PHYSICAL REVIEW B VOLUME 19, NUMBER 7 1 APRIL 1979

Systematical trends of nuclear quadrupolar relaxation in metallic liquid alloys of indium

M. v. Hartrott, J. Höhne, D. Quitmann, J. Rossbach, E. Weihreter, and F. Willeke
Institut für Atom- und Festkörperphysik Freie Universität Berlin
Boltzmannstrasse 20, D 1000 Berlin 33 Germany

(Received 8 May 1978)

Applying the method of perturbed angular distributions following the nuclear reaction $^{115}\text{In}(\alpha,2n)^{117}\text{Sb}^m$, systematic measurements have been made of the nuclear-quadrupolar relaxation rate R_Q for $^{117}\text{Sb}^m$ probe nuclei in liquid alloys of In, as a function of various parameters: the dependence of the rate enhancement on the partner element is established in 14 equicomposition alloys with I*b*, II*b*, II*a*, IV*a*, and V*a* group elements. The composition dependence of the rate in the In-rich domain has been recorded for $\text{In}_C X_{1-C}$, $X =$ Au, Hg, As, and Bi, and the temperature dependence of the rate is presented for $\text{In}_{0.5}\text{Bi}_{0.5}$ and $\text{In}_{0.5}\text{Hg}_{0.5}$. On the average we find a correlation of the rate enhancement to the valence difference between In and the partner element. The composition dependence confirms the characteristic deviation from a simple substitutional behavior described by a $C(1-C)$ rule which has been found in earlier NMR work. The temperature dependence of the rate in $\text{In}_{0.5}X_{0.5}$ alloys with enhancement, can be parametrized by an Arrhenius law where the activation energy is roughly a linear function of the alloy melting temperature; the proportionality factor, however, is about one half the factor occuring in diffusion. These results are examined in the frame of the Sholl and Warren theory for quadrupolar relaxation which we extend to alloys in its general form in terms of partial-dynamical structure factors taking advantage of analogies in the formulation of electrical resistivity. It is concluded from an evaluation of the formulas based upon a hard-sphere model that quadrupolar relaxation must be governed by the long-wavelength part of the structure factors. More specifically quadrupolar relaxation seems to be sensitive to the wave-number interval between the thermodynamical limit and the main peak of the static-pair correlation function of the liquid, a region which is poorly explored by other experimental techniques.

I. INTRODUCTION

It has been established in the past that nuclear quadrupolar relaxation in liquid metallic systems essentially originates from atomic dynamics.[1-3] It is therefore sensitive to microscopic structure and motion, and may be applied to complement other structural investigations, for instance x-ray and neutron scattering experiments. For several reasons however the information obtained is complex: (i) The relevant correlation functions,[4] which allow for structure and dynamics, differ from the Van Hove two-particle correlation functions familiar from scattering experiments. (ii) The relaxation rate depends on the strength of the electric-field gradient (EFG) produced by neighboring atoms at the probe. When comparing relaxation with scattering, the EFG function corresponds to the form factor; in contrast to the scattering, however, the form factor is strongly *k* dependent and not well known. (iii) The unambiguous experimental identification of the quadrupolar hyperfine interactions in metallic liquids is possible only for a few favorable cases.

Therefore, quadrupolar relaxation in metallic liquids has been so far a subject of investigation for its own sake rather than a tool to obtain information about systems. It is the aim of the present work to turn to more system-oriented problems, in particular concerning binary liquids. In the following we survey some points of view which contribute in our opinion to a promising resumption of the subject:

(a) *New approximations for correlation functions:* As has been recognized by Sholl,[4] the quadrupolar relaxation rate R_Q measures the correlation between *two* particles and the probe atom, i.e., a three-particle correlation function is involved. Considerable progress in linking quadrupolar relaxation in pure liquids to the theoretically and experimentally well studied pair correlations has been achieved by the work of Sholl[6] and Warren.[7] They extended the Kirkwood approximation and proposed an approximation for the time-dependent electric field gradient, which contains two time-dependent-pair correlation functions. This model has been tested extensively for pure liquid metals by an analysis of the predicted temperature dependence[5]; allowing for phononlike modes in the pair correlations, the theory reproduces reasonably well the experimental temperature dependence.

(b) *Theory of R_Q for binary alloys:* The work of Sholl[6] and Warren[7] has been motivated essentially[6] by the fact that the general relaxation-rate increment in alloys over the pure liquid value reveals a strong cancellation of contributions to the EFG from different ions in the pure liquid.[8] Thus, the application of this theory to alloys is obvious. Starting from very crude assumptions, such an extension, has been presented by Gabriel.[9] At this point the present paper continues by showing that a generalization of the formalism can be accomplished without any further approximation. We take advantage of the similarity of the theoretical expressions for the electrical resistivity in a liquid metal, and for the quadrupolar relaxation rate as derived by Sholl and Warren. As long as the EFG can be considered to have little or no change, the influence of alloying on quadrupolar relaxation is allowed for by the partial-dynamical structure factors which govern many other properties of alloys.

(c) *Extensive experimental material for binary alloys:* In the analysis of a limited set of experimental data,[10] it became apparent that the new approach is more appropriate for the interpretation of R_Q in alloys than the earlier formulation.[11] This has motivated a test of the theory on a larger body of experimental material.[12] In the present paper we report quadrupolar rates for 14 alloys $\mathrm{In}_{0.5}X_{0.5}$, the isothermal composition dependence in four alloys, and the temperature dependence in two equicomposition alloys. For the cases studied, the quadrupolar relaxation is the dominant relaxation process.

(d) *Perspectives for future interpretation:* The systematical inspection of the relaxation rates in alloys supports the earlier supposition[13] that in a first approximation the difference in valence is responsible for the magnitude of the alloy enhancement (i.e., the increase of R_Q over the average of the pure liquid metal values). It will be seen that this is in accord with the much stronger temperature dependence of R_Q, observed whenever there is an enhancement. It is also in qualitative agreement with the composition dependence. The dependence on partner, temperature and composition suggests, that the long wavelength part of the structure factors is heavily weighed by the EFG form factor.

