Nuclear Quadrupolar Relaxation in Liquid Alloys and Nearest Neighbour Dynamics*

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A theory of the quadrupolar relaxation rate, R_Q, for ideal liquid binary metallic mixtures is presented. The theory predicts cancellation after a few tenths of a picosecond of the two and three particle correlation terms in the fluctuation of the electric field gradient (EFG) for pure metals, and prevailing of the three particle term for binary mixtures. This is due to the high symmetry in the arrangement of the atoms around a probe nucleus. The prevailing of the three particle term in binary systems leads to a longer correlation time (a few picoseconds) of the fluctuating EFG and explains the experimentally observed higher values of R_Q and their quadratic concentration dependence. The validity of the theory has been confirmed by experimental data. Deviations for some real systems are discussed.

Introduction

The quadrupolar relaxation rate R_Q in liquids is proportional to the time integral of the correlation function of the electric field gradient (EFG) at the probe nucleus. The time dependence of the EFG is due to the relative motion of the neighbours of the probe atom which carries a nuclear quadrupole moment Q. In liquid metals and alloys one may restrict oneself to the nearest neighbours (n.n.). The EFG component V_2^m is the sum over all nearest neighbours, and the quadrupolar relaxation rate R_Q is given by [1]

$$R_Q = f(I,k)\,(eQ/\hbar)^2 \int c_{EFG}(t)\,\mathrm{d}t\,,$$

$$c_{EFG}(t) = \left\langle \sum_{m=-2}^{2} V_2^m(0)\; V_2^{-m}(t) \right\rangle, \tag{1a}$$

$$V_2^m(t) = \sum_i v_i(r_{ip}(t))\,\sqrt{4\pi/45}\; Y_2^m(\Theta_{ip}(t)\,\Phi_{ip}(t)). \tag{1b}$$

Here

$$f(I,k) = \frac{3}{80}\,k(k+1)\{4I(I+1) - k(k+1) - 1\} \cdot \{I^2(2I-1)^2\}^{-1}.$$

The sum i runs over the nearest neighbours, k is the multipole order observed ($k=1$ in NMR, $k=2$ in TDPAD). The main problem is the determination of the effective potential $\tilde{V}_i$ from which v_i is to be derived and of the space and time correlation function of the neighbouring particles which cause the relaxation.

A general theory of R_Q does not exist. The classical theories of Warren [2] and Sholl [3] are not well suited to describe the small value and weak temperature dependence of R_Q in pure metals [4]. Also, their extension to alloys [5, 6] does not cover the full range of phenomena observed in liquid binary alloys. For the latter problem it was helpful to introduce a thermodynamical point of view, particularly for mixtures which exhibit a strong concentration and temperature dpendence of R_Q. Starting from the phenomenological correlation between R_Q and the free energy of mixing, it was possible [7, 8] to attribute the typical behaviour of R_Q to the lifetime τ of associates, as suggested originally by Warren [9]. The concept of associates is used in order to explain, in the frame of the regular solution model, the thermodynamic properties of binary mixtures [10, 11]. A situation intermediate between metals and associated alloys prevails in athermal binary mixtures in which the enthalpy of mixing is small. Typically these alloys have a high number of n.n. atoms and nearly free electron properties. Concentrating on examples of such alloys, we describe and discuss a rather simple model [12, 13].

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Model Calculations

In liquid, because of the isotropy, (1 a) becomes

$$c_{\mathrm{EFG}}(t) = T_2(t) + T_3(t)$$
$$= \left\langle \sum_i (v_i(r_{ip}(0))\, v_i(r_{ip}(t))\, P_2(\cos\alpha_{ipi}(t)) \right\rangle + \left\langle \sum_{i\neq j} v_i(r_{ip}(0))\, v_j(r_{jp}(t))\, P_2(\cos\alpha_{ipj}(t)) \right\rangle, \tag{2}$$

where $\alpha_{ipj}(t)$ is the angle between $\boldsymbol{r}_{ip}(0)$ and $\boldsymbol{r}_{jp}(t)$. Because of the random and dense packing of atoms, $\langle V_2^m(t)\rangle = 0$. The instantaneous arrangement of the n.n. is almost always very symmetric (e.g. bcc-like). Also, the effect of angular motion is small compared to that of radial motion. It is therefore natural to set $\sum_j P_2(\cos\alpha_{ipj}) = 0$ for all times. This leads to opposite signs for T_2 and T_3 and to a considerable simplification of (2) [14]. The case of pure metals has been discussed elsewhere [13, 14].

