ELECTRIC FIELD FLUCTUATIONS IN LIQUID TELLURIUM ALLOYS -
A HINT TO BOND CHARACTER

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Atomic scale electric field fluctuations in liquid tellurium alloys are
detected as they induce nuclear spin relaxation rate \( R_Q \) in noble gas im-
purity atoms, via quadrupolar interaction. Results for \(^{132}\)Xe in liquid Ag, Ga,
In, Ti, Ge, Sn-Te alloys are discussed, assuming that bonding in these
alloys may be described as a mixture of metallic, covalent and ionic bond-
ing. Using an inhomogeneous model, and obtaining the metallic fraction from
electrical conductivity, the \(^{132}\)Xe \( R_Q \) data are used to derive estimates of the
ionic bonding fraction in the alloys studied.

I. INTRODUCTION AND THEORY

Quite a lot of semiconducting alloys are alloys of chalcogen elements.
Among these, the tellurium alloys differ widely in their electrical, thermo-
dynamic and structural behavior\(^1,2\). We will focus on liquid tellurium alloys
which show a metal-nonmetal transition. Its origin in \( M_x\text{-Te} \) (\( M_x\text{=Ag}_x,\text{Ti}_x,\text{Sn,Pb} \))
and \( M_2\text{-Te}_3 \) (\( M=\text{Ga,In} \)) is still a subject of controversial discussion\(^1,3,4\). In
order to introduce new information, we measured the nuclear spin relaxation
rate of implanted inert noble gas atoms (\(^{132}\)Xe) in Cu-, Ag-, Ga-, In-, Ti-, Ge,-, and Sn-Te alloys by a TDPAD technique. The quadrupolar part of the relax-
ation rate (\( R_Q \)) gives a measure of "far IR near field electric field fluctua-
tions", which reflect the electronic configuration of the nearest neighbor
atoms, surrounding the Xe-probe atom. We observe large increases in \( R_Q \) which,
by comparing with the drop in the electrical conductivity, allow to estimate
an effective charge transfer from the metal to the tellurium atoms. This possi-
bility suggests an extension of the concept of a two dimensional bond charac-
ter chart, known from solids (e.g.\(^5\)), to liquid alloys.

The well known expression for the quadrupole relaxation rate (see e.g.\(^6\))

\[
R_Q = \text{const} \times \int dt \ C_{EFG}(t)
\]  

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machine time.
(\(C_{\text{EFG}}\) is the correlation function of the electrical field gradient) can be expressed by means of two- and three-particle correlation functions:

\[
C_{\text{EFG}} = \sum_{i} v_{i}^{(i)}(r_{i,s}(0))v_{i}^{(i)}(r_{i,s}(t))P_{2}(\cos \alpha_{ij}(t)) + \sum_{i,j} v_{i}^{(i)}(r_{i,s}(0))v_{j}^{(j)}(r_{j,s}(t))P_{2}(\cos \alpha_{ij}(t)) = T_{2}(t) + T_{3}(t) \tag{2}
\]

In monatomic liquids \(T_{2}\) and \(T_{3}\) cancel to a high degree. \((T_{3}\) is always negative!) This cancellation reflects the facts that the EFG's are short ranged due to screening of the conduction electrons and that the surrounding has high symmetry. In liquid alloys the cancellation ceases to exist if the EFG's differ for A- and B-atoms giving an increase in \(R_{Q}\). We write \(C_{\text{EFG}}\) for an A-B alloy (for details see 7):

\[
C_{\text{EFG}} = C(T_{2}^{AA} + T_{3}^{AA}) + (1-C)(T_{2}^{BB} + T_{3}^{BB}) - C(1-C)(T_{2}^{AB} + T_{3}^{AB}) \tag{3}
\]

The first two terms are the interpolation of the EFG-correlation functions for pure constituents, the third is the alloy enhancement \(\sim C(1-C)\). Assuming similar dynamics for A- and B-atoms with respect to the inert Xe probe, and for simplification an \(r\)-independent ratio of the EFG's \(Z_{A}/Z_{B}\) one obtains

\[
R_{Q} \sim \frac{[CZ_{A}^{2} + (1-C)Z_{B}^{2}] \tau_{\text{met}} + (1-C)(Z_{A} - Z_{B})^{2} \tau_{3}(0) \tau_{3}]}{(CZ_{A}^{2} + (1-C)Z_{B}^{2})(\tau_{2}(0) + \tau_{3}(0))} \tag{4}
\]

\((\tau_{\text{met}} \) is the correlation time for the EFG-function \(C_{\text{EFG}}\) Eq. (2) and \(\tau_{3}\) is the correlation time for the term \(T_{3}(t)\) only.) For our purpose we only need the ratio of \(\tau_{\text{met}}/\tau_{3}\), \(\tau_{3}(0) = T_{3}(0)/Z_{A}^{2}\) etc.

