The equilibration of Co(II) ions between preferred tetrachloro- and tetranitrato-sites in 40 mol% Ca(NO₃)₂ - 60 mol% KNO₃ glass doped with Co(II) and chloride ions can be followed by monitoring the electronic spectra characteristic of Co(II) in these environments. Like most structural equilibria, this exchange is frozen out in the general glass transformation region of the solvent matrix. However, this element of the structure is characterized by relaxation times shorter on the average and of narrower distribution than those of the structure as a whole. The relaxation spectra are essentially unchanged when the chloride ligand is replaced with bromide. This contrasts with coordination equilibria in aqueous solutions which occur on time scales long with respect to the structural relaxation time of the solvent.

I. INTRODUCTION

Much interest has been shown recently in characterizing in detail the non-exponential, non-linear responses to perturbations from equilibrium of vitreous substances near their glass transitions. Of particular interest is the origin of pronounced differences between the response functions for perturbations of different character. Thus it has been shown that an electrical field stress applied instantaneously to the viscous molten salt 0.4 Ca(NO₃)₂ - 0.6 KNO₃ is dissipated much more rapidly than a shear stress. Both perturbations are relaxed rapidly in comparison with the relaxation to equilibrium after sudden changes in the temperature or pressure acting on a system near $T_g$. Moynihan, Macedo and co-workers have shown in general that the kinetics of return to equilibrium in the latter case depend on the particular property being monitored (e.g., volume $V$ or enthalpy $H$).
Why enthalpy should relax at a different rate and with a somewhat different spectrum of relaxation times than volume and why shear stress should be relaxed more rapidly than either but less rapidly than the electrical field is not yet entirely clear; the ideas are still in the formative stages. The subject area is a challenging one with the understanding of dynamic relations between different elements of aperiodic structures at stake. Greatly needed are more empirical data and, in particular, data which are selective for certain elements of the structure.

Barkatt and Angell\textsuperscript{11} have shown recently that the relaxation of a particular element of a glass structure can be monitored spectroscopically if that element gives rise to well defined absorption bands. They demonstrated in preliminary fashion that at least the later stages of the equilibration of a Co(II) cation with respect to two preferred sites (four-coordinated by NO\textsubscript{3} and four-coordinated by Cl\textsuperscript{-}) after a temperature jump proceeded more slowly than the equilibration of the structure as a whole in response to a shear stress. Because of the small optical density changes being monitored, this measurement suffered from the need for temperature displacements of some 7 degrees, which caused the responses to be distinctly non-linear. The development\textsuperscript{4-8} of an analysis by means of which the relaxation kinetics of a process can be extracted from the monitoring of a property during continuous cooling and heating is therefore of particular value for optical studies. The present short paper is based on the application of this analysis to the Co(II) site exchange relaxation problem.

II. EXPERIMENTAL SECTION

40 mol\% Ca(NO\textsubscript{3})\textsubscript{2} - 60 mol\% KNO\textsubscript{3} glass containing 1.2 mol \% Cl\textsuperscript{-} and 0.014 mol \% Co(II) was prepared as described previously\textsuperscript{11} by dehydration of an aqueous melt and transferred to a plastic optical cell containing two plastic U-tubes through which fluid from a controlled temperature bath could be passed. The use of plastic rather than glass cell materials is important since it minimizes expansivity differences between the cell and the melt and thereby obviates apparent changes in optical density arising from separation of the sample from the cell walls at low temperatures.

The population of the tetrachloro-coordinated Co(II) ions in the melt was monitored continuously by measuring the optical density \(D_{660}\) at the frequency of the 660 nm absorption band as the sample was cooled from a temperature above the transition region (356K) to a temperature below the transition region (317K) and subsequently reheated over the same range. Temperature \(T\) was monitored as a function of time \(t\) during cooling and reheating. \(T\) was not a linear function of \(t\), but in the range (320 to 337 K) where relaxation effects were observable (cf. Fig. 1) could be represented accurately as a quadratic function of time. Differentiation of a quadratic least squares fit of the \(T-t\)
data in this range gave the rate of temperature change $q(=dT/dt)$ as a function of $T$:

$$q(K/min) = -0.476[T(K) - 315.2]^{1/2} \quad (1)$$

$$q(K/min) = 0.506[349.6 - T(K)]^{1/2} \quad (2)$$

This corresponds to a gradual decrease in $q$ during cooling from -2.2K/min at 337K to -1.0K/min at 320K and a decrease in $q$ during subsequent reheating from 2.8K/min at 320K to 1.8K/min at 337K. Some small irreproducibility in $D_{660}$ (≈0.2%) was noted between the start and finish of the run. This was ascribed to a small irreversible plastic deformation of the optical cell at the high temperature limit of the experiment.

