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Nuclear Quadrupolar Spin Relaxation and Association in Binary Liquid Metallic Alloys

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Diffusion / Flüssigkeiten / Kernquadrupolrelaxation / Metalle / Thermodynamik

We present experimental data for the nuclear quadrupolar spin relaxation rate R_q in liquid $\text{In}_x\text{Sb}_{1-x}$, $\text{Hg}_x\text{K}_{1-x}$ and $\text{In}_{50}\text{Hg}_{50}$. The results for the concentration and temperature dependence of R_q can be qualitatively interpreted with the framework of association in these systems (quasi ternary solution model). We conclude that the relaxation is mostly due to the decay of associates in HgIn and to rotational diffusion of associates in Hg-K . In In-Sb , the corresponding correlation times seem to be equal so that both relaxation processes may contribute to the relaxation. The analysis of microscopic experiments using the concept of association may prove useful for a better understanding of the nature of the associates.

Introduction

A very successful model for binary liquids showing compound forming tendency is the model which introduces explicitly associates, the most recent development of the model being due to Sommer [1, 2]. It includes the enthalpy and entropy of the associates $A_\mu B_\nu$ ("short range ordered regions"), the interaction of the associates $A_\mu B_\nu$ with free atoms A, B and that among the free atoms A, B. The interaction parameters enter into the model via a quasi ternary regular solution model, the density of the associates being controlled by the law of mass action. This is a transcendental equation, if interaction of the alloying partners is included. No statement about the lifetime of the associates, however, is made within thermodynamics. But in order to speak about associates from a microscopic point of view, their lifetime must be definitely longer than the lifetime of nearest neighbour pairs in simple liquids, i.e., longer than a few 10^{-13} s. One should also expect a smaller distance between the atoms constituting the associate than the mean nearest neighbour distance of pairs of "free" A-B-atoms. However, this question will be controversially discussed unless all three partial structure factors of a liquid alloy with compound forming tendency are available.

An experiment which is sensitive to the dynamics of

distances between atoms – rather than positions as for the case of dynamical neutron

scattering – is nuclear spin relaxation. We are concerned here with nuclear spin relaxation rate due to quadrupolar interaction, R_q , which is (in the motional narrowing case) propor-

tional to the time integral of the correlation function of the electric field gradient (efg) at the probe nucleus. It is established, that in metallic systems the fluctuations of the efg are due to thermally agitated relative motion of the nearest neighbour atoms with respect to the probe atom. The important difference between R_q and dynamical neutron scattering comes in because the state of the surrounding of the probe is measured at the position of the probe atom (which of course exhibits itself thermal motion). The correlation function of the efg involves the probability to find an atom at a distance r_0 with respect to the probe atom for $t = 0$ and an atom at a distance r_t for $t > 0$. Dynamical neutron scattering on the other hand compares the positions of two atoms as different times. The momentum-energy-Fourier transform of the coherent scattering law is proportional to the probability that, if for $t = 0$ there is an atom at $\mathbf{R} = 0$ one finds an atom at \mathbf{R} for $t > 0$. The two situations are illustrated in Fig. 1.

The special character of the correlation function relevant for R_q makes this experiment very sensitive to possible formation of associates. If there are associates – and if the probe atom is bound in the associate – large effects on R_q are expected especially due to their extended lifetime.

Experimental Methods and General Results

Two experimental methods are used to measure the quadrupolar relaxation rate in liquid metals and alloys. One is conventional NMR [3] and the other one is the so called TDPAD-method [4, 5]. In the latter, to which we refer here mostly, the fact is used that a nuclear reaction (e.g. the reaction $^{204}\text{Hg}(\alpha, 2n\gamma)^{206\text{m}}\text{Pb}$), which in a certain fraction of cases produces a relatively long lived excited nucleus (here