Among different definitions of partial structure factors,[14,15,16] the formulation of Bhatia and Thornton is the one most appropriate for the present purpose. These structure factors are derived from the local density and concentration in the alloy; the alloy enhancement of R_Q is related intimately to the concentration fluctuation term as turns out from a hard-sphere calculation. The $k=0$ limits of these structure factors are connected to thermodynamical parameters of the binary alloy.[17] Thus, a relation may be established between macroscopic properties of the liquid alloy and quadrupolar hyperfine interactions.[18]

(e) *Treatment of the electric-field-gradient problem:* In principle, the liquid structure and the EFG are not independent since they both involve the outer part of the electronic shell. In practice, however, the two quantities are treated as independent; in metallic systems the main effect of the conduction electrons may be described as a shielding of ionic charges,[4,5] and a local antishielding (effective Sternheimer correction). The former effect can be estimated as long as the nearly free electron model applies. The enhancement data for the metallic alloys support the assumption that this way to proceed is essentially correct, though they seem to indicate that the procedure to derive the EFG form factor from the asymptotic form of a screened Coulombic potential[4,5] is too crude.

(f) *Combination of experimental methods:* Today there are two methods which can be applied to study quadrupolar relaxation in liquids — the classical NMR on stable ground states, and perturbed angular distributions (PAD) on nuclear isomers produced and aligned by nuclear reactions. Each of them has its specific advantages. From a physical point of view it is in general a superiority of NMR that the probe atoms are matrix atoms, while in PAD they will be an impurity in most cases. Occasionally however, the impurity probe is just what one needs in order to measure a complete composition dependence.[10,18,19] It appears that for systematic studies of metallic alloys the impurity problem seems to be of minor importance. We shall confine the discussion by considering only interactions between the probe and the alloy as a whole, and by disregarding possible effects due to the special combinations of the Sb probe and the respective alloy partner of In. It is an advantage of PAD that there exist several isomeric states (for instance $^{117}\mathrm{Sb}^m$, $^{132}\mathrm{Xe}^m$, and $^{207}\mathrm{Po}^m$), where the quadrupolar contribution to relaxation dominates strongly. In this case the decomposition of the observed rate into its magnetic and quadrupolar part is no problem, whereas in most classical NMR cases, both processes compete. It is also an advantage of PAD that the alignment effect, and thus the signal-to-noise ratio, is temperature independent in contrast to NMR. Throughout the present work the PAD method has been used, however, reference will be made to classical NMR results.

The outline of this paper is as follows: In Sec. II experimental details and results are presented. The extension of the Sholl and Warren formulation of R_Q to alloys is described in Sec. III. The experimental material — dependence of R_Q on the partner element, composition, and temperature, is discussed in Seec. IV. In Sec. V we describe and analyze a model calculation for R_Q based upon the hard-sphere approximation for the partial-static structure factors.

II. EXPERIMENTS AND RESULTS

(a) *Preparation of samples:* The samples for irradiation are of cylindrical size, 6 mm in diameter and 2 mm thickness. All of them have been composed from elementary material of $\geqslant 99.9\%$ purity. At about 100 °C above the melting point of the corresponding composition, the components have been molten together under ultrapure Ar flow at 1 atm in a graphite crucible. To attain homogeneity the melting procedure was repeated once after crushing the tablets. For details of target assembly, temperature calibration etc., see Ref. 10.

(b) *Measurement:* As described previously[10] we measured the nuclear quadrupolar relaxation of $^{117}\mathrm{Sb}^m$ by observing the spin rotation patterns from the decay of the 340-μsec isomer which was produced and aligned by the nuclear reaction $^{115}\mathrm{In}(\alpha,2n)$. The experiments have been performed at the Karlsruhe cyclotron. During the activation pulse (5 μsec width, $T_z=1600$ μsec repetition time) the beam intensity on the target was typically 1–5 μA. We observed two γ lines in the cascade of the isomer (1000 and 1325 keV) and used two 2-in × 2-in. NaI(Tl) detectors in order to collect as much information as possible. The intensity ratio $I(1000\text{ keV})/I(1325\text{ keV})$ is roughly 2. The signal-to-noise ratio is improved by suppressing the 3.5-min activity (^{118}Sb, 1230-keV γ line) by a beam on/off cycle of 3.5 minutes. The measuring time for one point in this mode of operation is about 1 h.

(c) *Data handling:* The time spectra are disturbed by dead time losses in the multichannel analyzer, and have been corrected by a procedure described elsewhere.[20] To fit them we used the usual expression[21] including an additional exponential background term. In the fits, so far unexplained correlations have been observed between the intensity of the γ line and the fitted nuclear lifetime. The resulting systematic errors in the relaxation rate could be reduced by calculating the composed rate

$$R_c=R_n^F+R_r^F \ , \tag{1}$$

with the fit results for the nuclear lifetime $1/R_n^F$, and the relaxation rate R_r^F. The final result for the relaxation rate R is then derived by

$$R=R_c-R_n \ , \tag{2}$$

using the value $1/R_n=(\ln 2)(340\pm 20)\,\mu$sec for the nuclear lifetime as given in the literature.[22]

(d) *Error considerations:* The statistical error for the relaxation time given by the fit program for each spectrum is usually consistent with the scatter among the results for the four spectra; the error bars plotted in the figures represent the mean-squared errors obtained from this scatter. For relaxation times, long compared with the nuclear lifetime, the uncertainty of the latter introduces a large systematic error into R. According to Eq. (2), an error ΔT_n in the nuclear lifetime T_n propagates into the rate in the form

$$\Delta R_n=\pm\Delta T_n/(T_n\mp\Delta T_n)^2=\pm 120\ \mathrm{sec}^{-1} \ , \tag{3}$$

independent of the relaxation rate.

As we are interested in the variation of R with different parameters, this systematic uncertainty is not included into the error bars shown in the plots; it must be taken into account additionally if absolute rates are considered.

(e) *Results:* As the relaxation time of $^{117}\mathrm{Sb}^m$ in pure In is long compared with the nuclear lifetime, its accurate determination is difficult. However its magnitude is important within this systematic investigation. Therefore, we remeasured the total rate $R\,(\mathrm{In}{:}^{117}\mathrm{Sb}^m)$ as a function of temperature obtaining values (Table I) which are smaller than those reported earlier.[10] One reason for this is the reduction of R_r^F to the literature value $1/R_n$ for the nuclear lifetime, which is somewhat smaller than the mean-fit results of our measurements $[1/R_n^F\approx(\ln 2)\times 360\ \mu\mathrm{sec}]$. Moreover, poor statistics and any distortion of the time spectra tend to simulate higher relaxation rates.

