DYNAMICS OF VITREOUS AND MOLTEN ZINC CHLORIDE

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The dynamics of vitreous and molten zinc chloride have been studied with inelastic neutron scattering at the Intense Pulsed Neutron Source. The results are analyzed in terms of the scattering function $S(Q,E)$ and the effective vibrational density of states $G(E)$. The vibrational spectra of both glass and liquid are dominated by broad features centered at 15 and 35 meV which are identified with F_2 modes of $ZnCl_4^{2-}$ tetrahedra. The other two normal modes are not observed because of inadequate resolution and broadening and overlap resulting from coupling between tetrahedra. The behavior of $ZnCl_2$ is contrasted with other tetrahedrally coordinated glasses that have been studied with the same technique.

Zinc chloride, $ZnCl_2$, has a tetrahedrally coordinated network structure in both vitreous and liquid states. Its structure has been thoroughly established by neutron diffraction measurements in the glass by Desa *et al.*¹ and in the liquid by Biggin and Enderby^{2a} and by Howe *et al.*^{2b}. It has also been investigated by Molecular Dynamics simulations³, on the basis of solely ionic forces. Its bond angle of approximately 110° ¹ places it intermediate between oxide glasses like SiO_2 ($\sim 150^\circ$)⁴ and chalcogenide glasses like $GeSe_2$ ($80-100^\circ$)⁵ and $SiSe_2$ ($\sim 70^\circ$)⁶. Relevant parameters for these glasses are listed in Table 1. From the point of view of transport properties, $ZnCl_2$ behaves as a relatively fragile liquid⁷ compared with other tetrahedrally coordinated glass formers, having a rapid drop in viscosity as the temperature is raised above the glass transition, T_g (390 K).

The aims of the present study were to investigate the dynamics of the glass and liquid by measuring the scattering function $S(Q,E)$ over a wide range of energy E and wave vector Q and to compare the results with those of similar studies of vitreous SiO_2 ⁸, $GeSe_2$ ⁹, and $SiSe_2$ ¹⁰. In addition, the low T_g of $ZnCl_2$ makes the liquid state more amenable to inelastic neutron scattering measurements than in the case of other tetrahedrally coordinated materials.

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Inelastic neutron scattering measurements on anhydrous ZnCl_2 were carried out on the Low-Resolution Medium-Energy Chopper Spectrometer (LRMECS) at IPNS with an incident energy $E_0 = 80.3$ meV. Time-of-flight data were collected in 41 groups of detectors placed at mean scattering angles ϕ ranging from 2.7° to 116.4° . Runs were made with the ZnCl_2 sample in the vitreous state at 298 K and in the liquid state at 620 K. This temperature, 230 K above the glass transition and 30 K above the melting point, $T_m = 590$ K, was chosen to avoid the possibility of crystallization. Runs were also made with an equivalent set of empty silica tubes at the same temperatures, with a vanadium standard, with no material in the beam and with a cadmium absorber covering the sample. Data were converted to the form of the scattering function $S(Q, E)$ and effective vibrational density of states $G(E)$ using standard procedures described in detail in Ref. 8. The energy resolution (FWHM) was 5.3 meV for elastic scattering ($E = 0$), decreasing to approximately 3.2 meV for energy transfers of 50 meV. The Q resolution was estimated to be $0.14 \text{ \AA}^{-1}$ at $Q = 5 \text{ \AA}^{-1}$.

Fig. 1 shows the elastic scattering, $S(Q, 0)$, for the glass and liquid as a function of Q . The general behavior is similar to that of the structure factors measured for the glass¹ and liquid² by neutron diffraction, the main difference being the fall-off in the intensity at large Q , due to the larger proportion of scattering occurring at larger E as Q increases.

The energy dependence of the inelastic scattering is most easily visualized from the effective neutron- and amplitude-weighted vibrational density of states $G(E)$ ⁸. For the glass, multi-phonon scattering was subtracted with an iterative procedure⁸ to give the function $G_1(E)$ shown in Fig. 2, which represents the best estimate of the effective one-phonon density of states for the glass. The low- E region, where the elastic scattering falls within the resolution function, has been excluded. $G_1(E)$ is seen to be dominated by two peaks centered approximately at 15 and 35 meV (~ 120 and 280 cm^{-1}) respectively. The same two features were observed by Galeener *et al.*¹¹ using a beryllium-filer spectrometer although the first peak occurs at a slightly lower energy (~ 11 meV) in their data.