In binary athermal A_cB_{1-c} metallic mixture the approximations mentioned are also fulfilled. Equation (2) will be modified in the sense that contributions to the terms T_2 and T_3 from A and B n.n.'s are now statistically weighted by c and $1-c$. Using $c^2 = c - c(1-c)$ and $1-c^2 = 1-c-c(1-c)$, one obtains instead of (2),

$$c_{\mathrm{EFG}}(t) = c\,\{T_2^{\mathrm{A}}(t) + T_3^{\mathrm{AA}}(t)\} + (1-c)\,\{T_2^{\mathrm{B}}(t) + T_3^{\mathrm{BB}}(t)\} - c(1-c) \cdot \{T_3^{\mathrm{AA}}(t) + T_3^{\mathrm{BB}}(t) - T_3^{\mathrm{AB}}(t) - T_3^{\mathrm{BA}}(t)\}, \tag{3}$$

where

$$T_2^{\mathrm{A}}(t) = K \int \mathrm{d}r_0\, r_0^2\, g_0^{\mathrm{A}}(r_0) \cdot \int \mathrm{d}r\, r^2\, W^{\mathrm{A}}(r_0; r, t)\, v^{\mathrm{A}}(r_0)\, v^{\mathrm{A}}(r), \tag{4}$$

$$T_3^{\mathrm{AB}}(t) = -K\,\{\int \mathrm{d}r_0\, r_0^2\, g_0^{\mathrm{A}}(r_0)\, v^{\mathrm{A}}(r_0)\} \cdot \{\int \mathrm{d}r_0\, r_0^2\, g_0^{\mathrm{B}}(r_0) \int \mathrm{d}r\, r^2\, W^{\mathrm{B}}(r_0; r, t)\, v^{\mathrm{B}}(r)\}\,. \tag{5}$$

K is the number of n.n.'s and $W(r_0; r, t)$ the probability to find one of the K atoms at the time t at a distance between r and $r + \mathrm{d}r$ if it was between r_0 and $r_0 + \mathrm{d}r_0$ at $t = 0$. g_0 is the first peak in the static pair distribution function. Assuming for a moment that $W^{\mathrm{A}} = W^{\mathrm{B}}$, $g_0^{\mathrm{A}} = g_0^{\mathrm{B}}$ and $v^{\mathrm{A,B}}(r) = Z_{\mathrm{A,B}}\, v(r)$, where $Z_{\mathrm{A,B}}$ represents an effective valence of the atom A and B, respectively, one obtains for the relaxation rate

$$R_{\mathrm{Q}} \sim (c\,Z_{\mathrm{A}}^2 + (1-c)\,Z_{\mathrm{B}}^2)\,(\tilde{T}_2(0) + \tilde{T}_3(0))\,\tau_{\mathrm{met}} - c(1-c)\,(Z_{\mathrm{A}} - Z_{\mathrm{B}})^2\,\tilde{T}_3(0)\,\tau_3\,, \tag{6}$$

where

$$\tilde{T} = T^{\mathrm{AB}}/Z_{\mathrm{A}}\,Z_{\mathrm{B}}\,, \quad \tau_3 = \int \frac{T_3(t)}{T_3(0)}\,\mathrm{d}t$$

and

$$\tau_{\mathrm{met}} = \int \frac{T_2(t) + T_3(t)}{T_2(0) + T_3(0)}\,\mathrm{d}t\,.$$

The implications of (6) depend – among other factors – on the magnitude of τ_3 relative to τ_{met}. Using the model described, calculations were carried out [12, 13, 14] for two forms of the effective electric potential:

$$\tilde{V}_1 = (Z/r)\exp(-\lambda r)$$

and

$$\tilde{V}_2 = Z\{(\varrho/r)^m - (m/n)\,(\varrho/r)^n\}$$

(for ϱ, the position of the maximum of $g_0(r)$ was taken). W was derived from solving a Smoluchowski equation [15]. The results are presented in Table 1.

Although the potentials $\tilde{V}$ considered here can only approximate the real form (for exact forms see e.g. [16]), the ratio $\tau_3/\tau_{\mathrm{met}} \approx 5$ is appearently independent of the specific form of $\tilde{V}$. This is in accord with [16, 17]. The model therefore predicts an increase of R_{Q} in binary mixtures over the value in single metals

$$\hat{R}_{\mathrm{Q}} = R_{\mathrm{Q}}(c)/R_{\mathrm{Q}}(c = c_{\mathrm{A}} = 0) = Z_{\mathrm{B}}^{-2} \cdot \left\{ c\,Z_{\mathrm{A}}^2 + (1-c)\,Z_{\mathrm{B}}^2 + c(1-c) \cdot (Z_{\mathrm{A}} - Z_{\mathrm{B}})^2\, \frac{\tau_3}{\tau_{\mathrm{met}}}\, \frac{\tilde{T}_3(0)}{\tilde{T}_2(0) + \tilde{T}_3(0)} \right\}. \tag{7}$$

Table 1. Results of the model calculation for τ_3 and τ_{met} for $\tilde{V}_1 = (Z/r)\exp\{-\lambda r\}$ and $\tilde{V}_2 = Z\{(\varrho/r)^m - (m/n)\,(\varrho/r)^n\}$. We have chosen $g_0(r_0)$ and $g(r)$ such as to represent liquid Ga at its melting point.