The relaxation rates R_Q (after correcting for the magnetic contribution, see below) are presented in Table II column 4 for $\mathrm{In}_{0.5}X_{0.5}$ alloys with 14 *sp* elements as alloy partners X. The data are taken at $T=900$ K, in all cases where the alloy is liquid at this temperature. Exceptions are $X=$ Cu, Ge, Te (1000 K), and As (1300 K). For $X=$ Cd and Hg, T was 720 and 300 K, respectively, to avoid decomposition of the alloy due to evaporation. The relaxation rates of the same systems measured near the melting point are quoted in column 6.

For some of the systems with a large enhancement ($\mathrm{In}_{0.5}X_{0.5}$, $X=$ As, Bi, Hg, and Au) we measured the isothermal composition dependence in the In-rich region; these data are presented in Fig. 1.

The temperature dependence of R at fixed composition has been measured for two systems ($\mathrm{In}_{0.5}\mathrm{Bi}_{0.5}$ and $\mathrm{In}_{0.5}\mathrm{Hg}_{0.5}$, see Fig. 2), where an appreciable temperature range (in units of the melting temperature T_m of the alloy) can be covered without decomposition of the sample.

(f) *Correction for magnetic contributions:* For pure In the quadrupolar relaxation rate is derived from the effective rate R_c according to

$$R_Q=R_c-R_n-R_m \ . \tag{4}$$

At 900 °K the magnetic rate R_m for $^{117}\mathrm{Sb}^m$ in In can be estimated by the Korringa relation, after extrapolating the experimental Knight shifts for Sb in $\mathrm{In}_C\mathrm{Sb}_{1-C}$ alloys[11] down to $C=1$. For the electron-

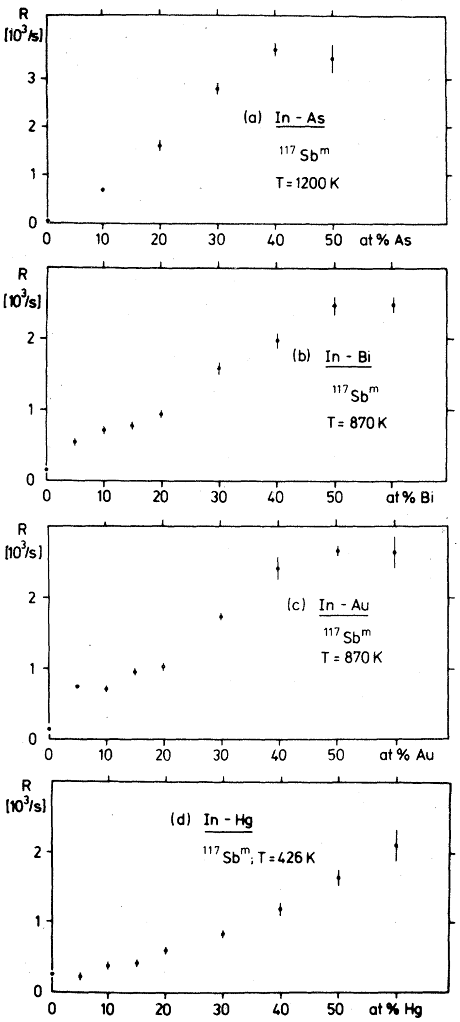

FIG. 1. Isothermal composition dependence of the total rate R in (a) In_CAs_{1-C}, (b) In_CBi_{1-C}, (c) In_CAu_{1-C}, and (d) In_CHg_{1-C}. The error bars represent the mean-squared error from averaging the four time spectra belonging to each point; the error due to the uncertainty in the nuclear lifetime is not included.

interaction factor $K(\alpha)$ the value 0.72 is adopted.[10] The temperature dependence of R_m is linear if we assume the Knight shift for Sb in In to vary as a function of temperature in a similarly slight manner as is the case for In in In. This has been tested experimentally.[23] The error assigned to R_m is essentially due to the uncertainty of $K(\alpha)$, which we estimate to be less than 30%. We find that the quadrupolar relaxation in pure In (Table I) is just on the limit of being detectable; the accuracy of the measurements is limited essentially by the large uncertainty in the nuclear lifetime of the isomer.

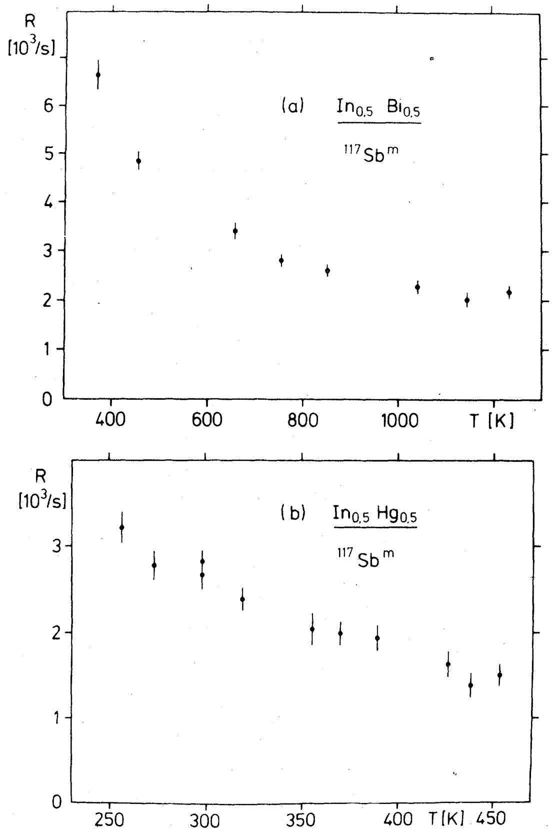

FIG. 2. Temperature dependence of the total rate R (a) in $In_{0.5}Bi_{0.5}$ and (b) $In_{0.5}Hg_{0.5}$. Error bars as in Fig. 1.

