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Nuclear-Magnetic-Resonance Studies of Bonding in Semiconducting Tl-As-Se Glasses

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^{205}Tl NMR measurements have been carried out on glasses of the semiconducting chalcogenide system Tl-As-Se. Chemical shifts and linewidths were measured as a function of composition and temperature. For a series of glasses in the pseudobinary system $(Tl_2Se)_x$-$(As_2Se_3)_{1-x}$ the isotropic component of the observed chemical shift ranges from -0.163% for $x = 0.33$ to -0.194% for $x = 0.66$. These relatively large paramagnetic shifts indicate that the thallium bonding configuration in this range of glass composition is highly covalent. For $x \leq 0.3$ the chemical shift drops (in magnitude) precipitously to about -0.09%, signaling the introduction of a more ionic-bonding configuration for lower thallium content. The ^{205}Tl NMR linewidths increase with increasing Larmor frequency as a result of anisotropic-chemical-shift contributions to the linewidth; these contributions are also an indication of the covalent nature of the thallium bonding. The observed chemical shifts and linewidths remain unchanged as the temperature is increased through the glass transition temperature and into the molten range. These unchanged shifts and linewidths demonstrate that the local structural order which involves the thallium bonding is preserved in the molten glass. Correlation times τ_c for the thallium bonds in these molten glasses are longer than 5×10^{-5} sec at temperatures up to 200 °C. These results are contrasted with those for selenium in which the ^{77}Se NMR becomes motionally narrowed in the melt, and the resulting correlation times are two orders of magnitude shorter than those for Tl-As-Se glasses at equivalent viscosity.

I. INTRODUCTION

Nuclear-magnetic-resonance (NMR) techniques have proven quite useful in the study of the structure of glasses.[1] The NMR spectra provide information concerning short-range (primarily nearest-neighbor) structural configurations, and in contrast to x-ray-diffraction spectroscopy, the application of NMR techniques is not hampered by the absence of long-range structural periodicity in glasses and liquids. The dipole-dipole, electric quadrupole, and chemical-shift interactions are all sources of spectral broadening which arise from the interaction of resonant nuclei with neighboring nuclear magnetic moments or bonding electrons. Studies of these interactions as a function of composition in glass-forming systems provide valuable information concerning changes in bonding configurations. In addition, these sources of spectral broadening can be strongly influenced by atomic reorientation or diffusive motions which occur in solids or liquids at elevated temperatures. Consequently, the study of the temperature dependence of NMR spectral broadening can provide quantitative estimates of the correlation times for the chemical bonding of resonant nuclei.

This paper presents the results of a systematic application of NMR to the study of chemical bonding in the chalcogenide glass system Tl-As-Se. Many of the principal constituents of chalcogenide glasses are unlikely subjects for NMR studies because of low natural abundance of resonant isotopes (S, Se, Te, Ge), extremely long spin-lattice relaxation times T_1 (Se, Te), or large nuclear electric quadrupole interactions which cause excessive broadening (As, Sb). However, thallium does have highly favorable NMR characteristics. The two resonant isotopes ^{203}Tl and ^{205}Tl are 29.52 and 70.48% abundant, respectively; both have spin $\frac{1}{2}$ (and therefore zero quadrupole moment), and both have large gyromagnetic ratios. Furthermore, because of the large nuclear charge of these nuclei, the NMR spectra exhibit large chemical-shift effects, which serve as a sensitive measure of the relative covalency or ionicity of the thallium chemical bonding configuration. The study of the compositional and temperature dependence of these chemical-shift effects in the Tl-As-Se glass system is of central importance in the discussion which follows.

