

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 impurity atoms, via quadrupolar interaction. Results for ^{132}Xe in liquid Ag, Ga, In, Tl, Ge, Sn-Te alloys are discussed, assuming that bonding in these alloys may be described as a mixture of metallic, covalent and ionic bonding. Using an inhomogeneous model, and obtaining the metallic fraction from electrical conductivity, the Xe R_Q data are used to derive estimates of the ionic bonding fraction in the alloys studied.

1. INTRODUCTION AND THEORY

Quite a lot of semiconducting alloys are alloys of chalcogen elements. Among these, the tellurium alloys differ widely in their electrical, thermodynamic and structural behavior^{1,2}. We will focus on liquid tellurium alloys which show a metal-nonmetal transition. Its origin in $M_x\text{-Te}$ ($M_x = \text{Ag}_2, \text{Tl}_2, \text{Sn}, \text{Pb}$) and $M_2\text{-Te}_3$ ($M = \text{Ga}, \text{In}$) 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 (^{132m}Xe) in Cu-, Ag-, Ga-, In-, Tl-, Ge-, and Sn-Te alloys by a TDPAD technique. The quadrupolar part of the relaxation rate (R_Q) gives a measure of "far IR near field electric field fluctuations", 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 possibility suggests an extension of the concept of a two dimensional bond character chart, known from solids (e.g.¹²), to liquid alloys.

The well known expression for the quadrupole relaxation rate (see e.g.⁵)

$$R_Q = \text{const} \times \int dt C_{\text{EFG}}(t) \quad (1)$$

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(C_{EFG} is the correlation function of the electrical field gradient) can be expressed by means of two- and three-particle correlation functions⁶

$$C_{EFG} = \langle \sum_i v_2^{(i)}(r_{is}(0)) v_2^{(i)}(r_{is}(t)) P_2(\cos \alpha_{ii}(t)) \rangle + \langle \sum_{i \neq j} v_2^{(i)}(r_{is}(0)) v_2^{(j)}(r_{js}(t)) P_2(\cos \alpha_{ij}(t)) \rangle =: T_2(t) + T_3(t) \quad (2)$$

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_{EFG} for an A-B alloy (for details see⁷)

$$C_{EFG} = C(\tau_2^A + \tau_3^{AA}) + (1-C)(\tau_2^B + \tau_3^{BB}) - C(1-C)(\tau_3^{AA} + \tau_3^{BB} - \tau_3^{AB} - \tau_3^{BA}) \quad (3)$$

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

$$R_Q \sim [(CZ_A^2 + (1-C)Z_B^2)(\tilde{T}_2(0) + \tilde{T}_3(0)\tau_{met} - C(1-C)(Z_A - Z_B)^2 \tilde{T}_3(0)\tau_3)] \quad (4)$$

(τ_{met} is the correlation time for the EFG-function C_{EFG} Eq.(2) and τ_3 is the correlation time for the term $T_3(t)$ only.) For our purpose we only need the ratio of τ_{met}/τ_3 , $\tilde{T}_3(0) = T_3(0)/Z_A^2$ etc.

2. RESULTS AND DISCUSSION

For ^{132m}Xe 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 alloy¹⁴, 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 Tl-Te and Sn-Te the data can be

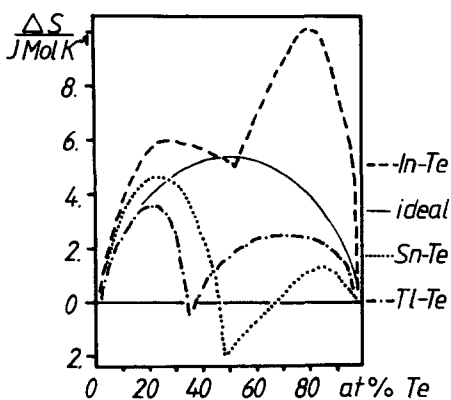


FIGURE 1 Entropy of mixing from refs. 9,10,11

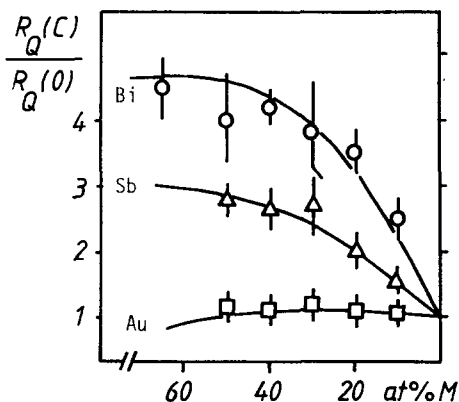


FIGURE 2 Quadrupolar relaxation of ^{132m}Xe in metallic Te alloys M_CTe_{1-C}

fitted by two curves of ideal mixing binary systems M-M_xTe and M_xTe-Te. (ΔS 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_{Au}=1, Z_{Bi}=5, Z_{Sb}=5 and an effective valency of 3 for Te, Eq.(4) was fitted to the experimental data. A mean value of τ₃/τ_{met} ≈ 7 was obtained which agrees with the values from different model calculations for liquid metals^{7,8}.

The striking fact that a large increase in R_Q was mainly observed when solid tellurium compounds exist which crystallize in ionic structures¹², 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 ^{132m}Xe 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.¹⁴ who determined a fraction of nonmetallic regions X₁

$$X_1 = 1 - X_0 = 1 - [\sigma(C)/\sigma(0)]^{1/2}$$

(X₀ being the fraction of metallic regions, σ(C) the conductivity at the measured concentration and temperature and σ₀ an interpolation

$$\sigma_0 = [C/\sigma_M + (1-C)/\sigma_{Te}]^{-1}.$$

The measured relaxation rates show a linear dependence on X₁ (Fig. 3). As there is - within the experimental errors - a linear dependence [R_Q(C)-R_Q(0)]~X₁ it is justified to assume incoherent superposition R_Q = R_{Q0} X₀ + R_{Q1} X₁.

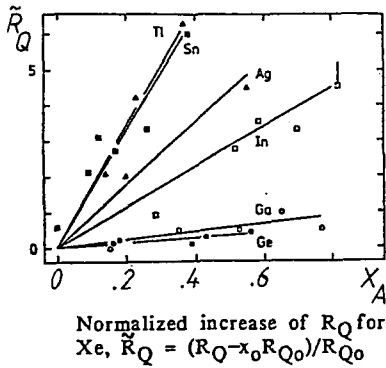


FIGURE 3
Quadrupolar relaxation rates R_Q vs. fraction of nonmetallic regions.

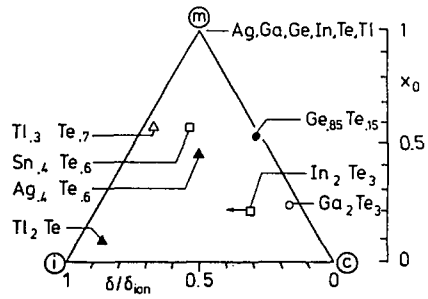


FIGURE 4
Bond character chart.

In the frame of the model all nonmetallic regions in the alloy have the same stoichiometry M_xTe_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. $\sqrt{R_{Q1}} \sim (Z_A - Z_B)$ is then proportional to an effective charge transfer $\delta = \frac{1}{Z}(Z_A - Z_B)$. For liquid Tl_2Te the value of δ was given by Robertson¹³ $\delta=1.34$ ($Tl_2^{+0.89}Te^{-1.78}$). 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. δ_{ion} is the charge transfer for the nominal ionic charges.

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