For In-X alloys magnetic contributions to $R(^{117}Sb^m)$ are estimated in the alloys starting from the Knight shift κ on In in the respective systems. We use again the Korringa relation and assume, that the variation of κ(Sb) with composition and temperature is of the same order as that of κ(In). This may be justified by noting that the variation of κ(A) and κ(B) generally is of the same order in metallic binary A_CB_{1-C} alloys, where both shifts have been measured.[24] Further, we assume we have $K(\alpha) \leq 1$, which is supported experimentally by the measurement of Knight shifts and magnetic relaxation on Sb in InSb (Ref. 3), and in GaSb (Ref. 25); here the magnetic relaxation has been identified by isotopic separation.

Knight shifts on In in liquid alloys of In are available[24] for the systems listed in Table II except for X = As, Cu, Ge, and Zn. The variation of the known shifts is less than 15% in all cases; an exception is semiconducting In-Te, which has been considered elsewhere.[26] Thus, we estimate possible enhancements of the magnetic part of $R(^{117}Sb^m)$ in the alloys

TABLE I. Deduction of quadrupolar rate for $^{117}\mathrm{Sb}^{m}$ in pure In.[a]

Measuring temperature T (K)	R_c (sec^{-1})	R_n (sec^{-1})	R_m (sec^{-1})	R_Q (sec^{-1})
434	3210 ± 150	2940 ± 120	71 ± 21	200 ± 190
527	3170 ± 120	2940 ± 120	86 ± 26	140 ± 170
878	3090 ± 100	2940 ± 120	143 ± 43	10 ± 160
1118	3080 ± 100	2940 ± 120	183 ± 55	0 ± 170

[a] The rates R_Q are derived according to Eq. (4). Errors: column 2: statistical error; column 3: error quoted by Fromm *et al.*[22]; column 4: uncertainty in $K(\alpha)$; column 5: propagated error from columns 2–4.

to be at most 50% of the magnetic rate in pure In at the same temperature. For definiteness we take the value $R_m = 150 \pm 120$ sec^{-1} in Table II.

III. REPRESENTATION OF QUADRUPOLAR RELAXATION RATES IN LIQUID ALLOYS

In the liquids of interest here the extreme narrowing limit applies. The quadrupolar relaxation rate of a nuclear spin I with quadrupole moment Q is then given by

$$R_Q = (3\pi/40)(eQ/\hbar)^2 f(I,\lambda) J(\omega=0) \ , \tag{5}$$

where

$$f(I,\lambda) = \frac{\lambda(\lambda+1)[4I(I+1) - \lambda(\lambda+1) - 1]}{2I^2(2I-1)^2} \tag{6}$$

and we have $\lambda = 1$ for NMR and $\lambda = 2$ for the present PAD measurements.[27] Our interest is directed to $J(\omega=0)$, which is the low-frequency limit of the time fluctuations of the electric-field gradient at the probe nucleus. We shall discuss $J(0)$ as a function of the alloy partner, composition, and temperature of the alloy. Its Fourier transform is the EFG time correlation function which is written (notation adopted from Ref. 4)

$$J(t) = \int\int U(\vec{r}_0) U^*(\vec{r}_1) P(\vec{r}_0, 0, \vec{r}_1, t) \times d^3r_0 d^3r_1 \ , \tag{7}$$

assuming that the time fluctuations of the EFG originate from atomic motions of the probe, and the $N-1$ other atoms in the sample relative to each other. We begin the discussion of R_Q in alloys by considering current approximations for P in pure metals.

Sholl[6] and Warren[7] proposed a representation of P for a monatomic liquid using time-dependent total and self-correlation functions $G(\vec{r},t)$ and $G_s(\vec{r},t)$, respectively,[28] and the static-radial distribution function $g(r)$,

TABLE II. Quadrupolar relaxation rates in liquid $\mathrm{In}_{0.5}X_{0.5}$ alloys.[a]

Alloy partner	Melting temperature of the alloy (K)	Measuring temperature (K)	R_Q (sec^{-1})	Measuring temperature (K)	R_Q (sec^{-1})
Cu	910	1000	2450 ± 200	1000	2450 ± 200
Ag	770	870	750 ± 130	870	750 ± 130
Au	770	870	2280 ± 260	870	2310 ± 260
Zn	620	870	380 ± 160	680	230 ± 185
Cd	450	720	200 ± 140	500	200 ± 170
Hg	250	300	2570 ± 160	275	2850 ± 160
Ga	340	870	$\lesssim 120$	370	$\lesssim 120$
Tl	470	870	180 ± 160	510	400 ± 250
Ge	940	1000	460 ± 160	1000	460 ± 160
Sn	400	870	260 ± 180	450	750 ± 160
Pb	510	870	300 ± 130	560	400 ± 190
As	1210	1210	3250 ± 300	1210	3250 ± 300
Sb	800	870	4490 ± 180	800	5850 ± 230
Bi	380	870	2410 ± 180	380	6650 ± 230
Te	970	970	>20000	970	>20000
Pure In	430	970	$\lesssim 120$	430	200 ± 190

[a] After correcting for the magnetic rate, see Sec. II f, R_Q is given in column 4 at constant absolute temperature whenever possible (Sec. II e), and in column 6 near the melting point. The quoted errors include the uncertainty due to magnetic contributions, but not due to ΔR_n.

$$P(\vec{r}_0, 0, \vec{r}_1, t) = \rho g(r_0) g(r_1) \times \int G_S(\vec{r}, t) G(\vec{r} + \vec{r}_1 - \vec{r}_0, t)\, d^3r \quad . \tag{8}$$

In this approximation we have

$$R_Q \propto J(\omega = 0) \propto \int \int k^2 V^2(k) S_s(k, \omega_0) \times S(k, \omega_0)\, dk\, d\omega_0 \quad , \tag{9}$$

with the EFG form factor

$$V(k) = \int_0^\infty r^2 V_2(r) g(r) j_2(kr)\, dr \quad . \tag{10}$$

$S(k, \omega)$ is the space-time Fourier transform of $G(\vec{r}, t)$, and $V_2(r)$ is the radial part of the EFG $U(\vec{r})$. For pure metals, Eq. (9) has recently[5] been evaluated with a variety of models for $S(k, \omega)$ and $S_s(k, \omega)$. While from the assumption underlying Eq. (8), correlations between the probe atom and the surroundings are not included in detailed form, Eq. (9) can account for correlated motions of the surrounding liquid through $S(k, \omega)$. Taking for $S(k, \omega)$ and $S_s(k, \omega)$ single Lorentzians with equal widths, Eq. (10) yields[7]

$$R_Q \propto \tfrac{1}{2} \int k^2 V^2(k) S(k, \tfrac{1}{2}\omega = 0)\, dk \quad . \tag{11}$$

We quote this formula, since it has also been taken as a starting point for numerical calculations of absolute rates,[7] as well as of temperature dependences[29] in pure liquid metals.

