co, and Cu glasses, while structures of the form MO_n, where M is the TMI, dominate glasses formed with Ti, V, Mo, and W. This

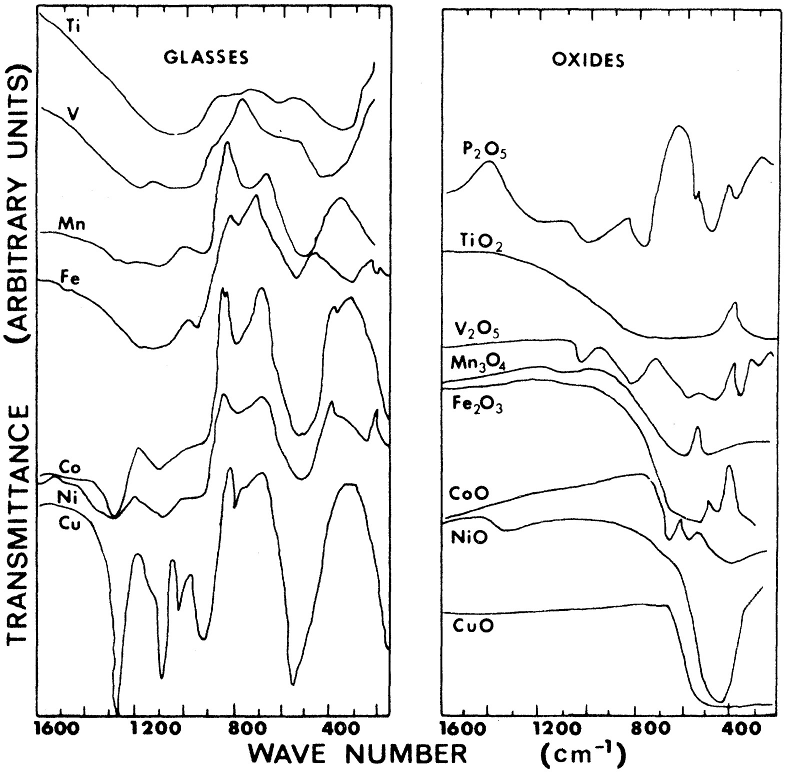

FIG. 8. Infrared absorption spectra for 50 mol % glasses and for constituent oxides.

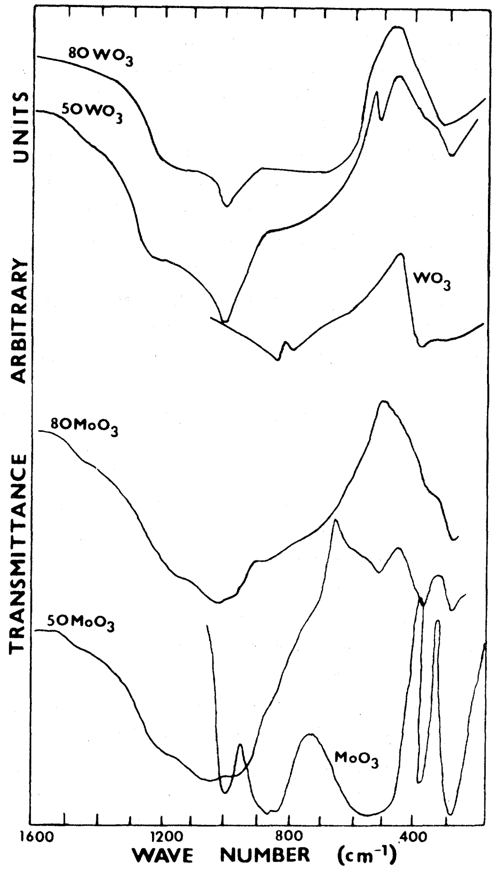

FIG. 9. Infrared absorption spectra for two compositions of WO_3 and MoO_3 glasses and the constituent oxides.

suggestion of a fundamental difference in a glassy structure is of interest since the activation energies for conduction differ quite markedly in the two groups, being lower in the TMI-dominated glasses.