Arsenic trisulfide and arsenic triselenide glasses, based on the layer structure compounds As_2S_3 and As_2Se_3, may be regarded as the parent glasses for all the chalcogenide glasses of the arsenic-group elements.[2] With the exception of glassy selenium, these glasses have been studied more extensively than any other chalcogenide glass; the study of their structural, optical, and electrical properties is considered fundamental to an understanding of the entire class of vitreous chalcogenide materials. For the reasons given above, these glasses are not well suited for NMR studies, although the authors have recently reported the first observations of ^{77}Se NMR in glassy Se and As_2Se_3,[3-5] which will be referred to later in this paper. However, early investigation by Goryunova *et al.* of the extent of glass-forming regions in the glass systems formed by adding a third element to the systems As-S and As-Se revealed that particularly large regions existed for

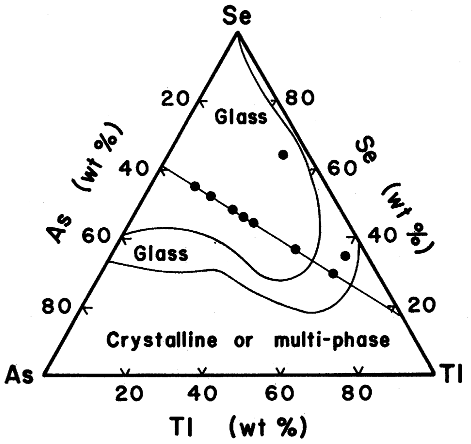

FIG. 1. Glass-forming region in the system Tl-As-Se (Flaschen *et al.*, Ref. 7). The upper boundary line is for 200-g batches, the lower for 20-g batches.

the addition of Tl.[6] Hence, it is possible to introduce large numbers of thallium nuclei, with highly favorable NMR characteristics, into the As-S and As-Se glass-forming networks.

Flaschen *et al.*[7] have carried out a more detailed determination of these glass-forming regions and their results for the Tl-As-Se system are presented in Fig. 1. They discovered that the addition of thallium markedly reduces the melt viscosity; temperatures corresponding to 30 P viscosity are as low as 185 °C for selenium-rich compositions of low arsenic content. Flaschen and co-workers suggested that the structure of these glasses may be based on long chains involving Se-Se linkages, with arsenic entering into the chains. They further hypothesized that the thallium might enter the chains as a weak link, the rupture of which causes low melt viscosities. However, the chemical-shift data to be presented here demonstrate that there is a substantial difference between the thallium bonding configurations of the thallium-rich and thallium-poor regions of the system, and the temperature dependence of the NMR spectra indicates that the thallium bonding configuration remains stable at temperatures well above the glass transition temperature.

II. INTERPRETATION OF NMR SPECTRA

In the absence of electric quadrupole effects, the chemical shift is the only electron-nuclear interaction that need be considered for the interpretation of the NMR spectra to be presented. When an atom is contained in a solid, the magnetic-resonance line of its nucleus may exhibit a small but significant chemical shift relative to the hypothetical resonance line of the atom in free space. This shift is usually defined for fixed frequency as

$$\Delta H/H=(H_{\mathrm{samp}}-H_{\mathrm{ref}})/H_{\mathrm{ref}}. \tag{1}$$

The shift arises because the resonant nucleus is subjected not only to the externally applied field $\vec{H}_{\mathrm{app}}$, but also to a local magnetic field produced at the nuclear site by the circulation induced in the orbital electrons by $\vec{H}_{\mathrm{app}}$. This shift will be a diamagnetic effect[8] because of Lenz's law. In addition, there is a second-order paramagnetic contribution[9] to the shift which arises from the magnetic interaction of the applied field with excited paramagnetic states that are mixed into the ground state of the free ion by its electrostatic interaction with neighboring ions. The size of this paramagnetic contribution of the chemical shift provides a measure of the relative ionicity or covalency of the chemical bonds which involve the resonant nuclei.