2. RESULTS AND DISCUSSION

For \(^{132}\text{mXe}\) as a probe atom quadrupolar relaxation is the essential relaxation channel.

In semiconducting Te alloys the described formalism does not fit the experimental data. Neither the large increase in \(R_{Q}\) nor the differences between Ge-Te and Sn-Te, or between Ga-Te and In-Te can be explained satisfactorily. To get a simple quantitative treatment of quadrupolar relaxation on Xe atoms, we will use a model for an inhomogeneous liquid alloy 14, starting by giving arguments for using this model: In metallic alloys or liquid noble gases only nearest neighbor atoms contribute decisively to the EFG. Inhomogeneity of the alloy does therefore not mean to use a cluster model (with about 30 or more atoms in a cluster), but to allow different regions in the liquid on a nearest neighbor length and a correspondingly short time scale. Such a form of inhomogeneity is in agreement with thermodynamic data: For Ti-Te and Sn-Te the data can be
fitted by two curves of ideal mixing binary systems M-M\textsubscript{X} and M\textsubscript{X}-Te-Te. (\(\Delta S\) for In-Te is more difficult to explain as there are probably volume effects included.) See Fig. 1.

Taking for the metallic Te-alloys of Fig. 2 the formal valencies \(Z\text{Au}=1\), \(Z\text{Bi}=5\), \(Z\text{Sb}=5\) and an effective valency of 3 for Te, Eq.(4) was fitted to the experimental data. A mean value of \(\tau_{3}/\tau_{\text{met}} \approx 7\) was obtained which agrees with the values from different model calculations for liquid metals\textsuperscript{7,8}.

The striking fact that a large increase in \(R_{Q}\) was mainly observed when solid tellurium compounds exist which crystallize in ionic structures\textsuperscript{12}, leads to the assumption that charged complexes may cause the bigger field gradients.

To check if covalently bonded atoms can produce also large EFG-fluctuations, \(R_{Q}\) of \(^{132}\text{mXe}\) in As-Te and Se-Te alloys was measured, too. Only a slight increase was observed at temperatures close to the liquidus temperatures.

Searching for a correlation between \(R_{Q}\) and the decrease of electrical conductivity we follow the ansatz of Tsuchiya et al.\textsuperscript{14} who determined a fraction of nonmetallic regions \(X_{1}\)

\[
X_{1} = 1 - X_{0} = 1 - \left[\sigma(C)/\sigma(0)\right]^{1/2}
\]

(\(X_{0}\) being the fraction of metallic regions, \(\sigma(C)\) the conductivity at the measured concentration and temperature and \(\sigma_{0}\) an interpolation \(\sigma_{0} = \left[C/\sigma_{M}+(1-C)/\sigma_{Te}\right]^{-1}\).)

The measured relaxation rates show a linear dependence on \(X_{1}\) (Fig. 3). As there is - within the experimental errors - a linear dependence \([R_{Q}(C)-R_{Q}(0)]\approx X_{1}\), it is justified to assume incoherent superposition \(R_{Q} = R_{Q_{0}} + R_{Q_{1}} X_{1}\).
In the frame of the model all nonmetallic regions in the alloy have the same stoichiometry $M_x Te_y$. Eq.(4) was applied to determine the charge transfer from the slope of the curves. For this purpose the ratio $(T_2(0)+T_3(0))/T_3(0)=0.7$ was taken from model calculations. In principle one has to take into account differences in the dynamics in different alloys, but as there is no correlation of $R_Q$ with viscosity changes this was neglected. $\sqrt{R_{Q1}^2 - (Z_A - Z_B)^2}$ is then proportional to an effective charge transfer $\delta = \frac{1}{2}(Z_A - Z_B)$. For liquid Tl$_2$Te the value of $\delta$ was given by Robertson $\delta = 1.34$ (Tl$^{+3.39}$Te$^{-1.78}$). We can now use the $R_Q$ data for the other alloys to derive the charge transfer as a second coordinate for a bond character chart, see Fig. 4. $\delta_{ion}$ is the charge transfer for the nominal ionic charges.

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