We turn now to metallic alloys. The observed enhancement of R_Q in many systems[10,11,13,30–33] increases smoothly to a maximum value in the intermediate range independently from the existence of intermetallic compositions in the solid state. This supports the view that the effect is dominated by an essentially random replacement of atoms of a pure liquid by the alloy partner: Solute atoms destroy the highly symmetrical arrangement around the probe as they differ in their properties from the solvent atoms, for example in charge or size, and therefore, in the EFG they induce.[8,13] The extensions of Eqs. (9) and (11) given below account especially for this replacement effect.

For pure monatomic liquids the formal structure of Eqs. (9) and (11) resembles the corresponding expressions for the scattering cross section of x rays[34] or of neutrons, or of electrons, as needed in the calculation of electrical resistivity.[14] In these cases the scattering probability is given by an integral over the product of a form factor times a structure factor, and the effect of alloying is to substitute identical scattering centers by a mixture of different ones. This is appropriate if no change in the form factors belonging to the components A, B (compared to the pure materials) occur in the alloy, an approximation which is fulfilled well for scattering of neutrons, and to a very good approximation for x-ray scattering. For conduction electron scattering, on the other hand, the pseudopotential enters the form factor for scattering; it also enters the intercomponent forces, which determine the structure (and dynamics) of the liquid. For systems where the NFE model is a good approximation, the form factors and structure factors may be treated independently (Faber-Ziman theory). For quadrupolar relaxation we expect much the same situation as for resistivity, since here the pseudopotential is involved in $V(k)$, the equivalent to the form factor for electron scattering. We assume, therefore, the separation into form factor and structure factor to work for R_Q approximately as long as it works for electrical transport properties. Utilizing the formal analogy to scattering, we refer in the following to well-known developments[14,16] in the scattering formalism. The expressions for R_Q, which we shall give in the following, differ in that one may either first introduce approximations for $S(k, \omega)$ into Eq. (9) and then generalize to the alloy, or vice versa.

We start from Eq. (11) and introduce the static structure factor $a(k)$ by the Vineyard approximation

$$S(k, \omega) \approx a(k) S_s(k, \omega) \quad . \tag{12}$$

Now the substitution of like atoms by different ones is allowed for[9,10] by replacing $a(k)$ by the three partial structure factors $a_{ij}(k)$, which are multiplied by the corresponding products of the EFG form factors $V_i(k)$, $V_j(k)$ belonging to the $i, j = A$, and B component. In general, the self-function $S_s(k, \omega)$ will also be altered, which we indicate by use of $\tilde{S}_s$ in the alloy instead of S_s; however, $\tilde{S}_s$ does not break up into several terms. One obtains[8,11] (C_A, C_B atomic concentrations, $C_A + C_B = 1$)

$$R_Q \propto \tfrac{1}{2} \int [C_A^2 V_A^2 a_{AA} + C_B^2 V_B^2 a_{BB} + 2 C_A C_B V_A V_B a_{AB} + C_A C_B (V_A - V_B)^2] S_s k^2\, dk \quad . \tag{13}$$

In Eq. (13) the Faber-Ziman definition of partial structure factors is used, which, however, cannot be generalized directly to dynamical-partial structure factors. Therefore, we rewrite Eq. (13) in the number-concentration structure factors $S_{NC}(k)$ etc. as defined by Bhatia and Thornton[16]. We have

$$R_Q \propto \tfrac{1}{2} \int [(C_A V_A + C_B V_B)^2 S_{NN}(k) + (C_A V_A + C_B V_B) \times (V_A - V_B) S_{NC}(k) + (V_A - V_B)^2 S_{CC}(k)] \times \tilde{S}_s(k, \tfrac{1}{2}\omega = 0) k^2\, dk \quad . \tag{14}$$

One may as well start from Eq. (11), however, avoid the Vineyard approximation and generalize the dynamical structure factor $S(k,\omega)$ directly to partial-dynamical structure factors $S_{ij}(k,\omega)$ (Ref. 16), i.e.,

$$R_Q \propto \frac{1}{2}\int [(C_A V_A + C_B V_B)^2 S_{NN}(k,\tfrac{1}{2}\omega=0) + (C_A V_A + C_B V_B)\cdot(V_A - V_B) S_{NC}(k,\tfrac{1}{2}\omega=0) + (V_A - V_B)^2 S_{CC}(k,\tfrac{1}{2}\omega=0)] k^2\, dk \quad . \quad (15)$$

Finally, the transition to the alloy can be performed already for the dynamical structure factor $S(k,\omega)$ [Eq. (9)] which represents the motion of the surrounding of the NMR atom, i.e.,

$$R_Q(\omega) \propto \int\int [(C_A V_A + C_B V_B)^2 S_{NN}(k,\omega_0) + (C_A V_A + C_B V_B)(V_A - V_B) S_{NC}(k,\omega_0) + (V_A - V_B)^2\ S_{CC}(k,\omega_0)] \tilde{S}_s(k,\omega-\omega_0) \times d\omega_0\, k^2\, dk \quad . \quad (16)$$

Equation (16) is obtained without any assumption for $S(k,\omega)$, and may be considered to be the best description of the alloy in the sense of the theory of Warren[7] and Sholl.[6] Due to poor theoretical and experimental information about dynamical-partial structure factors in alloys, the practical applicability of Eq. (16) is limited. To our knowledge analytical expressions have been given only for the hydrodynamical limit ($k \to 0$, $\omega \to 0$).[35] Applying these representations the S_{CC} term in all three expressions (14) – (16) yields the same composition and essentially the same temperature dependence in the approximation, where thermal diffusion is neglected (see Appendix).