	λ (Å^{-1})	τ_3 (ps)	τ_{met} (ps)	$\tau_3/\tau_{\mathrm{met}}$
$\tilde{V}_1$	0.5	3.18	0.58	5.5
	1.0	2.57	0.49	5.3
	1.5	2.20	0.41	5.4
	2.0	1.98	0.36	5.5
$\tilde{V}_2$	$m = 4$, $n = 2$	1.15	0.23	5.0

The present model and computer simulations [18] give a value of about 1.5 for $|\tilde{T}_3(0)|/|\tilde{T}_2(0)+\tilde{T}_3(0)|$. The parameters which are predicted to determine sensitively R_Q are thus Z_A, Z_B, and $c(1-c)$ as in the earlier theories [5].

Results and Discussion

A typical system with low enthalpy of mixing is Cd–Sn ($\Delta H \approx 300$ J/mole, $\Delta G = -3$ kJ/mole, at $c = 0.5$ and $T = 773$ K; eutectic alloy [19, 20]). The nuclear quadrupolar relaxation rate can be measured on the isomer ^{115m}Sn ($T_{1/2} = 159\,\mu$s, $g = -0.249$, produced by an $(\alpha, 3n)$ reaction from ^{114}Cd) using the TDPAD technique [21]. The measured rate in pure Cd is $R = R_M + R_Q = 1.5\ \mathrm{ms}^{-1}$ (temperature independent) [22]. Correcting for the magnetic rate R_M using the Korringa relation and the Sn Knight shift ($R_M = 0.82\,T(\mathrm{K}^{-1}\,\mathrm{s}^{-1})$), the quadrupolar relaxation rate is thus $R_Q = 1\ \mathrm{ms}^{-1}$ at the melting point ($T = 595$ K). We have measured the rate in liquid $Cd_{66}Sn_{34}$; it has, within the error bars, the same value as in pure Cd, and it is also temperature independent ($T = 465-1000$ K). Correcting as above for R_M [23], the same value for R_Q is obtained as in the single metals $\hat{R}_{exp} \approx 1$.

Another athermal system is Hg–Pb ($\Delta G \approx -2.5$ kJ/mole at $c \approx 66\%$ Pb; $T = 597$ K; peritectic phase at 66% Pb [14, 15]). Figure 1 shows the temperature dependence of the relaxation rate of ^{206m}Pb ($T_{1/2} = 123\,\mu$s, $g = -0.0127$, produced by an $(\alpha, 2n)$ reaction from ^{204}Hg) in pure Hg and $Hg_{50}Pb_{50}$. Because of the small g value, the magnetic rate is negligible here. The measured enhancement is $\hat{R}_{exp} = 3$, taking the respective melting points, and a small temperature dependence is observed.

Besides the results obtained with the TDPAD technique, we show (Table 2) the main results for NMR measurements on the quadrupolar relaxation rate in some s-p liquid alloys. For a better survey our TDPAD results are also tabulated. The summarized results are presented with emphasis on thermodynamical properties.

If we consider the screening effect of the conduction electrons, the effective charges of the atoms will be reduced. If the screening is strong, reducing all effective charges to small and similar values, the values $\hat{R} > 1$ become difficult to explain. From the

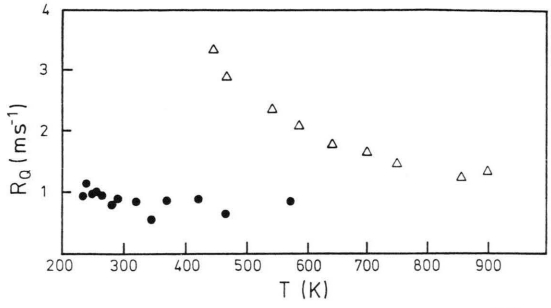

Fig. 1. Measured quadrupolar relaxation rate of ^{206m}Pb in liquid Hg (●) and Hg_5Pb_{50} (△) [24].