The chemical-shift interaction is a tensor quantity which may give rise to shifts which depend strongly upon the orientation of the principal axes of the tensor, relative to the direction of the applied magnetic field. It is most convenient to discuss the chemical-shift tensor in the principal-axes system in which it is diagonal and has the principal components σ_1, σ_2, and σ_3. In a polycrystalline material, there will exist nuclear sites having all possible orientations of the principal axes of the chemical-shift tensor relative to the direction of the applied magnetic field. In the calculation of the anisotropically chemically shifted resonance line shape one must therefore perform an average over all possible orientations, obtaining the so-called powder pattern. If it is assumed that the disorder in the glass is only orientational, then the resonance line shape in the glass will be equivalent to the polycrystalline case. This assumption neglects the additional broadening due to local variations in bond length and bond angle, but has no effect upon the qualitative conclusions to be drawn from the analysis of the anisotropically chemically shifted NMR spectra to be presented here. The analytic expression for this line shape is equivalent to that for satellite transitions in the first-order nuclear quadrupole powder pattern[10] and to that for the anisotropic Knight-shift powder pattern.[11,12] The field positions of the shoulders (edges) of this powder pattern can be written (for $\sigma_1<\sigma_2<\sigma_3\ll 1$) approximately as[11]

$$H_1=H_0\,(1+\sigma_1) \tag{2}$$

and

$$H_3=H_0\,(1+\sigma_3)\ , \tag{3}$$

and the position of the divergence is given by

$$H_2=H_0\,(1+\sigma_2)\ . \tag{4}$$

These expressions are for an experiment carried out at fixed frequency ν_0, where

$$H_0 = 2\pi\nu_0/\gamma\ , \tag{5}$$

and γ is the nuclear gyromagnetic ratio. The total width of the powder pattern is given by

$$\Delta_{cs} = H_3 - H_1 = H_0\ (\sigma_3 - \sigma_1)\ . \tag{6}$$

The width of the powder pattern is proportional to the frequency ν_0, and this allows one to observe the presence of anisotropic-chemical-shift effects in the frequency dependence of the linewidth.

The observed resonance line shape will also be broadened by the effects of the nuclear dipole-dipole interaction.[13] Resulting line shapes can vary substantially, depending upon the relative sizes of the chemical shift and dipolar interactions. A complete discussion of the derivation of the analytical expressions for these powder patterns as well as graphical representations of expected line shapes are presented in Ref. 14. In general, when the ratio of the chemical-shift width Δ_{cs} to the dipolar width δH (the peak-to-peak width of the derivative curve) is small, a single asymmetric resonance results, whose width increases as $\Delta_{cs}/\delta H$ is increased. For large $\Delta_{cs}/\delta H$ ($\Delta_{cs}/\delta H > 2$ for axial symmetry), a shoulder appears in the spectrum.

It is possible to separate the analytical expression for the chemical shift into an isotropic part and an angularly dependent part. This means that for a powder pattern the angularly dependent terms will be responsible for the broadening of the line shape, while the isotropic term simply shifts the entire resonance envelope bodily in field. The powder patterns to be considered in this paper will consist of simple, nearly symmetric resonances (no shoulders, small $\Delta_{cs}/\delta H$). In this case it is not possible to measure precisely the isotropic component of the chemical shift. Therefore, the approximation will be made that the isotropic chemical shift is given by the position of the zero crossing of the experimental derivative curve.

In addition to the Van Vleck[13] dipole-dipole interaction, there is another source of broadening for thallium NMR spectra in solids which is termed the indirect interaction.[15] The strength of this interaction depends upon the amount of electron-orbital overlap between thallium atoms. It will suffice for the purposes of this paper to mention that when this interaction becomes important the NMR spectrum of the less abundant isotope, ^{203}Tl, will be broadened relative to that of the more abundant one, ^{205}Tl.

III. EXPERIMENTAL PROCEDURE

The glasses studied in these experiments were prepared from 99.999%-pure elemental materials. The constituents were sealed in evacuated quartz ampoules, melted and fired in a rocking furnace, and air quenched. None of the compositions exhibited any tendency to devitrify and an examination of selected specimens with a scanning electron microprobe revealed no evidence of crystallinity. Electrical conductivities of all the glasses were low enough to ensure adequate penetration of radio-frequency (rf) fields into solid bulk samples.[7]

Nuclear-resonance spectra were obtained at frequencies ranging from 6.0 to 16.0 MHz, using a standard cw broad-line nuclear-induction NMR spectrometer (Varian Associates model V-4200). For extremely weak signals (low thallium content) a computer of average transients was employed in a repetitive-sweep signal-averaging technique. Chemical shifts were measured relative to the resonance position of Tl ions in a 2.5M solution of thallium acetate in water. Elevated sample temperatures were obtained with a hot-nitrogen-gas flow system; the temperature was monitored with a copper-constantan thermocouple.