IV. COMPARISON WITH EXPERIMENT

A well suited starting point for comparison with experiment is Eq. (14), with the additional assumption that the alloy is substitutional. "Substitutional" means that we have

$$a_{AA}(k) = a_{AB}(k) = a_{BB}(k) = S_{NN}(k) = S(k)$$

and that the components differ only in their form factors. We then obtain

$$R_Q \propto (1-\gamma_{\text{eff}})^2 \int [(C_A V_A + C_B V_B)^2 S(k) + C_A C_B (V_A - V_B)^2] S_s(k,\omega) k^2\, dk \quad . \quad (17)$$

Here γ_{eff} is the effective Sternheimer factor, which up to here was absorbed into the form factor, and $S(k)$ is the static structure factor. $S(k) = S_{NN}(k)$ is the only partial structure factor which depends on the wave number k because $S_{CC}(k)$ reduces to $C_A C_B$, and $S_{NC}(k)$ vanishes. In spite of these crude simplifications Eq. (17) reproduces characteristic features of the observed composition dependence[10,13,31–33] and temperature dependence[3,10,11,26] of R_Q.

(a) *Dependence of R_Q on the alloy partners:* The alloy enhancement has been considered systematically in liquid alloys of *sp* metals by Cartledge *et al.*[33] and earlier occasionally by Heighway and Seymour,[13] and Claridge *et al.*[11] On ^{69}Ga, in five Ga alloys doped with 8% of the partner element, a linear correlation has been observed between the alloy enhancement and the difference of the atomic volume of Ga and of the partner element.[33] Heighway and Seymour[13] found in some systems a correlation between the alloy-partner valence difference and the enhancement, however, they noticed that the correlation is not very convincing and suspected that some other effect must also be involved. In later work[11,32] the conclusion was reached again, that there is no clear relation between the valence difference and the alloy enhancement.

As we shall see in Sec. V, the occurrence of a sizeable alloy enhancement requires that the second term of Eq. (17) is dominant at intermediate composition. It will be expected then that the function $[V_A(k) - V_B(k)]^2$ in fact plays a decisive role. Modifications of this view will be considered in Sec. V. We confine our attention to metallic systems in the sense that the electronic transport properties can be described by the nearly-free-electron (NFE) model since this allows a straightforward estimation of the EFG variations in the alloy. Then the strength of the EFG will be given by the charge of the neighbor ion, which is screened by conduction electrons, thus we have $V_i \propto Z_i/N(E_F)$. The dependence of V on composition through $N(E_F)$, and the electron density of states at the Fermi level, will be neglected; that $N(E_F)$ is nearly constant can be seen from Hall-effect data.[36] Furthermore, within the NFE model the alloy is characterized by only one k_F and therefore the k dependences of the EFG functions are the same. Accordingly, the relaxation is expected to be proportional to the square of the difference in the valence between the alloy partners $(Z_{\text{In}} - Z_X)^2$.

The data in Table II and Fig. 3 confirm these expectations in their tendency, though not in detail. Quantitatively the average alloy enhancement for the different groups is stronger than the squared valence difference at the right side (polyvalent elements), and weaker at the left side (mono and divalent elements). This, as well as the scatter within the groups, does not follow the regularity predicted by the preceding arguments. Because large alloy enhancements are accompanied by a considerable temperature dependence of R_Q (Sec. IV c) it may be appropriate to compare the rates at a constant temperature in units of the melting temperature (same "reference temperature") rather than at the same absolute temperature. However, also in such a comparison (Table II) the irregularities within the groups are not removed.

Our observations conform essentially with the findings of Heighway and Seymour.[13] The limited data on the Ga alloys,[33] in fact show no correlation to the valence. The conclusion about the lack of correlations of R_Q to the valence in Bi alloys[11] may partly result from the difficulty of separating R_Q(Bi) from the dominating magnetic rate, lacking the possibility of isotopic separation.

We have tried, using different definitions of atomic or ionic radii,[37] to find correlations between the difference in atomic volume and the rate enhancement.[33,38] There appears, however, in no case a significant correlation. Kerlin and Clark[25] assume in their discussion of R_Q in liquid Ga and GaSb that the electronegativity difference between the alloy partners causes charge transfer. However, using any of the common electronegativity scales,[39,40] no simple correlations were found for the present data.

Finally, we consider the possibility of an alloy-partner dependence of the Sternheimer factor of the probe atom. The Sternheimer correction will contain a contribution due to the ionic core[41] Sb^{5+}, $\gamma_{\rm ion}$, for which a composition independence is evident immediately, and an additional contribution $\gamma_{\rm met}$ due to the conduction electrons. For an estimation of possible changes of $\gamma_{\rm met}$ we follow the discussion of Watson *et al.*[42] putting (in their notation),

$$\gamma_{\rm met} \approx -e^2 \tfrac{4}{25}[\langle r^2\rangle \langle r^{-3}\rangle N(E) f_p]_F \ . \tag{18}$$

Changes of $\langle r^2\rangle$ and $\langle r^{-3}\rangle$ can be expected to be small for the present cases, maybe of the order of 10%. In order to estimate the variation of $f_p N$ one may consider the orbital, i.e., p contribution to the Knight shift, κ_p; although strictly speaking both, κ_p and $\gamma_{\rm met}$ contain contributions from below the Fermi level, the discussion of Watson *et al.*[42] leads us to consider for the changes mainly the region around E_F, as in Eq. (18). Thus, the changes of $\gamma_{\rm met}$ should be not very different from those of κ_p. As an example for large alloy enhancement of R_Q we mention the system InSb, where a sizeable p contribution to κ(Sb) has been assumed.[31] There, the variation of κ(Sb) with composition is known to be monotonous and only 10% (see Ref. 11); the temperature dependence of κ(Sb) in InSb is also small.[3] Thus, we conclude that large changes of R_Q(Sb) with concentration, alloy partner, and temperature cannot stem from the antishielding factor of the Sb atom.

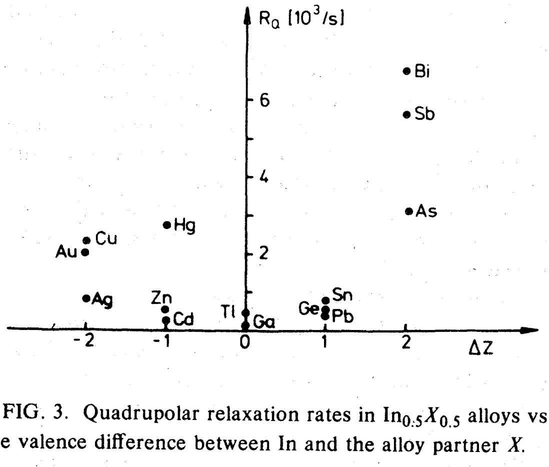

FIG. 3. Quadrupolar relaxation rates in $In_{0.5}X_{0.5}$ alloys vs. the valence difference between In and the alloy partner X.