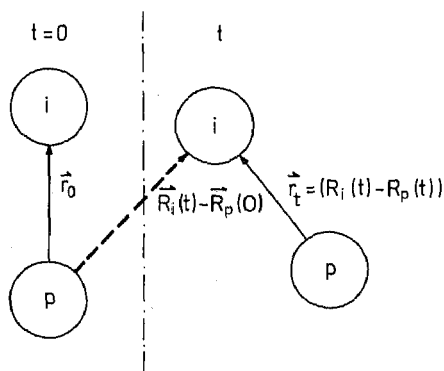


Fig. 1

Atomic correlations for R_q and for the distinct part of the neutron scattering law $S(k, \omega)$. Left side $t = 0$, right side $t > 0$. The vector important for neutron scattering is $R_i(t) - R_p(0)$, indicated by a broken arrow. $R_i(0)$ is the position vector of particle i at time $t = 0$ referred to a laboratory fixed frame, $r_0 = R_i(0) - R_p(0)$. The distance vectors, the correlation of which is decisive for R_q in associating liquid alloys are r_0 and r_t , indicated by solid arrows. p marks the probe atom

^{206}mPb), aligns in this production process the spin of the resulting excited nucleus. If the nuclear lifetime is in the range of the quadrupolar relaxation rate, the latter can be conveniently measured by determining the decay of the alignment, since the γ -radiation emitted when the aligned nuclei decay into the groundstate is anisotropic.

Concentrations of the probe atoms are extremely low ($< 10^{-8}$).

Some of the results for R_q obtained from NMR and TDPAD in liquid metals and metallic binary alloys may be summarized as follows:

1. In pure liquid metals "small" rates are observed with a weak temperature dependence, which may be described approximately by a relation $R_q \propto T^{-1/2}$ (T = temperature) [6].
2. In alloys which behave like ideal or regular mixtures ($RT_M \gg \Delta H$, ΔH = heat of mixing) generally the same results as in pure metals are obtained. Enhancements of R_q as compared to the pure metal are small, say smaller than a factor 5 [7].
3. In the alloys mentioned under 2, the temperature dependence of R_q remains similar if one uses different probe atoms (e.g. Hg or Tl or Pb in pure liquid Hg [8]).
4. In liquid alloys which form intermetallic compounds in the solid state, generally large enhancements of R_q as compared to the pure metals are found. Typically, R_q at concentrations near the stoichiometric composition of the intermetallic phase is 10 to 100 times larger than in the corresponding pure metals [3, 9].
5. The enhancement, point 4, is accompanied by a much steeper temperature dependence, which may be described by a T^{-2} - or an Arrhenius law with an activation energy of the order of $\geq 10^3$ K.
6. In compound forming alloys, marked changes of the temperature dependence of R_q with the probe atoms can be observed ([8], see also concluding paragraph).

Discussion within the Association Model

The small R_q and the weak temperature dependence in monoatomic liquids very probably arise because of the highly symmetrical arrangement of the neighbour atoms around the probe atom. Already slight motions of the nearest neighbour atoms change the symmetry enough to change the efg considerably, so that the fluctuations of the efg have very short correlation times [6, 10–12].

If the atoms however bind in the associates, the symmetry of the surrounding is strongly reduced. If they stick together a long time a corresponding enhancement of the time integrated efg correlation, thus of R_q , is to be expected. Note that the probe atom must be a member of the associate in order that maximum enhancements of R_q are produced.

If we assume an association, the quadrupolar relaxation rate R_q is given by

$$R_q = \text{const.} (w_A \langle \text{efg}_A^2 \rangle \tau_A + (1 - w_A) \langle \text{efg}_M^2 \rangle \tau_M) \quad (1)$$

Here the subscript "A" refers to the associates, w_A is the probability, that the probe atom is bound in an associate. We expect w_A to be proportional to the density of the associates, n , which is controlled by the law of mass action. τ_A is the corresponding correlation time to be discussed below. efg_M and τ_M are the metallic efg and the metallic (short) correlation time. Obviously we expect $\tau_A \gg \tau_M$. In view of the bonding, we expect also $\langle \text{efg}_A^2 \rangle \gg \langle \text{efg}_M^2 \rangle$. Thus we neglect the second term.