V. DISCUSSION

The general features of the conduction process which emerge from the present experiments and from previous work may be summarized as follows.

(a) The activation energy for conduction plays a dominant role in determining both the ac and dc conductivity.

(b) An exponential dependence of conductivity on TMI spacing is not observed.

(c) For a glass of given composition, the conductivity varies with the number of reduced TMIs. For vanadate glasses a maximum in conductivity is observed when the fraction of TMIs in the reduced state is between 0.1 and 0.2, depending on the system.[10,30]

(d) The effect of short-range order at different types of sites in the glass may have to be considered.

(e) The value of the dielectric constants increases with conductivity and increased concentration of the transition-metal oxide. This increase occurs despite evidence for a decrease in both site spacing and number of electrons contributing to the dipole moment.

(f) Effects of the disordered nature of the lattice are apparent at low temperatures but are not in evidence at high temperatures.

A. Activation Energy

The temperature dependence of conductivity shown in Figs. 1 and 2 is consistent with a polaron model for conduction in all the glasses. The polaron model predicts that an appreciable departure from a linear $\ln\sigma$-vs-$1/T$ plot should occur below a temperature of $\frac{1}{2}\theta_D$, where θ_D is given by $\hbar\omega = k\theta_D$ and ω is the mean frequency of longitudinal-optical phonons. In the vanadate system this temperature was deduced to be of the order of $\frac{1}{2}\theta_D = 300\,^\circ\mathrm{K}$,[11] and Figs. 1 and 2 show that a temperature-dependent activation energy is only observed in glasses which have a measurable conductivity below this temperature. The major assumption in this statement is that the optical-phonon distribution does not differ appreciably between phosphate glasses. This assumption can be justified by the similarities between the infrared spectra for different compositions within the vanadate system[12] and between the spectra of vanadate glasses and Ti, Mo, and W glasses. The assumption is less easily justified for Ni, Co, Fe, Cu, and Mn, where a larger density of vibrational modes is evident in the lowest energy range of the infrared spectra.

In a generalized polaron model, the activation energy $W = W_H - J$, where J is a polaron bandwidth related to the electron wave-function overlap on adjacent sites. Theories have been proposed to cover both nonadiabatic[36] and adiabatic[37] hopping processes. Friedman and Holstein[36] derive an expression for the mobility,

$$\mu = \frac{3}{2}\,\frac{ea^2J^2}{kT}\left(\frac{\pi}{kT\,W_H}\right)^{1/2} e^{-W_H/kT}\,, \tag{7}$$

for the case of nonadiabatic hopping, while Emin and Holstein[37] show that in the adiabatic regime

$$\mu = \frac{4}{3}\,\frac{ea^2\,\omega_0}{kT}\,e^{-(W_H-J)/kT}\,. \tag{8}$$

The form of Eq. (1) proposed by Mott clearly represents hopping in the nonadiabatic regime, since $J \approx e^{-\alpha a}$. However, the present experimental results follow Eq. (8) much more closely, with a thermal activation energy W which varies with the TMI concentration. A dependence of this type was originally proposed by Killias[38] and has been investigated more recently by Bjorck.[39] The condition for adiabatic hopping given by Emin and Holstein is that

$$J > \left(\frac{2kTW_H}{\pi}\right)^{1/4}\left(\frac{\hbar\omega_0}{\pi}\right)^{1/2} , \tag{9}$$

with the condition for the existence of a small polaron being $J \lesssim \frac{1}{3} W_H$. The limiting value of J for a 76-mol%-V_2O_5 glass at 500 °K is 0.04 eV, and therefore the condition for the existence of a small polaron in the adiabatic regime can be met. An unambiguous decision as to whether the polaron is actually in the adiabatic regime requires an estimate of the value of J. An upper limit can be deduced by assuming that the entire concentration dependence of the activation energy is due to variations in J. In vanadate glasses (Table II), this corresponds to a change in W from 0.29 to 0.42 eV, a possible variation in J of 0.13 eV. However, since W_H is likely to change with composition, the true value is probably smaller than this, although it may be large enough that the adiabatic hopping theory may be most appropriate to describe polaron mobilities in vanadate glasses. Measurements of Hall mobility may be useful in finally resolving the matter.