Table 2. Experimental quadrupolar relaxation rate increase $\hat{R}_{exp}$ for some s-p liquid alloys. $\hat{R}_Q$ was derived from (7), considering that Z_A and Z_B correspond to the normal valencies. ΔG and ΔH were taken from [19]. The NMR data of ^{209}Bi and ^{69}Ga [5, 26, 27] show a quadratic dependence on the concentration; $\hat{R}_{exp}$ culminates for the concentration presented.

Probe nucleus	$\hat{R}_{exp}$ (Method)	$\hat{R}_Q$	Thermodynamical properties ΔH, ΔG (J/mole)
^{114m}Sn	$R_Q(\mathrm{Sn}\mathbf{Cd_2Sn})/R_Q(\mathrm{Sn}\mathbf{Cd}) \approx 1$ (TDPAD)	1.2	eutectic alloy $\Delta H \gtrsim 0$
^{206m}Pb	$R_Q(\mathrm{Pb}\mathbf{HgPb})/R_Q(\mathrm{Pb}\mathbf{Hg}) \approx 3$ (TDPAD)	1.2	peritectic β ($Hg_{66}Pb_{34}$) phase, $\Delta G(c = 0.6) = -2500$, $T = 597$ K
^{209}Bi	$R_Q(\mathrm{Bi}\mathbf{BiSb})/R_Q(\mathrm{Bi}\mathbf{Bi}) \approx 4$ (NMR)	1	completely miscible in the solid and liquid states
^{209}Bi	$R_Q(\mathrm{Bi}\mathbf{BiPb})/R_Q(\mathrm{Bi}\mathbf{Bi}) \approx 6$ (NMR)	1.1	eutectic alloy, $\Delta H(c = 0.5) = -1200$ $T = 700$ K
^{209}Bi	$R_Q(\mathrm{Bi}\mathbf{BiIn})/R_Q(\mathrm{Bi}\mathbf{Bi}) \approx 10$ (NMR)	1.1	two intermediate solid phases; $\Delta H(c = 0.55) = -1800$, $T = 623$ K
^{69}Ga	$R_Q(\mathrm{Ga}\mathbf{GaIn})/R_Q(\mathrm{Ga}\mathbf{Ga}) \approx 1$ (NMR)	1	eutectic alloy

systematics of R_Q in many liquid alloys of s-p metals it appears to us that a least one of the reasons for the discrepancies is to be sought in the thermodynamical properties.

We remind that Hg–Pb and Bi–In show intermetallic compounds in the solid state. Moreover, ΔG in Hg–Pb is asymmetric in its concentration dependence. Ascribing such effects to local bonding in the liquid alloy [10] as discussed by Sommer [11], one supposes for Hg–Pb and Bi–In a tendency to develop associates, which is absent in Cd–Sn, Bi–Sb, Bi–Pb and Ga–In. In the frame of the model discussed here for R_Q, there is an additional attractive potential between A and B (the probe being, say B), $\varphi \to \varphi + \psi_{AB}$. Therefore a different dynamic behaviour develops for W_{AB} cmpared to the rest. When ψ_{AB} is attractive and nonnegligible compared to φ, the nucleus will experience a quadrupolar relaxation rate which is increased compared to the usual τ_3 determined value. As long as $\varphi \approx \psi_{BA}$ ($\varphi = -k_B T \ln g$) the increase is not large, but when $\psi_{BA} \ll \varphi$, the dynamics of the probe atom is primarily determined by ψ_{BA}. In this case the dynamics of the bonded neighbour is thermally activated, $\tau_3 \to \tau \sim \exp\{-\psi_{BA}/k_B T\}$. Along this line, it was demonstrated [7, 8] that for systems with large enthalpy of mixing, i.e. associated mixtures, the lifetime of the associates plays a major rôle in R_Q. From the results presented above, we conclude that even in systems with only incipient association there is sufficient deviation from ideal mixing so that the change of the dynamic behaviour may explain the experimental results in R_Q.

It is not clear, which mechanism determines the enhancement in Bi–Sb and Bi–Pb. It is possible that the covalent short range order observed in liquid Sb [25] prevails also in the Bi–Sb mixture, and that the lifetime of this configuration leads to an increased correlation time for the c_{EFG}. For the latter system, if we try to explain the behaviour of R_Q in the frame of the model discussed, we may be obliged to adopt $Z_{Bi}/Z_{Pb} \approx 2.2$, a rather high value. On the other hand, if we take into account that some Pb eutectic alloys form metallic glasses at the eutectic point (e.g. $Sb_{10}Pb_{90}$, $Ag_{10}Pb_{90}$ [28]), the same behaviour is not excluded for Bi–Pb. In this case, again our attention must be concentrated rather on τ than on c_{EFG}.

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