The dynamical processes which are responsible for the relaxation may be broadly grouped into reorientation, i.e. rotational diffusion, of an associate, and decay (vibrational motion in the associate is ineffective). For the former process, the correlation time can be estimated by the classical formula [13]

$$\tau_A^{\text{rot}} = v\eta/k_B T \quad (2)$$

where η and V are viscosity of the alloy and the volume of the associate, respectively.

A derivation of the decay time is less obvious. But we may consider the law of mass action as a *rate* equation for the thermal formation and destruction of the associates, and from it we expect for the temperature dependence of the lifetime of an associate

$$\tau_A^{\text{dec}} = v_0^{-1} \exp(-C_A/RT) \gamma_1'' \gamma_2^y \gamma_3^{-1} \quad (3)$$

The γ 's are the activity coefficients, the indices 1, 2 and 3 refer to free A- and B-atoms and $A_\mu B_\nu$ -associates, respectively. C_A is the formation enthalpy of the associates. The activity coefficients contain the parameters for the interaction of free A- and B-atoms (C^{reg}) and for the interaction of free atoms with the associates (C'^{reg} and C''^{reg}). For the description of the thermodynamics of the alloys we use the same model (quasi-ternary solution model) as Sommer [1, 2].

Evidently, the shorter of the two processes, decay or rotational diffusion, will dominate the relaxation rate.

Results

The model is illustrated for three cases for which sufficient thermodynamical and R_q data are available. These are In–Sb-alloys (probe Sb) [14, 15], Hg–K alloys (probe Pb) [16], and InHg (probe Sb) [8].

1. In–Sb. We have used thermodynamical data for ΔH , ΔS [17], and Δc_p [18] at 50 at.-% and 1000 K to derive the parameters for the model. Only one kind of associates is considered in the present work, namely InSb. The following set of data is obtained: $S_0 = 0$, $C_A = -15.0$, $C^{\text{reg}} = -4.6$, and $C'^{\text{reg}} = C''^{\text{reg}} = 7.5$ (kJ/mol). Data for the viscosity as a function of concentration and temperature are also available [19], so that both models can be tested against the R_q data. Since the mean squared efg's in metallic systems are not known, the curves taken from eqns. (2) and (3), which fix temperature and concentration dependence of R_q together with eq. (1), have to be normalized. The normalization point is taken here at 1100 K and 50 at.-%, which gives the best overall agreement for

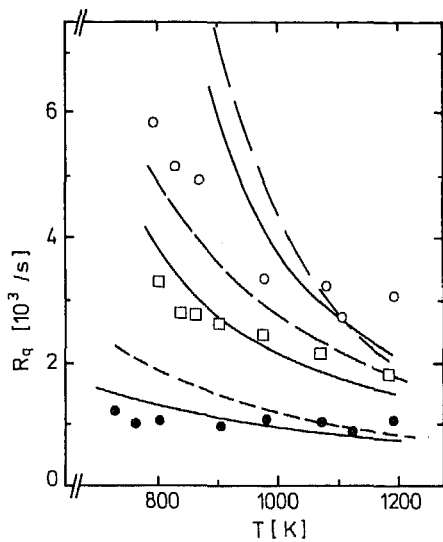


Fig. 2

R_q in In-Sb alloys, probe: ^{117m}Sb . Full lines represent the "decay picture" and broken ones the "rotational picture". The legend for the experimental points is: \bullet : 20 at.-% Sb, \square : 35 at.-% Sb, \circ : 50 at.-% Sb. The normalisation point for the theoretical curves is $x_{\text{Sb}} = 50$ at.-% and $T = 1100$ K. NMR-results exist for $\text{In}_{50}\text{Sb}_{50}$, Warren and Clark [3], and give essentially the same temperature dependence for R_q .