IV. EXPERIMENTAL RESULTS

A. Chemical Shift

^{205}Tl and ^{203}Tl NMR spectra were studied in selected compositions throughout the glass-forming system. These compositions are shown in Fig. 1 and they include seven samples on the pseudobinary line Tl_2Se-As_2Se_3, with one glass near the limit of maximum thallium content (60 wt% Tl), and two low-arsenic-content glasses (7 wt% As).

The room-temperature thallium NMR spectra (both ^{203}Tl and ^{205}Tl) from three of the glasses on the Tl_2Se-As_2Se_3 pseudobinary line are shown in

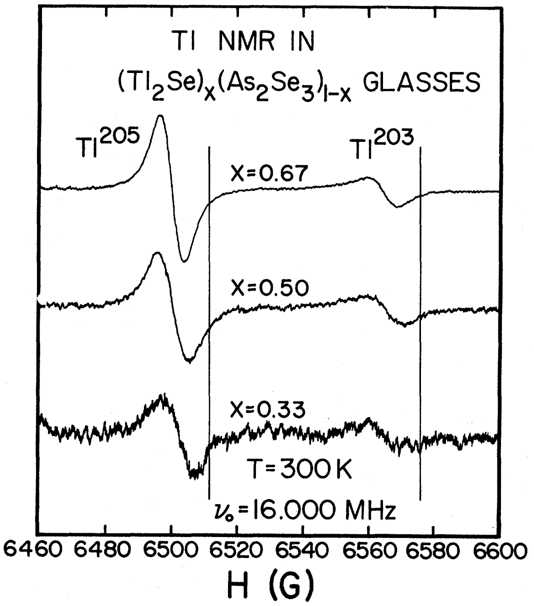

FIG. 2. Thallium NMR spectra in glasses of the Tl-As-Se system. The vertical lines represent the positions of the thallium NMR lines in a thallium acetate reference sample.

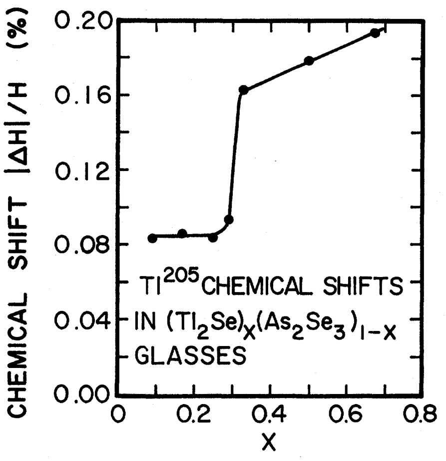

FIG. 3. Magnitude of the ^{205}Tl NMR isotropic chemical shift in Tl-As-Se glasses plotted as a function of Tl_2Se content.

Fig. 2. These spectra were obtained without the aid of the signal averager. All glasses with 0.3 molar fraction Tl_2Se or less had to be studied in the repetitive-sweep averaging mode. In all cases, because of the field-modulation technique, the traces represent the derivative of the absorption spectrum. The vertical lines designate the resonance positions of the two thallium isotopes in the thallium acetate reference sample. All of the resonances are structureless (exhibit no shoulders) and relatively symmetric, which indicates that the ratio $\Delta_{cs}/\delta H$ is small. That is, the dipolar interaction makes a substantial contribution to the linewidth.