In the Raman scattering data of Galeener *et al.*¹¹, the spectrum with HV polarization, which usually resembles the true density of states¹², shows principal peaks at 110 and 280 cm^{-1} , in good agreement with the peaks in the neutron measurement. Smaller peaks are observed around 80, 230 and 320 cm^{-1} ; the peak at 230 cm^{-1} dominates the HH spectrum. By analogy with GeSe_2 ⁹, which has a rather similar spectrum, the latter can be identified with the A_1 tetrahedral breathing mode. Peaks at similar energies are observed in the later measurements of Cacciola *et al.*¹³, who identify the peaks around 70, 100-120, 230 and 270 -

320 cm^{-1} in the glass with tetrahedral modes of $E(\nu_2)$, $F_2(\nu_4)$, $A_1(\nu_1)$, and $F_2(\nu_3)$ symmetry, respectively. The splitting of the two F_2 modes is ascribed to TO-LO splitting. In the neutron effective density of states, only the two F_2 modes appear to be present. The same features, slightly shifted, are observed in the Raman spectra of the liquid at 592K.

The far-infrared spectra measured by Angell *et al.*¹⁴ for ZnCl_2 glass and liquid show features generally similar to the Raman spectra. In the glass at room temperature, the principal peaks are at 105 and 265 cm^{-1} with shoulders at 75 and 120 cm^{-1} ; in the liquid at 593K, the principal peaks are at 90 and 260 cm^{-1} with a shoulder around 120 cm^{-1} . The main difference from the Raman spectra is that the several Raman peaks observed in the 230-320 cm^{-1} region in both glass and liquid are replaced by a broad spectrum centered around 260 cm^{-1} .

Sen and Thorpe¹⁵ have shown that, under a certain set of simplifying conditions, the dynamics of AX_2 glasses can be described in terms of the AX_4 tetrahedra. A necessary condition for this to be applicable is that the AXA bond angle θ lie below the critical value $\theta_c = \cos^{-1}(-2M_X/3M_A)$, which has the value 111° for ZnCl_2 , very close to the observed value of θ . If we adopt this approach nevertheless, the frequencies and structure factors of the normal modes can be calculated in terms of isolated AX_4 tetrahedra following the procedure followed for GeSe_2 in Ref. 9. With values for the two valence force constants of $f_1''' = 110$ and $f_2''' = 30$ N/m, we obtain frequencies for the four tetrahedral modes of 104 (E), 112 (F_2), 230 (A_1) and 310 (F_2) cm^{-1} , respectively, in reasonable agreement with the optical frequencies and with the two neutron peaks if these are ascribed to the two modes of F_2 symmetry. We discuss below the structure factors of these two modes.

Fig. 3 shows the total effective density of states $G(E)$ for the liquid, which is related to the Fourier transform of the weighted average velocity autocorrelation function. In spite of the difference in the state of the sample, the functions shown in Figs. 2 and 3 have some similarity. In particular, the features at 15 and 35 meV observed in the glass survive the melting process, confirming the conclusion of Biggin and Enderby that the ZnCl_4^{2-} tetrahedra continue to play a significant role in the structure of the liquid.

The wave-vector dependence of the inelastic scattering is best viewed by considering the Q dependence of $S(Q, E)$ for a particular energy E . For the present purpose, we examine the scattering associated with the main peaks in $G(E)$. Figs. 4 and 5 show the Q dependence of $S(Q, E)$ for the glass at energies $E = 15.9$ and 35.6 meV, respectively. The Q dependence shows the expected Q^2 dependence at small Q , followed by the drop-off at high Q arising