(b) *Temperature dependence of* R_Q *at* $C=0.5$: For pure liquid metals, a proportionality of $R_Q(T)$ to the reciprocal diffusion constant has been suggested originally.[1,2,4] However, experiments in a number of liquid metals[3,43,44] have disproved this idea. In alloys, on the other hand, the existence of a different temperature dependence becomes more and more evident for systems with an appreciable enhancement.[3,10,25] In Eq. (17) the main temperature dependence enters through $S_s(k,\omega)$, and within the model of free diffusion, this is proportional to $1/D(T)$, $D(T)$ being the coefficient for self-diffusion. The temperature dependence of the S_{NN} term is assumed to resemble the weak variation observed in pure metals[3,43,44] [constant b in Eq. (19)]. Thus, the relaxation rate in alloys is expected to vary with T as

$$R_Q(T) = b + a/D(T) \ . \tag{19}$$

It is known,[45] that D shows certain common properties for quite different simple liquids like metallic alloys or salt melts: its absolute value differs only moderately from system to system, the concentration dependence is weak, and its temperature dependence may be parametrized fairly well by an Arrhenius law (k_B is the Boltzmann constant), i.e.,

$$D(T) = D_0 \exp(-W/k_B T) \ . \tag{20}$$

Since we are interested here in general trends, the following analysis is based on this form, where the activation energy parameter W/k_B for diffusion is related by an empirical rule[45] to the melting temperature T_m of the liquid by:

$$W/k_B \approx 3.7\, T_m \ . \tag{21}$$

Using Eqs. (19) and (20) we analyzed $R_Q(T)$, measured on Sb probe nuclei in the alloy InSb,[10] InBi, InHg (present work), GaSb,[25] and Sb_2Te_3.[46] Treating a and b and the activation energy as free parameters, reasonable fits for all systems are obtained.

We find the following trends (i): There exists a clear correlation between the activation energy and the melting temperature of the alloy. However, the activation energy for R_Q is about half that occurring in diffusion, see caption to Fig. 4. This correlation is established only for alloys with relaxation enhancement. (ii) The density fluctuation parameter b turns out to be zero in systems investigated by the Sb probe nucleus. The only exception requiring a definitely positive value b is the nonequicomposition alloy Sb_2Te_3.

It will be argued in Sec. Vc that for the quadrupolar relaxation process, the low k hydrodynamical range of the structure factors is of main importance, which is equivalent to saying that the alloy enhancement originates essentially from the concentration fluctuation contribution. Therefore, instead of starting from Eq. (17) one may return to Eqs. (14) – (16) and introduce the expressions for $S_{CC}(k,\omega)$ derived in the hydrodynamical limit.[35] The S_{NC} term will be neglected because it is small and the S_{NN} term is assumed again to depend only weakly on temperature. As shown in the Appendix, the temperature dependence predicted then, is very similar to the form inferred from Eq. (17). The only difference is the meaning to be given to the diffusion coefficient: if the hydrodynamical model is introduced into Eq. (14) it is the self-diffusion D, if it is introduced into Eq. (15) it is the interdiffusion D^+, and if it is introduced into Eq. (16) it is the mean value of self- and interdiffusion.

Following the model underlying Eqs. (9) and (10), it is most reasonable to insert the mean value of the self- and interdiffusion coefficients:

$$R_Q = b + a/\tfrac{1}{2}[D(T)+D^+(T)] \quad . \tag{22}$$

The temperature dependence of interdiffusion may be represented satisfactorily by an Arrhenius law with an activation energy which correlates with the melting temperature of the alloy in a similar way, as in the case for self-diffusion (see the detailed investigation[48] of Sb_CBi_{1-C}). Therefore, one expects much the same temperature dependence for $C=0.5$ [Eqs. (19) and (20)] as derived above with more crude arguments.

(c) *Composition dependence:* Again we start from the substitutional model Eq. (17). The main composition dependence expected then stems from the concentration fluctuation term which is proportional to C_AC_B. In In_CSb_{1-C}, where the composition dependence of R_Q could be observed over the entire composition range,[10,11] the above predictions are confirmed on the whole; a maximum of the rate is found at about $C=0.5$ and in the Sb-rich region the composition dependence is compatible with the C_AC_B rule.[11] In the In-rich region, however, the slope of $R_Q(C)$ is less than expected, if a C_AC_B dependence holds. In fact, this characteristic "sharp maximum" in the intermediate range or "increasing slope" for small C has been found in several other systems[13,30,33] where an enhancement exists. On the In-rich side, to which our measurements are limited, the four alloys show again an upward curvature (see Fig. 1). The dependences of $R_Q(C)$ quoted here have been taken at constant absolute temperature. Since the relaxation in the investigated alloys depends sensitively on the temperature, we tried to account for this effect correcting the measured values with the empirically found temperature dependence from above. However, comparing, e.g., along the liquidus curve the consistency with the expected C_AC_B behavior is not improved.

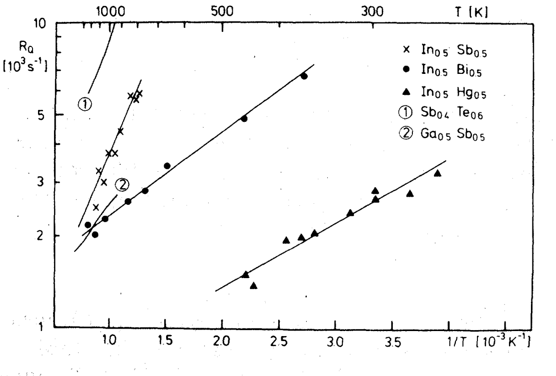

FIG. 4. Fit of the temperature dependence of the relaxation rate on Sb probe nuclei in some $A_{0.5}B_{0.5}$ alloys according to Eqs. (19) and (20). The fit results for $W/3.7T_mk_B$ are 0.68 for InSb, 0.43 for InBi, 0.50 for InHg, 0.41 for GaSb, and 0.72 for Te_3Sb_2. Corresponding fits of $R_Q(T)$ detected on ^{209}Bi yield 0.47 in InBi (Ref. 11) and in BiPb the values 0.54 and 0.78 (Refs. 11 and 47, respectively).