In order to simplify the ensuing discussion, the isotropic chemical shift $\Delta H/H$ in the glass is defined simply as the measured separation of the zero crossing of the ^{205}Tl derivative curve and the position of the ^{205}Tl thallium acetate reference line. All of the spectra observed throughout the glass-forming system exhibited paramagnetic, isotropic chemical shifts with respect to the reference line.[16] In other words, a lower applied magnetic field is required to produce a resonance in the glass; the local chemical-shift field is aiding the applied field. Then according to the definition in Eq. (1), all of the shifts are negative. This paramagnetic nature of the chemical shift indicates that there is a large second-order paramagnetic contribution arising from low-lying excited electronic-orbital states which opposes the diamagnetic contribution from the core electrons. The measured values of the isotropic shift $|\Delta H|/H$ for seven glasses ranging from 0.1 to 0.67 molar fraction Tl_2Se are plotted in Fig. 3. At low Tl_2Se content, the chemical shift remains relatively constant at about -0.085%. Then as the molar fraction of Tl_2Se reaches 0.3, the shift suddenly rises (in magnitude) steeply to roughly twice its value for low Tl_2Se content. The chemical shift exhibits a linear dependence on Tl_2Se content in the range of 0.33 to 0.67 molar fraction Tl_2Se.

B. Linewidths

In four of the samples containing the highest amounts of thallium, the experimental signal-to-noise ratio was large enough to permit the measurement of the peak-to-peak linewidth of the ^{205}Tl NMR spectra at Larmor frequencies ranging from 6.0 to 16.0 MHz. The results of these measurements are presented in Fig. 4 for the $x=0.67$ and 0.5 glasses on the $(Tl_2Se)_x$-$(As_2Se_3)_{1-x}$ line and the two low-arsenic-content glasses. The linewidths are observed to increase (broaden) in all samples as a function of increasing frequency. Hence there are substantial anisotropic-chemical-shift contributions to the linewidths. With the use of the curve-fitting procedure of Ref. 14, these data can be extrapolated to zero frequency to obtain the purely dipolar linewidths δH and the anisotropic components of the chemical shifts Δ_{cs}. The dipolar linewidths δH range from about 3.0 G in one of the low-arsenic glasses (60Tl-33Se-7As, wt%) to 5.0 G in a glass on the pseudobinary line with $x=0.5$. Scatter in the linewidth data of Fig. 4 precludes an accurate determination of the anisotropic component of the chemical shift Δ_{cs}. In general, Δ_{cs} is of the order of 0.05%, but it is not possible to determine the magnitude of the deviation from axial symmetry.

The total linewidth of the ^{205}Tl NMR spectrum also exhibits a dependence upon the composition of the glass. Along the pseudobinary line $(Tl_2Se)_x$-$(As_2Se_3)_{1-x}$ the linewidth increases from 7.3 G at $x=0.67$ to a maximum of 10.2 G at $x=0.33$. Below $x=0.33$ it decreases somewhat, reaching 9.3 G at $x=0.1$. Another compositional trend along this line is observed in the relative sizes of the ^{205}Tl

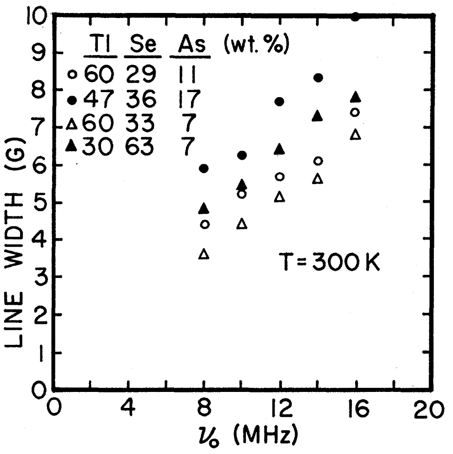

FIG. 4. Linewidths of the ^{205}Tl NMR spectra in Tl-As-Se glasses plotted as a function of Larmor frequency ν_0.

and ^{203}Tl linewidths. At low values of x ($x \leq 0.29$) the NMR linewidths for the two isotopes are approximately equal. But as x exceeds 0.5 the ^{203}Tl linewidth increases relative to the ^{205}Tl linewidth, and becomes 30% larger at $x = 0.67$.