from the Debye-Waller factor, with a small amount of short-period oscillation, which can be ascribed to correlated displacements of nearby atoms in the normal modes of vibration^{8,9}. In Figs. 4 and 5 we show the structure factors for the $F_2(\nu_4)$ and $F_2(\nu_3)$ modes computed with the tetrahedral model discussed above. There are some similarities between the observed and calculated structure factors, but the agreement is not as striking as in the case of GeSe_2 ⁹, perhaps because the condition for the validity of the isolated tetrahedral model ($\theta \ll \theta_c$) is not as well fulfilled. We note that SiSe_2 ¹⁰ also does not agree as well with the isolated tetrahedral model, perhaps because the tetrahedra are predominantly edge-sharing and therefore more strongly coupled. For SiO_2 , on the other hand, $\theta > \theta_c$ and the dynamics are more suitably discussed in terms of OSi_2 units⁸.

The value of the bond angle in ZnCl_2 may account for the fact that only two peaks are visible in density of states $G_1(E)$ as measured by neutron scattering, compared with the four or more observed for GeSe_2 ⁹. Sen and Thorpe¹⁵ showed that, as θ approaches θ_c , the $\nu_1(A_1)$ and $\nu_3(F_2)$ tetrahedral modes broaden and in fact overlap at $\theta = \theta_c$, the condition which applies for ZnCl_2 . In particular, the delta-function component of the $\nu_1(A_1)$ mode overlaps with the continuous component of the $\nu_3(F_2)$. This appears to make the $\nu_1(A_1)$ mode indistinguishable in the neutron density of states. The lower two tetrahedral modes, $E(\nu_2)$ and $F_2(\nu_4)$ are, according to the optical data^{12,13}, separated by about 30 cm^{-1} which is less than the resolution of the present measurement. The shoulder which can be barely identified in the neutron density of states at 11 meV (90 cm^{-1}) may be an indication of the $E(\nu_2)$.

In conclusion, the vibrational spectra of both vitreous and liquid ZnCl_2 are dominated by broad features centered at 15 and 35 meV . Taking into consideration the optical data and the Q dependence of the structure factors at these energies, these features are ascribed to the two F_2 modes of the ZnCl_4^{2-} tetrahedra. The other two normal modes are not observed, the lower one possibly due to inadequate resolution, the upper one due to broadening and overlap resulting from coupling between tetrahedra, which is expected to be strong because the bond angle is nearly equal to the critical angle for inter-tetrahedral coupling.

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TABLE 1. Characteristics of tetrahedrally coordinated AX₂ glass formers

AX ₂	Ref. ^a	Ref. ^b	$\frac{\bar{b}_A}{\bar{b}_X}$ ^c	$\frac{M_A}{M_X}$ ^d	θ ^e	θ_c ^f
SiO ₂	4	8	0.71	1.76	150°	112°
ZnCl ₂	1	This work	0.59	1.84	110°	111°
GeSe ₂	5	9	1.03	0.92	80-100°	136°
SiSe ₂	6	10	0.52	0.36	70°	>180°

^a Reference to neutron diffraction

^b Reference to inelastic neutron scattering

^c Ratio of neutron scattering lengths

^d Ratio of atomic masses

^e Average bond angle A- $\hat{X}$ -A

^f Critical angle $\theta_c = \cos^{-1} (-2M_X/3M_A)$ (Ref. 15).

FIGURE CAPTIONS

FIGURE 1. Elastic scattering $\langle S(Q,0) \rangle$ for (a) vitreous and (b) liquid ZnCl_2 . Curve (a) is displaced vertically by 100 units. The solid lines through the symbols represent cubic spline fits to the data.

FIGURE 2. One-phonon effective vibrational density of states $G_1(E)$ for vitreous ZnCl_2 .

FIGURE 3. Effective vibrational density of states $G(E)$ for liquid ZnCl_2 .

FIGURE 4. Scattering function $\langle S(Q,E) \rangle$ for vitreous ZnCl_2 measured at $E = 15.9$ meV (symbols), compared with model calculations for the ν_4 mode (dashes). The solid line through the symbols represents a smooth cubic spline fit to the data.

FIGURE 5. Scattering functions $\langle S(Q,E) \rangle$ for vitreous ZnCl_2 measured at $E = 35.6$ meV (symbols), compared with model calculations for the ν_3 model (dashes). The notation is the same as for Fig. 4.

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