Two methods of calculating the polaron binding energy have been suggested. The most general expression is that of Holstein[40]:

$$W_p = (2N)^{-1}\textstyle\sum_q |\gamma_q|^2 \hbar\omega_q , \tag{10}$$

where $|\gamma_p|^2$ is the electron-phonon coupling constant, ω_q is the frequency of optical phonons of wave number q, and N is the site density. Mott[3] has derived a more direct estimate:

$$W_p = \tfrac{1}{2} e^2/\epsilon_p r_p , \tag{11}$$

where r_p is the polaron radius and ϵ_p is an effective dielectric constant given by $1/\epsilon_p = 1/\epsilon_\infty - 1/\epsilon_0$. Bogomolov *et al.*[41] have shown that an expression of the form of Eq. (11) can be derived from Eq. (10) for the case of a nondispersive system of frequency ω_0. The polaron radius is given by

$$r_p = \tfrac{1}{2}(\tfrac{1}{6}\pi)^{1/3} a , \tag{12}$$

where a is the site spacing. Equation (12) is obviously oversimplified for a complex lattice but the infrared spectrum of the vanadate system with the strong absorption band at 380 cm^{-1} linked with the presence of V^{4+} ions in the glass[12] suggests that this approximation may fit the vanadate glasses fairly well. This conjecture is supported by the fact that the basic structural units of the glass lattice are V-O_5 groups and phosphorous groups having a fourfold coordination with oxygen,[12,13,17] and recent calculations[42,43] suggest that the vibrational modes of such groups are well localized. The value of the polaron radius calculated from Eq. (12) using the average TMI spacing as an estimate for a is shown in Table III. An experimental estimate[3] of the polaron radius may be obtained from Eq. (11) taking $W = W_H = \frac{1}{2} W_p$ and assuming that $W_H \gg J$. The values obtained are included in Table III. Where possible, ϵ_p was calculated fully, but in the cases where ϵ_∞ was not known, the approximation $\epsilon \sim \kappa^2$ was used, where κ is the refractive index. For the vanadate system, the experimental value of r_p for different composition glasses is constant within experimental error and has a value of about 2.1 A. The value calculated from Eq. (12) is about 1.7 A and the discrepancy may arise in the difficulty of defining the lattice spacing a in a noncubic system. The experimental and theoretical values for tungsten and iron glasses are comparable to those of the vanadate system, but considerable differences are observed for glasses having higher activation energies. The polaron radii are about one-half those for the vanadate system and the agreement between the experimental values and those calculated from Eq. (12) is very poor. A possible reason is that a large dispersion exists in the phonon spectrum, as suggested by the infrared results, and that Eq. (12) is not applicable.

Although the possible effects of disorder have been neglected in the above calculation, the small values of the polaron radii suggest that the polaron is highly localized. The implications of such strong localization may now be considered, first for the vanadate system since the data available are most complete, and then for other glass systems.

If the polaron energy is determined to first order by nearest-neighbor interactions, the existence of well-defined structural groups implies that the

TABLE III. Polaron radius r_p for different glasses calculated from Eq. (9) and substituting experimental values in Eq. (8).

Glass	W_H (eV)	ϵ_p	r_p (Å)	r_p (expt.) (Å)
88 V_2O_5	0.29	5.8	1.6	2.1
81 V_2O_5	0.34	4.6	1.6	2.3
76 V_2O_5	0.36	4.5	1.6	2.3
64 V_2O_5	0.39	4.7	1.7	2.0
58 V_2O_5	0.41	4.4	1.8	2.0
49 V_2O_5	0.42	4.0	1.9	2.1
50 Fe_2O_3	0.60	3.3	1.8	1.8
50 TiO_2	0.76	3.9	1.7	1.2
50 CoO	1.23	2.5	2.0	1.1
50 NiO	1.32	2.6	2.2	1.0
50 Mn_3O_4	1.24	2.5	1.9	1.1
50 CuO	1.06	2.6	2.0	1.3
80 WO_3	0.39	4.3	1.7	2.0
50 MoO_3	0.59	3.9	1.8	1.6