C. Temperature Dependence

The ^{205}Tl NMR spectra in the $0.67Tl_2Se$-$0.33As_2Se_3$ (molar fraction) sample and the $0.25Tl_2Se$-$0.75As_2Se_3$ glass were studied at elevated temperatures. The $0.67Tl_2Se$ glass was chosen as representative of those samples which exhibit large ($\sim|0.18|$ %) chemical shifts, while the $0.25Tl_2Se$ glass represents the range of compositions for which the isotropic shift has the smaller value ($\sim|0.09|$ %). In both cases there was no apparent change in either the linewidth or the anisotropic chemical shift as the temperature exceeded the glass transition temperature T_g and climbed into the molten phase. This behavior is consistent with that reported previously by the authors for ^{205}Tl NMR in Tl_2Se-As_2Te_3 glass.[17]

At temperatures in the vicinity of 200 °C and above, the ^{205}Tl NMR spectra became unobservable in both samples. This behavior is also exactly analogous to that reported for ^{205}Tl NMR in Tl_2Se-As_2Te_3 glass. In that case it was demonstrated by measuring the spin-lattice relaxation time T_1 as a function of temperature that the free carriers provide the dominant relaxation mechanism, and since the carrier concentration is an exponential function of temperature, T_1 decreases rapidly with increasing temperature. This leads to lifetime broadening of the ^{205}Tl NMR line at high temperature, which probably sets the high-temperature limit on the observability of the resonance. Because the electrical conductivities of the glasses in the Tl-As-Se system are lower than that of vitreous Tl_2Se-As_2Te_3, the high-temperature limit is somewhat higher in the Tl-As-Se system.

V. DISCUSSION

A. NMR Evidence for Covalent Bonding

The large, paramagnetic isotropic chemical shifts exhibited by the ^{205}Tl NMR spectra in the glasses with high thallium content indicate that the bonding configuration for the thallium atoms in these glasses is highly covalent. It would appear that the thallium atoms are covalently bonded into the structural network of the glass and do not exist as interstitial ions in the voids of the glass network. This result seems eminently reasonable since it would be difficult to understand the incorporation of over 60 wt% thallium in some of these glasses without the benefit of covalent bonding on the part of the thallium atoms. However, the precipitous drop in the chemical shift below about $x = 0.3$ on the $(Tl_2Se)_x$-$(As_2Se_3)_{1-x}$ line strongly suggests that a thallium site with somewhat less covalent character is being introduced for glasses of low thallium content. In fact, the introduction of small amounts of this less covalent site could explain the linear drop in the chemical shift as x decreases from 0.67 to 0.33; the observed shift would be a weighted average of the shifts for the two types of sites. This might also explain the broadening of the ^{205}Tl spectrum in the vicinity of $x = 0.3$. The superposition of two unresolved NMR spectra with different isotropic chemical shifts can result in one broad spectrum. Attempts to resolve two lines in the vicinity of $x = 0.33$ were unsuccessful. Even if two lines do coexist, there must be a very sudden change in their relative intensities at $x = 0.3$ in order to explain the precipitous drop in the measured chemical shift at that composition.

A qualitative justification for identifying the 0.16–0.20% shifts as representative of covalent bonds and the 0.09% shifts as somewhat less covalent is provided by a comparison with the chemical shifts measured in some thallium salts (halides) where the relative covalency and ionicity of the chemical bonds is known. In ionic thallous chloride (TlCl) the ^{205}Tl isotropic chemical shift is about 0.06%, while in largely covalent thallic chloride ($TlCl_3$) the chemical shift of the ^{205}Tl NMR is 0.28%.[18] One might infer from this comparison that the thallium atoms enter the glass as Tl^{1+} ions for low thallium content but assume the Tl^{3+} valence state for high thallium content; however, the evidence is not conclusive.