III. RESULTS AND DISCUSSION

A plot of $D_{660}$ versus $T$ during cooling and subsequent reheating is shown in Fig. 1. The optical density, $D_{660}$, is analogous to the glass configurational enthalpy insofar as both quantities reflect the proportion of high energy configurations which have been excited at temperature $T$. Comparison with Fig. 2 of Ref. 8 shows that the $D_{660}$-T plot exhibits relaxational effects during cooling and reheating in the glass transition region qualitatively similar to those observed when monitoring enthalpy. Above 337K the $D_{660}$-T curves for cooling and heating coincide, so that $D_{660}$ in this range is a measure of the temperature dependence of the tetrachloro Co(II) population in the equilibrium liquid and could be represented by the linear equation:

$$D_{660e}(cm^{-1}) = L_e + M_e T = 2.9586 - 6.40 \times 10^{-3}T(K) \quad (3)$$

Below 320K the $D_{660}$-T curves for cooling and heating also coincide, so that in this range the tetrachloro Co(II) population can be considered to have ceased exhibiting any temperature dependence, i.e., the tetrachloro Co(II) population has been frozen-in at a constant value in the glass. The temperature dependence of $D_{660}$ for the glass could be expressed by the linear equation:

$$D_{660g}(cm^{-1}) = L_g + M_g T = 1.0646 - 6.6 \times 10^{-4}T(K) \quad (4)$$

Addition of 1.2 mol% Cl and 0.014 mol% Ca(II) shifts the glass transition temperature $0.4Ca(NO_3)_2 \cdot 0.6KNO_3$ by a negligible amount, so that it is valid to compare the spectroscopic probe ion relaxational data with the enthalpy relaxation data for an undoped nitrate melt. To facilitate this comparison we have plotted in Fig. 1 the evolution of the fictive temperature determined from the enthalpy, $T_{fH}$, during a rate cool and subsequent reheat through the transition region at 2K/min, approximately the mean rate of temperature change for the spectroscopic measurements. (The $T_{fH}$-T curve was calculated using the parameters in line 3 of Table II of Ref. 8.) The relaxation region for the respective
D₆₆₀ and Tₚₘ plots may be taken as the region of hysteresis between the heating and cooling curves. We may note, first, that the temperature region of structural relaxation effects for the Co(II) probe ion coordination rearrangement (320 to 337K) is much narrower than, but falls within the relaxational region for enthalpy (305 to 350K). Second, the relaxation region for the probe ion measurements occurs in the low temperature end of the enthalpy relaxation region, indicating that on the average the exchange of nearest anion neighbors in the transformation of the Co(II) probe ion from a chloride to a nitrate coordinated species is considerably more rapid than whatever configurational changes are involved in the structural relaxation of the enthalpy.

To make the comparison between the relaxation involving the Co(II) coordination state and the enthalpy relaxation data more quantitative we have fit the former data to the same kinetic equations used to treat the latter data (cf. Eqs. (8) and (12) of Ref. 8):

\[
T_{f\text{Co}}(T) = T_o + \frac{T}{D_{660}(T)}
\]

\[
\tau_{0\text{Co}} = A_{\text{Co}} \exp\left(\frac{x_{\text{Co}} \Delta h^*}{RT} + \frac{(1 - x_{\text{Co}}) \Delta h^*}{RT_{\text{fCo}}}\right)
\]

where subscript "Co" indicates that the parameters refer to the Co(II) probe ion relaxational data. \( T_{f\text{Co}} \) is the fictive temperature assessed from Co(II) relaxational data and is given by (compare Eq. (4) and Fig. (2) in Ref. (8)):

\[
T_{f\text{Co}}(T) = \frac{L_e - D_{660}(T) + M_T}{M_e - M_g}
\]