form of the potential well for the electron at a TMI site should be similar within the same type of group independent of its orientation with respect to its surroundings, with the nature of the linking network determining the energy only to second order. The constant value of the polaron radius for vanadate glasses of different compositions is consistent with this proposal. A simple interpretation of the variation of activation energy with composition is also obtained on this basis. A configurational coordinate diagram similar to that discussed by Austin and Mott[3] is shown in Fig. 10, in which the energy of an electron at a V^{4+} site is plotted as a function of distance from the equilibrium position of the ion *after all lattice relaxation has taken place*. On such a diagram the energy required for electrons to transfer between sites is given by the intersection of the potential-energy curves appropriate to adjacent wells. Experimentally the variation of activation energy with spacing (Fig. 11) is not particularly rapid. This may be accounted for by assuming that a strong potential variation with distance occurs up to a radius a_0 owing to tne specific structural unit surrounding the TMI (V-O_5), with a subsequent weaker variation influenced by next-nearest neighbors taking place at larger distances. The minumum activation energy in a glass should therefore be given by a random packing of the structural units appropriate to the oxide. Some evidence for this is found in the vanadate system in that the graph of activation energy versus vanadium spacing in Fig. 11 attains the value for polycrystalline V_2O_5[44] at a lattice spacing which is the arithmetic mean of the V-V distances along the three crystal axes of crystalline V_2O_5.

In the above connection, it is of interest that both the empirical classification of TMI glasses proposed earlier based on the infrared spectra and the magnitude of the hopping activation energy reflect the tendency for the TMI concerned to form covalently bonded complexes and, in some cases, compounds based on a chain structure. This tendency is well documented for V, Mo, and W,[25,26] while Ni, Co, and Mn oxides form cubic lattices with tendency to form tetrahedral-type complexes. It is likely that the definition of a structural grouping affects the hopping probability in a number of ways—by maintaining site energies within narrow limits, by reducing dispersion in the local phonon frequencies, and also by separating the TMI from direct interaction with the more polarizable phosphate complexes. It is suggested that any theoretical calculation of the hopping activation energy in phosphate glasses will have to take the detailed structural nature of the glass into account. A further factor in the case of Fe, W, Ni, Co, and Mn glasses is the possibility of magnetic interactions such as those proposed by Friebele *et al.*[22]

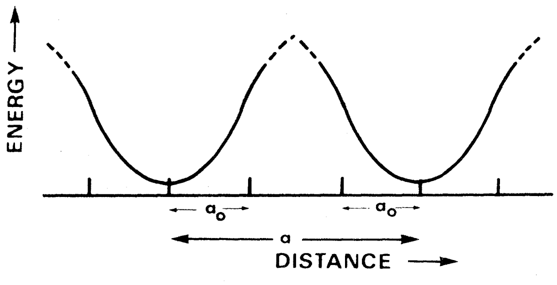

FIG. 10. Electron energy near V^{4+} sites after all lattice relaxation has occurred. a represents V^{4+}-V^{4+} spacing. a_0 represents the average radius of a specific structural unit located about the TMI site.