Flaschen *et al.*[7] have reported the 30-P points for many glass compositions throughout the Tl-As-Se system. An examination of their viscosity data along the pseudobinary line $(Tl_2Se)_x$-$(As_2Se_3)_{1-x}$ reveals that there is a drop in the 30-P temperature from 285 to 240 °C near the composition $x \simeq 0.3$ for which the sudden transition in the ^{205}Tl chemical shift occurs. The data of Flaschen *et al.* are not sufficiently detailed to allow a determination of how abrupt this change in viscosity is. It can only be said that for $x > 0.3$, $|\Delta H|/H \simeq 0.18\%$, and the 30-P point $T < 240$ °C, and for $x < 0.3$, $|\Delta H|/H \simeq 0.09\%$ and the 30-P point $T > 285$ °C. The implication is that the depression of the melt viscosity in the thallium-rich half of the pseudobinary line is somehow associated with the introduction of the more covalent thallium bonding configuration in these compositions.

The increase in the NMR linewidth with increasing Larmor frequency provides additional evidence for the occurrence of a largely covalent thallium bonding situation in most of these glasses. The broadening of the resonance is attributed to anisotropic-chemical-shift effects, which are characteristic of a large anisotropy in the electronic configuration of the thallium atoms that occurs in highly directed bonding.

It is not possible to relate the measured dipolar linewidths to the structural configuration of the glass, because a detailed knowledge of the local structural configuration or environment of the resonant nuclei is lacking. Estimates of Tl-Tl dipolar interactions indicate that this interaction alone is probably sufficient to account for the observed dipolar linewidths. Furthermore, the increase in the width of the ^{203}Tl spectrum relative to that of the ^{205}Tl spectrum with increasing x along the line $(Tl_2Se)_x$-$(As_2Se_3)_{1-x}$ indicates that substantial effects of the indirect interaction[15] are present. These effects arise from molecular-orbital overlap between thallium atoms, which is a consequence of the increasingly covalent-bonding configuration of these atoms in the glasses with high thallium content. The presence of these effects further complicates any attempt to relate observed dipolar linewidths to local structure.

B. Implications of Temperature Dependence

The lack of any significant temperature dependence of the observed isotropic shift confirms its identification as a chemical shift rather than a Knight shift. The Knight shift involves the interaction between the nuclear magnetic moment and the conduction electrons and would be expected to be highly temperature dependent because of the exponential temperature dependence of the carrier concentration in these glasses.[2]

Since there is no change in either the chemical shift or the linewidth as the temperature passes through T_g and well up into the molten phase, the covalence of the thallium bonding and the local structural order are apparently preserved in the melt for viscosities as low as 30 P. If the correlation time τ_c, which characterizes the atomic reorientation rate within the thallium structural units in the molten glass, were to fall below 5×10^{-5} sec, the linewidth would narrow, due to the averaging of the static dipolar and anisotropic-chemical-shift interactions.[19,20]

This evidence for the preservation of local structural order in molten Tl-As-Se glasses is consistent with similar NMR results in liquid Tl_2Se-As_2Te_3,[17] and with the observation of identical far-infrared vibrational bands in solid and liquid layer-structure glasses.[21] The temperature dependence of ^{205}Tl NMR in liquid Tl-As-Se and Tl_2Se-As_2Te_3 glasses is in striking contrast with the temperature dependence of ^{77}Se NMR in elemental selenium, which occupies one corner of the Tl-As-Se system. The structure of glassy selenium is thought to comprise a mixture of helical chains (trigonal Se structure) and eight-membered rings (α-monoclinic Se structure). The authors have recently observed a broad ^{77}Se NMR line in solid glassy selenium which becomes motionally narrowed in molten selenium.[3–5] In this case the NMR measurements demonstrate that correlation times for atomic reorientation in the melt are in the range 10^{-5}–10^{-7} sec for temperatures above the 217 °C crystal melting point.