where \( L_e, M_e, \) and \( M_g \) are taken from Eqs. (3) and (4). The \( A_{\text{Co}} \) parameter is fixed by matching the limiting fictive temperature, \( T_{f\text{Co}}(\sim 330.0K) \), while the \( \tau_{0\text{Co}} \) and \( x_{\text{Co}} \) parameters are picked by matching the shapes of the heating and cooling curves. \( \Delta h^* \) was set equal to the shear viscosity activation enthalpy. The values of \( q \) were taken from Eqs. (1) and (2). The best fit parameters are

\[
\begin{align*}
A_{\text{Co}} &= 1.01 \times 10^{-91} \text{s} \\
\Delta h^* &= 141 \text{ kcal/mol} \\
\beta_{\text{Co}} &= 0.63 \\
x_{\text{Co}} &= 0.86
\end{align*}
\]

The \( D_{660}-T \) cooling and heating curves calculated from these parameters are shown in Fig. 1.

The \( \beta_{\text{Co}} (= 0.63) \) parameter is considerably larger than the \( \beta \) parameter for the enthalpy (≈ 0.42-0.48), so that the spectrum of relaxation times is much narrower for the Co(II) probe ion relaxation than for the enthalpy structural relaxation. This is reflected in Fig. 1 in the much smaller range of temperature of relaxation effects for the probe ion.
relaxation. At 330K the mean equilibrium probe ion relaxation time $<\tau_{Co^2+}>_e$ (cf. Eq. (15) in Ref. 8) is $3.5 \times 10^2$s, compared to the corresponding $<\tau_{H^+}>_e$ value of $7.0 \times 10^2$s. That is, as noted above, the Co(II) coordination rearrangement takes place on the average much faster than the enthalpy relaxation.

One possible reason for this is that the Co(II) coordination rearrangement might involve transport of only the more mobile ions in the melt, e.g., NO$_3^-$ anions moving out of the Co(II) coordination sphere and being replaced by Cl$^-$ ions. This calls to mind the explanation proposed$^9$ for the fact that the electric field in this system near $T_g$ relaxes much faster than does the shear stress, namely, that the electric field relaxes via movement of the more mobile K$^+$ cations, while the shear stress relaxation involves in addition motion of the less mobile Ca$^{2+}$ cations. This in turn suggests that the appropriate activation enthalpy $\Delta h^*$ for the Co(II) ion rearrangement might be that obtained for the electric field relaxation$^9$ and presumably characteristic of the transport of fast ions in this system, viz., 78 kcal/mol. We attempted a fit (Eqs. (5) - (7)) to the data of Fig. 1 using this $\Delta h^*$ value, but were unable to obtain good agreement between the experimental and calculated curves.

With the idea in mind that the rate of the Co(II) probe ion relaxation might depend on the mobility of the foreign anion in the melt, we have carried very recently a spectroscopic relaxation experiment at heating and cooling rates comparable to those for Fig. 1 in which the Cl$^-$ ion was replaced by Br$^-$ ion and the experiment monitored at the absorption wavelength (662nm) of the tetrahedral CoBr$_4^{2-}$ species. The results of this experiment are shown in Fig. 2. Unfortunately the scatter in the data is so large as to mask the hysteresis between heating and cooling curves and preclude a detailed kinetic analysis. However the temperature ($T_f^*$ or $T_g$) of intersection of the extrapolated equilibrium and glass curves is about 330K, the same as for the data of Fig. 1, so that we may conclude that substitution of Br$^-$ for Cl$^-$ does not appreciably affect the rate of the Co(II) ion relaxation. In retrospect this is perhaps not surprising, since Cl$^-$ and Br$^-$ ions are both spherical and smaller than the planar NO$_3^-$ ion. That is, it could be that the rate of migration of the larger NO$_3^-$ ion determines the rate of rearrangement of the Co(II) environment, so that a more meaningful experiment might be to study the effect on the rate of relaxation of replacement of Cl$^-$ with an asymmetric coordinating anion of considerably larger size, e.g., SCN$^-$. It is, on the other hand, quite possible that an entirely different explanation is needed to account for the difference in relaxational rates between enthalpy and the Co(II) ion coordination process. In this regard it is significant to note (Fig. 1) that, although the enthalpy relaxation is on the average slower than the Co(II) ion relaxation, the enthalpy relaxation occurs over a wider temperature range, and there are elements of the enthalpy relaxation (occurring at low temperatures on
Fig. 1) which are considerably faster than Co(II) ion rearrangement. It is conceivable that the enthalpy structural relaxation begins with highly localized, rapid configurational changes, insufficient to accomplish the replacement of the Co(II) coordination sphere, and proceeds eventually at much longer times to an adjustment of the structure over a region much larger than the region which must undergo rearrangement to permit replacement of the NO$_3^-$ ions with Cl$^-$ ions in the coordination sphere of a Co(II) ion. This is the picture of structural relaxation proposed by Majumdar$^{13,14}$, who suggested that a stress field giving rise to relaxation could be decomposed into elementary modes of wavelength $\lambda$, each with an associated relaxation time $\tau$ proportional to $\lambda^2$. The relaxation is presumed to first occur in small local areas (small $\lambda$ and $\tau$) and then to extend to larger areas (larger $\lambda$ and $\tau$) by adjustment of the mismatch between the local areas. Hence the Co(II) ion rearrangement might involve only those modes intermediate in size and time scale between the smallest and the longest modes involved in the enthalpy relaxation.