B. Effective Polaron Concentration

The conclusion that the terms outside the factor $e^{-W/kT}$ in the expression for dc conductivity change little for different glasses may now be examined in terms of the experimental values of the other parameters listed in Tables I and II. This may be done with most confidence for the vanadate glasses, in that complete data for a range of compositions are available. A second experimental check of the terms involved may be obtained from a measurement of the static dielectric constant, since Eqs. (1) and (6) include the same parameters, with the exception of the frequency factor ν_0 and some numerical factors. Table IV shows a comparison of experimental data for vanadate glasses with theoretical values for $\epsilon_0 - \epsilon_\infty$ and frequency factor ν_0 calculated from Eqs. (6) and (1), respectively. The trend of the calculated values of dielectric constant with composition differs from that observed experimentally, and at lower TMI concentrations the discrepancy between theory and experiment is greater than a factor of 10. The frequency factor ν_0 is also found to vary with composition. It is generally assumed that this parameter is related to the phonon frequencies at the hopping site.[4] Since the infrared data suggest that no change in these frequencies occurs for glasses of different compositions, it is more reasonable to expect that ν_0 should be constant for the range of glasses.

It is recognized in both Eqs. (1) and (6) that the probability of hopping is determined by the presence of an electron at an initial site and by the absence of an electron at the final site. However, as seen in Table I, many glasses have values of c between 0.01 and nearly unity, which implies a polaron density corresponding to one polaron every one or two lattice sites. At such high densities the possibility of interactions between polarons must be considered. Such interactions may take the form of direct Coulomb effects or

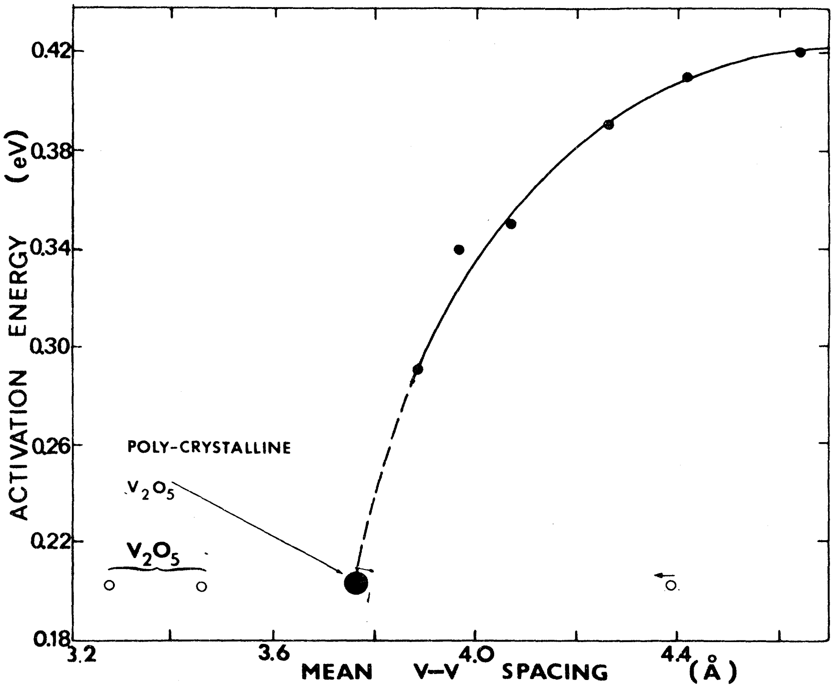

FIG. 11. Activation energy vs mean V-V spacing for glasses of different composition. Open circle represents lattice spacings for three crystallographic axes of V_2O_5, while closed circle shows the arithmetic mean of the three spacings.

indirect correlations occurring through the electron-lattice interaction, for example, by means of changes induced in the lattice relaxation at a given site due to the presence of a polaron on an adjacent site. If such interactions are large enough, it may be energetically unfavorable for a site adjacent to a polaron to accept an electron, thereby becoming barred from participation in the hopping process. Quantitatively, this effect can be treated in two ways—by defining a "correlation volume" about a polaron within which the probability of finding a second polaron is very small, or in terms of hopping on a lattice. In the first case, the effective volume of the lattice available for hopping is reduced by a factor depending on the number of polarons, and the hopping process can be visualized as the motion of spheres of appropriate size through the TMI lattice. Since the polaron is highly localized in the glass, it is likely that the correlation volume will correspond primarily to nearest-neighbor interactions. In terms of a lattice one might require that for hopping to occur from an occupied site (probability c) to an unoccupied site (probability $1-c$), the n nearest neighbors of the final site must also be unoccupied [probability $(1-c)^n$], resulting in a total hopping probability