The occurrence of the motional narrowing of NMR spectra in liquid Se and its absence in liquid thallium-containing glasses at equivalent viscosity clearly demonstrates that quite different atomic reorientation rates prevail in these two types of materials. It is inferred from this fact that the structures of the materials are fundamentally different. While a ring-chain structure is almost certainly applicable to glassy and liquid selenium, such a structure is apparently not appropriate for the Tl-As-Se and Tl_2Se-As_2Te_3 glasses and liquids. The NMR results yield no evidence to support the model of Flaschen *et al.*[7] of As-Se chains with weak thallium bonds that rupture at elevated temperatures. Local structural order in the Tl-As-Se glasses is probably more closely related to that of the layer-structure compound As_2Se_3 and the structure of the crystalline compounds of the Tl-As-Se system than to the chain structure of glassy selenium. Rawson[22] has suggested that the structural environments or bonding configurations of the thallium atoms in the Tl-As-Se glasses may be similar to those found in the compound TlSe.[23] However, although TlSe is the most stable compound of the Tl-Se system, the compound Tl_2Se also exists in the thallium-rich alloys[24]; in addition, the composition Tl_2Se-As_2Se_3 forms a crystalline compound[25] and very recently the synthesis of single crystals of Tl_3AsSe_3 (or $3Tl_2Se\cdot As_2Se_3$) has been reported.[26] Clearly the thallium bonding environment in Tl-As-Se glasses cannot be identified *a priori* with that of a single-crystalline compound, and as demonstrated by the chemical-shift data, there is a substantial difference between the thallium bonding configurations of the thallium-rich and thallium-poor regions of the system.

VI. SUMMARY

The ^{205}Tl NMR spectra have been studied in glasses of the system Tl-As-Se at room temperature and in the molten state. Relatively large paramagnetic isotropic chemical shifts were observed for high thallium content which indicate that the thallium bonding configuration in these glasses is highly covalent. At lower thallium content there is a striking transition to a less covalent-bonding configuration. Frequency dependence of the NMR linewidths revealed a large anisotropic-chemical-shift contribution to the linewidth, which is characteristic of a highly anisotropic electronic configuration of the thallium and is also an indication of covalent bonding.

Temperature dependence of the NMR spectra demonstrated that the local structural order, characterized by the covalent thallium bonding, is preserved in the molten glass. Atomic reorientation rates for the thallium bonding configurations in the melt are characterized by correlation times τ_c longer than 5×10^{-5} sec at temperatures up to 200 °C. The results of the temperature-dependence study are contrasted with those for chain-structure selenium, in which the ^{77}Se NMR becomes motionally narrowed in the melt. Correlation times for atomic reorientation in liquid selenium are nearly two orders of magnitude shorter than those for molten Tl-As-Se glasses at equivalent viscosity. On the basis of the striking contrast of the NMR temperature dependences, it is suggested that the structure of Tl-As-Se glasses is more closely related to that of glasses based on layer-structure compounds, such as As_2Se_3 and As_2S_3, than to that of glasses based on chain structure compounds such as Se and S.

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Approximate Expression for the Binding Energy of Isotropic Biexcitons*

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A formula which gives the binding energy of the biexciton as a function of the electron-to-hole mass ratio σ is obtained for the case of isotropic effective masses of the carriers. The expression which contains powers of $[\pi/4 - \arctan(\sigma)^{1/2}]^2$ satisfies the requirements imposed by the Schrödinger equation and by the known results of variational calculations for the hydrogen and positronium molecules.

I. INTRODUCTION

The binding energy of biexcitons in a semiconductor with isotropic effective masses of the electrons and holes, m_e and m_h, has been calculated variationally by Sharma[1,2] with the method of James and Coolidge.[3] The variational reservoir allowed by this method, with five parameters, is better suited for certain values of the ratio $\sigma \equiv m_e/m_h$ than for others. Thus, certain features of the analytic dependence of the binding energy obtained by Sharma for $0 \leq \sigma \leq 1$ can be incorrect, even though excellent approaches to the actual ground-state energy may have been obtained for