It appears that relaxational studies of properties that are sensitive only to local elements of the structure may be critical to gaining an understanding of the molecular events involved in the structural relaxation. For the 0.4 Ca(NO$_3$)$_2$ - 0.6 KNO$_3$ system one such potentially informative investigation might involve a relaxational study similar to the one carried out here of the NO$_3^-$ ion n$\rightarrow$$\pi^*$ absorption band, which is sensitive to the local NO$_3^-$ ion environment$^{14}$.

Acknowledgements. This research was supported at Purdue University by the NSF-MRL Block Funding Program, DMR 72-03018 A04, and at Catholic University by Office of Naval Research Contract N00014-75C-0856.

REFERENCES

1. R. Gardon and O.S. Narayanaswamy, J. Am. Ceram. Soc., 53, 380 (1970).
2. O.S. Narayanaswamy, J. Am. Ceram. Soc., 54, 491 (1971).
3. R.W. Douglas, "Amorphous Materials", R.W. Douglas and B. Ellis, Eds., Wiley-Interscience, New York, 1972, pp. 3-22.
4. O.V. Mazurin, S.M. Rekhson, and Yu. K. Startsev, Fizika i Khimiya Stekla, 1, 438 (1975).
5. C. Moynihan, P. Macedo, N. Saad, M. DeBolt, B. Dom, A. Easteal, and J. Wilder, Fizika i Khimiya Stekla, 1, 420 (1975).
6. C.T. Moynihan et al., Proceedings of the Workshop on the Glass Transition and the Nature of the Glassy State, R. Simha and M. Goldstein, Eds., New York Academy of Sciences, in press.
7. M.A. DeBolt, A.J. Easteal, P.B. Macedo, and C.T. Moynihan, J. Am. Ceram. Soc., 59, 16 (1976).
8. C.T. Moynihan, H. Sasabe, and J. Tucker, this volume.
9. F.S. Howell, R.A. Bose, P.B. Macedo, and C.T. Moynihan, J. Phys. Chem., 78, 2673 (1974).
10. A. Weitz and B. Wunderlich, J. Polym. Sci: Polym. Phys., 12, 2473 (1974).
11. A. Barkatt and C.A. Angell, J. Phys. Chem., 79, 2192 (1975).
12. C.K. Majumdar, Solid State Commun., 9, 1087 (1971).
13. R.W. Douglas, J. Non-Cryst. Solids, 14, 1 (1973).
14. J. Wong and C.A. Angell, J. Non-Cryst. Solids, 7, 109 (1972).
Figure 1. Variation with temperature of optical density $D_{660}$ at 660nm CoCl$_4^{2-}$ absorption peak and of fictive temperature $T_{fH}$ determined from enthalpy during cooling and reheating in the glass transition region of a 0.4 Ca(NO$_3$)$_2$ - 0.6 KNO$_3$ melt.
Figure 2. Variation with temperature of the optical density $D_{662}$ at the 662 nm absorption peak of CoBr$_2^-$ during cooling and reheating of a 0.4 Ca(NO$_3$)$_2$ - 0.6 KNO$_3$ melt in the glass transition region. ● cooling, ○ heating.