$$P_{\text{hop}} = c(1-c)^{n+1} \,. \tag{13}$$

For an approximately cubic lattice, $n = 5$ and the exponent in Eq. (13) equals 6, but for a general lattice it is likely that the exponent will differ from this value depending on the structure. The final columns of Table IV show values of static dielectric constant and frequency factor calculated from Eqs. (1) and (6) modified according to Eq. (10) with $n = 5$. Agreement with the experimental values for dielectric constant is obtained within a factor of 3 and the variation with composition is in closer agreement with experiment, except in the low and high ranges of V_2O_5 concentration. Incipient phase separation and increased experimental error are most likely at these limits. Apart from the 49-mol%-V_2O_5 glass, the frequency factor varies little with composition, having a value of about 1.5×10^{12} sec^{-1}. This is of the same order of magnitude as the characteristic phonon frequency of 9×10^{12} sec^{-1} corresponding to the infrared absorption band at 380 cm^{-1}.

TABLE IV. Experimental values of static dielectric constant $\epsilon_0-\epsilon_\infty$ compared with values of dielectric constant and frequency factor ν_0 calculated from Eqs. (1) and (10), respectively.

Glass	$(\epsilon_0-\epsilon_\infty)_{\text{expt}}$	$P_{\text{hop}}=c(1-c)$ $\epsilon_0-\epsilon_\infty$	 $\nu_0\times$ (10^{-12} sec)	$P_{\text{hop}}=c(1-c)^6$ $\epsilon_0-\epsilon_\infty$	 $\nu_0\times$ (10^{-12} sec)
88 V_2O_5	41	21.3	1.3	17.6	1.6
81 V_2O_5	16.5	35.8	1.1	25.6	1.5
76 V_2O_5	15.6	41.6	0.7	27.6	1.0
64 V_2O_5	12.4	80.1	0.4	29.6	1.1
58 V_2O_5	11.6	77.1	0.6	29.0	1.6
49 V_2O_5	11.1	120.8	0.4	9.1	6.1
50 Fe_2O_3	13.8	159.0	0.4	8.7	8.4
50 MoO_3	12.8	6.46	0.049	6.07	0.052

Previous authors[10] have suggested that a fraction of the TMIs in phosphate glasses is rendered inactive with respect to the hopping process, possibly due to structural effects such as the formation of polymeric complexes within the glass structure. However, little independent experimental evidence has been put forward for sites whose static characteristics differ in such an extreme manner. The present proposal represents a dynamic effect imposed upon a uniform site distribution which may be physically more realistic.

The value of c for which the conductivity is a maximum is given by differentiating Eq. (13) with respect to c and equating to zero. The result obtained is that the hopping probability should be a maximum for

$$c = 1/(2+n) \; . \qquad (14)$$

Linsley *et al.*[10] have published the most comprehensive data on the conductivity maximum in vanadate glasses. They have shown that the value of c at maximum conductivity varies from about 0.11 to 0.18 for the range of glass compositions 90-60 mol% V_2O_5. This corresponds to a change in n from 7 to 3.5. This is consistent with the physical situation, since increasing TMI concentration implies a decreased spacing between the TMI and a higher possibility of polaron interactions. The effect of a reduced value of n upon the calculations made in Table IV is to increase the dielectric constants of low-vanadium-content glasses and decrease those having a higher content of vanadium. However, since data were not available to allow a calculation of n for the glasses described in this paper, any such detailed calculation would be speculative at best.