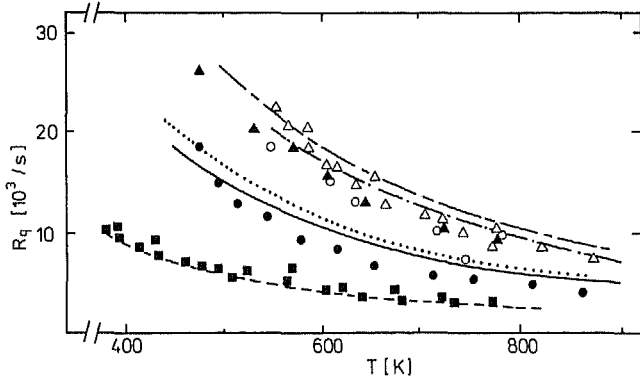


Fig. 3

R_q in Hg-K alloys, probe: ^{206m}Pb . The legend is: \blacksquare (---): 10 at.-% K, \blacktriangle (.....): 20 at.-% K, \triangle (—): 33 at.-% K, \circ (—): 40 at.-% K, \bullet (—): 50 at.-% K. The lines are for the rotational picture, the normalisation point is 10 at.-% K and 378 K.

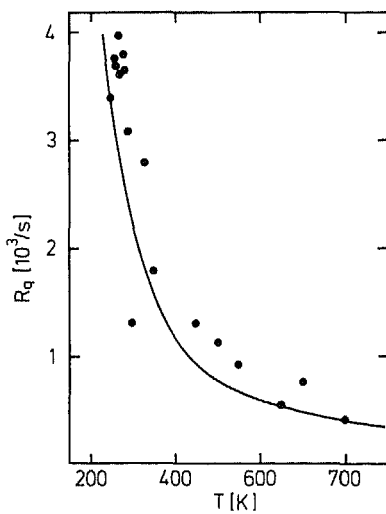


Fig. 4

R_q in $\text{In}_{50}\text{Hg}_{50}$, probe: ^{117m}Sb . The full curve is obtained from the "decay picture", the normalisation point is 700 K.

the choice $\tau_A = \tau_A^{\text{dec}}$, the "decay picture". It is seen in Fig. 2 that the overall agreement is satisfactory apart from showing too steep a temperature dependence of R_q at 50 at.-%. This deviation is probably due to the fact that the model for the thermodynamics gives too large ΔH at low temperatures. The dashed curves in Fig. 2 are for the "rotational picture" which works less well. One may estimate the decay time τ_A^{dec} by assuming that the efg on Sb in pure liquid In is approximately the same as in the InSb-associate and from a correlation time calculation in pure metals: $\tau_M \approx 10^{-13}$ s [20]. Then τ_A is roughly 10^{-11} s, at 50 at.-% and 800 K; the same value is derived from eq. (2). This is also in accord with an earlier estimate by Warren [3] who had used the magnitude of the efg from an Sb compound to derive $\tau_A = 0.25 \cdot 10^{-11}$ s.

2. Hg-K. The information about thermodynamical properties of this system is somewhat poor, but ΔS is very probably negative and in Hultgren et al. [17], ΔH is estimated to be of order -25 kJ/mol. This huge heat of mixing suggests that the decay time is larger than the rotational diffusion time so that $\tau_A \approx \tau_A^{\text{rot}}$. In Fig. 3 we show the good correspondence of the rotational diffusion model, eq. (2), with the R_q data. We have assumed maximal association of Hg_2K associates (corresponding to the maximum of the liquidus), which seems reasonable because ΔH is so large. Here we have treated the probe atom (Pb) as not distinct essentially from a Hg-matrix atom because the phase diagrams Pb-K and Hg-K are of similar character whereas HgPb is almost ideal.