It must be noted that some caution must be exercised in the application of Eq. (11) to the conductivity maximum, since Linsley *et al.*[10] have also suggested that a variation with activation energy occurs with c, such that the activation energy goes through a minimum when the conductivity passes through a maximum. Unfortunately, complete data for a single system have not been published, but a tentative evaluation of the data of Linsley *et al.* for a 90-mol%-V_2O_5 glass in terms of Eq. (10) is shown in Fig. 12. If a value of n is calculated from the position of the maximum, the variation of conductivity with c according to Eq. (10) is shown by the dotted curve which is normalized at the maximum. The theoretical peak is asymmetric, as is generally observed experimentally,[5,30] but is broader than the experimental peak. Linsley *et al.* have not published activation-energy data for the 90 mol% glass, but if the published 70-mol%-glass data are taken as a model for the variation of W with c, one might expect a change of W with c for the 90 mol% glass of the form shown in the inset of Fig. 12. This variation in

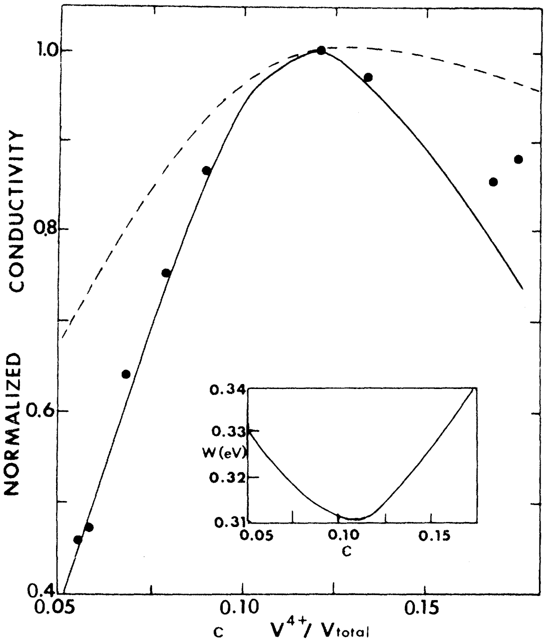

FIG. 12. Experimental data for the variation of conductivity and activation energy with V^{4+}/V^{5+} ratio taken from Linsley *et al.* (Ref. 10). The conductivity data are for a 90-mol%-V_2O_5 glass, but the activation-energy variation is estimated from the general form shown by Linsley *et al.* for a 70-mol%-V_2O_5 glass. Theoretical curve (dashed) is calculated from Eq. (13) normalized at the peak; the solid curve includes the variation of activation energy.

activation energy is found itself to produce a peak if the preexponential term is assumed to be constant, but again the theoretical curve is too broad compared with the experimental data. However, weighting the dotted curve obtained from Eq. (10) with a factor $e^{-W(c)/kT}/e^{-W(c)_{\text{peak}}/kT}$, where $W(c)$ and $W(c)_{\text{peak}}$ are the activation energy at any value of c and at the peak value of c, respectively, gives relatively good agreement with the experimental data. This is shown by the solid curve in Fig. 12. This analysis is tentative, but it does indicate that variations in hopping probability and activation energy must both be considered in analyzing the experimental data.

The Seebeck coefficient on the above model is given by[3]

$$\alpha = \frac{k}{e}\left(\ln\frac{n_0}{P} + \alpha'\right) = \frac{k}{e}\left(\ln\frac{c}{1-(n+1)c} + \alpha'\right) \; , \qquad (15)$$

where α' is a constant, n_0 is the number of carriers, P is the density of unoccupied states, and n is the number of neighbors within the correlation volume defined earlier. The final equation arises from $n_0 = cN$ and $P = N - c(n+1)N$, since the sites within any correlation volume do not participate in the conduction process. Previous measurements on vanadate glasses have indicated that $n = 0$,[45] but recent data by Linsley *et al.*[10] show a deviation from this behavior which is greater for the higher-vanadium-content glasses. This is consistent with our previous considerations, since the value of n associated with such glasses is large. The general trend of the data[10] of Linsley *et al.* is in agreement with Eq. (15) for $\alpha' \sim -1.0$ but with n between 1 and 3. In light of the associated change in activation energy it is likely that further experimental studies will be necessary before tnis problem can be resolved.

Calculations similar to the above have been carried out for Mo and Fe glasses, these being the materials for which the most reliable data on reduced TMI concentration were available. The agreement between theory and experiment for ν_0 and $\epsilon_0 - \epsilon_\infty$ is shown in Table IV. A more detailed comparison requires further experimental work on glasses prepared with a range of compositions.

VI. CONCLUSION

An examination of the conduction processes in phosphate glasses containing TMIs suggests that a polaron model is generally applicable, with some evidence that hopping occurs in the adiabatic regime. It is found that polaron interactions have to be considered. The over-all results are best described by an equation of the form

$$\sigma = \nu_0 \frac{Ne^2a^2}{kT} c(1-c)^{n+1} e^{-[W(a)+W_D]/kT} ,$$

where for vanadate glasses $n = 5$ and the disorder energy W_D has a major effect only at low temperatures.

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Crossed-Field Acoustic Amplification in Nondegenerate Semiconductors in Strong Magnetic Fields[*]

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A quantum-mechanical derivation is given for the conductivity and diffusion tensors of a nondegenerate free-electron gas which is subjected to crossed electric and magnetic fields. We use this formalism to obtain an explicit expression for the absorption coefficient for the quantum case of strong magnetic fields, i.e., when $\hbar\omega_c \gg k_B T$. It is seen from our results that the value of the absorption coefficient may increase by a factor of 3 by taking into account the relevant energy dependence of the relaxation time for the case of acoustic-phonon scattering.

I. INTRODUCTION

In the last decade a sizable number of papers have been published on the attenuation of acoustic waves in solids (for a review of the work the reader is referred to an article by Spector[1]). Most of these papers were restricted to the case of an extremely degenerate electron gas, i.e., metals; recently, however, some papers[2–12] have been published which are applicable to nondegenerate semiconductors. The main reason for this interest in the study of attenuation of acoustic waves in semiconductors is the experimental observation[13–16] of two modes of acousto-electric-current oscillations in InSb under a transverse magnetic field. Hammar and Weissglas[7] and Abe and Mikoshiba[8,9] have proposed that mode I is due to Doppler-shifted amplification. However, all of these theories are valid only for low magnetic fields, i.e., for $\hbar\omega_c \ll k_B T$ (where ω_c is the cyclotron frequency, T is the temperature, and k_B is the Boltzmann constant). Recently, Nill and McWhorter[17] and Spector[18] have investigated this phenomenon for nondegenerate semiconductors in strong magnetic fields (i.e., $\hbar\omega_c \simeq k_B T$), where quantum effects become important. Both of these authors have assumed a constant relaxation time. More recently, Jacobini and Prohofsky[19] have studied the longitudinal magnetoacoustic absorption for the limiting case of very strong magnetic fields taking into account the energy dependence of relaxation time when electrons are scattered either by acoustic phonons or by impurities. They have, however, not considered the case of crossed electric and magnetic fields.

In this paper we develop a theory for the phenomenon of magnetoacoustic amplification in nondegenerate semiconductors which is valid for magnetic fields for which $\hbar\omega_c \gg k_B T$. We consider a geometric configuration where the wave vector of the acoustic wave is perpendicular to both electric and magnetic fields. For the sake of simplicity we assume that the energy surfaces in k space are spherical and the energy bands are parabolic.

The procedure used for the evaluation of the conductivity tensor is essentially the self-consistent-field method given by Ehrenreich and Cohen,[20] applied by Quinn and Rodriguez[21] and also Spector[22] to degenerate metals. Starting from the equation of motion of the density matrix which takes into account the effect of electron collisions and expanding the density matrix into time-dependent and time-independent parts, we obtain an expression for the time-dependent part of the density matrix which is further used to derive expressions for the conductivity and diffusion tensors. In order to calculate the absorption coefficient these general expressions are then evaluated using nondegenerate statistics for the specific case of the high magnetic fields and acoustic mode of lattice scattering. Our results reduce to those of Nill and McWhorter[17] in the limit of zero electric field and a constant relaxation time. It is seen from our results that taking into account the energy dependence[23] of the collision frequency considerably modifies the attenuation.