3. InHg. Thermodynamical data are available from Hultgren et al. [17]. Sommer's model gives the following parameters: $S_0 = -1.2$ J/molK, $C_A = -5.9$, $C^{\text{reg}} = -4.2$, $C'^{\text{reg}} = C''^{\text{reg}} = -2.9$ (kJ/mol). These values are used to calculate the temperature dependence of the decay time via eq. (3). The results are shown in Fig. 4. Agreement is excellent in this case. This is not trivial in view of the metallurgical differences between the probe (Sb) and the matrix. Under the same assumptions about the efg and the correlation time in pure metal, we can estimate a life time of the associates to be $0.8 \cdot 10^{-11}$ s at 50 at.-% and T_M .

We conclude with some remarks to the role of the probe atom. In all cases mentioned above, the probe atom binds to one (and only one) of the alloying partners, but in the two latter cases the probes are impurities. Treating the probe atoms as we did, i.e. as matrix atoms, is by no means obvious. There is even a problem regarding Sb as a probe atom in pure In - R_q gives no indication that impurity Sb atoms exhibit appreciably longer living bonding (e.g. no strong temperature dependence of R_q). Having the success of our treatment in mind, we see a possibility for reconciling matrix bonding with impurity bonding by remembering that associate formation in a cooperative effect. The hypothesis is that impurities only bond to associates if there are already these structures. That chemical short range order is of longer spatial range is known from neutron scattering [21, 22].

The properties of the probe atoms however remain very important. E.g., R_q in Ga-Te alloys have been measured on the probe atoms: Ga [23], As [24], and Xe [25]. R_q is greatly enhanced on As and Ga, but not on the Xe probe. The Xe atoms experience essentially repulsive interactions with associates, and will consequently have small w_A and τ_A , thus no large R_q enhancements. It is the good agreement between the consequences

of the model and the experimental R_q -systematics – metals, regular alloys, associated alloys and the last mentioned, rather extreme case – which we take as a strong support of the assumption that most of the enhancements observed for R_q are indeed due to association in liquid metallic alloys.

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Self-Consistent Solution of Sommer's Partial Associated Model. New Approach of the Configurational Entropy

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Metalle / Phasenumwandlungen / Thermodynamik

We have worked with Sommer's partial associated model [1, 2]. Considering that the adjustable parameters of this model are not real independent ones we have looked at iteration mathematical procedure to assure the self-consistency with the formalism of the model. With respect to such a procedure, one isothermal enthalpy curve, for example, is mathematically sufficient to determine all the adjustable parameters. So we shall emphasize that all the results are strongly dependent on the choice of the configurational entropy model. Ours is coherent with the initial chemical assumption.

1. Introduction

1.1. Motivations

For the last ten years our laboratory has been concerned with thermodynamic studies of some stoichiometric intermetallic compounds. For example Notin has measured the enthalpies of formation of AlBa and AlCa compounds by direct reaction calorimetry in solid-liquid mixtures. Both enthalpy and entropy of such compounds can also be attained simultaneously by E.M.F. measurements using fluoride electrolytes. Notin has studied the properties of calcium compounds with Ag, or Cu, or Au, or Ni, or Al [3]. In another field Gachon measured the enthalpy of formation of transition metal compounds in Ti or Zr systems alloyed with Fe, or Co, or Ni [4]. He used the drop reaction calorimetry at very high temperatures, taking pellets of sintered powders.

In order to test the consistency of our data and to extend the thermodynamic information attained by direct measurements we have started to calculate phase equilibrium diagrams considering these diagrams as "Gibbs-meters". Charles chose a pure mathematical formalism without a physical support, using Legendre's polynomial development to represent the excess free enthalpy of the liquid phases [5].

On the other hand, Cunat has conducted enthalpy studies of glassy alloys, taking into account estimates of thermodynamic properties of undercooled liquid phases as, for example, for the Fe–B system [6]. This is another important reason why our laboratory has focused on the thermodynamics of liquid phases. We emphasize that in all the cases in which the liquid alloys are short range ordered ones, we can also look at a physical support to attain a good representation of the proper-