V. SIMULATION OF THE COMPOSITION AND PARTNER-ELEMENT DEPENDENCE OF R_Q USING A HARD-SPHERE MODEL

So far we have considered a liquid mixture of atoms with different EFG form factors V, but equal mutual interaction and equal size. This describes some of the essential trends, while it misses much of the prominent particularities. It is therefore worthwhile to attempt an analysis of some of the details starting from the model used. In the following we shall describe calculations which allow for different atomic size in the partial structure factors. For this purpose we use as a starting point Eq. (14) instead of Eq. (17).

(a) *Model expressions and assumptions:* In order to assess the content of Eq. (14) we need analytical forms for the three static structure factors S_{ij}. Tractable expressions have been deduced from the Percus-Yevick equation for a binary mixture of hard spheres with different diameters.[15,49]

Three parameters enter in the hard-sphere alloy model: the ratio of the hard-sphere diameters of the two species α, the composition C, and the packing fraction η. The latter must be chosen[50] close to 0.46; in the following this quantity will be kept fixed. The occurrence of C in the partial structure factors leads to a complicated composition dependence of R_Q, in addition to that stemming from the difference in the form factors.

As the EFG form factor [Eq. (10)] characteristic for the species i we adopt the parametrized form proposed by Schirmacher[5] for Ga,

$$V_i(k) = A_i j_2(kr_i) e^{-0.112k} , \qquad (23)$$

where k is measured in Å^{-1}; the A_i's are experimentally and theoretically scarcely-known quantities. However, in order to simulate the difference in strength of the EFG originating from In and the alloy partners, relative values will be sufficient. The range parameter r_i is expected to correlate closely with the size of the EFG source atom. We assume that the $V_i(k)$ are composition independent functions for both constituents throughout the whole composition range.

(b) *Selection of parameters:* It is convenient to introduce the following ratios as parameters for model calculations, i.e., $R_A(j) = A_{\text{In}}/A_j$, for the alloy partner j. In linear screening the variation of R_A will be between $R_A = 3$ for the alloy with the Ib metals, and $R_A = 0.6$ for those with the Va elements. The average agreement with the observed alloy enhancement suggests that this interval for R_A is reasonable. Further, the ratio of the EFG-size parameters is given by $R_{\text{EFG}}(j) = r_{\text{In}}/r_j$. Since the r_j depend on the atomic size, we vary $R_{\text{EFG}}(j)$ with the hard-sphere diameter, i.e., we put $R_{\text{EFG}} = \alpha$. We estimate the region for reasonable variations of α from the atomic radii r_D, as deduced from the density ($r_D^3 = 3/4\pi$ times atomic mass divided by bulk density). Finally, the ratio σ/r is of interest which scales the EFG-size parameter to the hard-sphere diameter. It should not depend much on the particular element under consideration. Therefore, we estimate it for Ga, where data for both σ and r are available, and apply the obtained value for all the other metals. We find $\sigma/r = 0.82$, using[51] $\sigma = 2.3$ Å and[5] $r_{\text{Ga}} = 2.8$ Å. Though these absolute values of lengths refer to the case — which is not given here—that the probe and surrounding consist of the same atomic species this is no objection for the present purpose since here only ratios of such distances enter the calculations.

(c) Results: With the EFG strength factor ratio R_A proportional to the valence ratio, diameter ratios α which vary according to the density diameter r_D and $\sigma/r = 0.82$, Eq. (17) yields a monotonic composition dependence for almost all alloys (Fig. 5). Remarkably, R_Q, at $C = 0.5$, increases or decreases from the pure In value depending on whether the alloy partner has a larger or smaller valence than In. This contradicts the data, which never show a lowering of the rate on the In-rich side when a valence difference is present. Now the three contributions to R_Q depend differently on the overlap between the form factors and the structure factors; all V's and S_{NN} depend strongly on k, while S_{CC} is only weakly k dependent and S_{NC} is small. This is displayed in Fig. 6. Therefore, the NN term depends on details of the overlap, and varies sensitively if the scaling parameter σ/r is altered. As seen from Fig. 6 the NN contribution to R_Q will be weakened, if σ/r is lowered, i.e., if the form factor is compressed on the k scale. Accordingly, we performed the above calculations again adopting smaller values for σ/r ($\sigma/r = 0.65$, 0.5, and 0.3). Indeed, the CC term then becomes more and more important, [see Figs. 5(a)–5(d)] and for $\sigma/r = 0.3$, the typical alloy enhancement appears for all systems with a valence difference. The maximum of the enhancement occurs around $C = 0.5$ within an interval of $\Delta C \approx 0.15$. Deviations from the strict correlation of the enhancement to the valence difference occur; the scatter of these deviations compared to the absolute enhancement appears to be realistic (Table III). Remarkably, the calculated increment of R_Q in the Ib alloys is on the average somewhat smaller than that in the Va alloys in accord with the observed tendency; this is due to the more pronounced difference in size between In and the Ib metals compared to In and the Va elements. So at first sight the above calculations suggest some relevance of this account for atomic size effects. There are, however, obvious shortcomings of the approach: (i) In detail the calculated deviations from the trend governed by the valence difference do not correlate with the observations. (ii) Even with $\sigma/r = 0.3-0.5$ the alloy enhancement turns out to be too small. (iii) Only for a few systems the calculated shape of $R_Q(C)$ exhibits the tendency of increasing slope at low C.

A more general conclusion, however, may be drawn as the essential result of the above analysis, namely, that the main contribution to the overlap integral for the NN term to R_Q must originate from the low k (hydrodynamical region of $S_{NN}(k)$: as seen from Figs. 5(a)–5(d), the integral of $S_{NN} V_{NN}$ yields always a monotonic composition dependence, the slope of which depends on the valence difference between the alloy partners. This is true in particular, if the form factor weighs heavily the region around the first peak of S_{NN} which is represented reliably by the hard-sphere model. If, however, this region is weighed heavily, the NN term becomes strongly dominating, and with some confidence, a monotonic composition dependence is expected for the total rate R_Q in contradiction to the observation. We conclude, therefore, that actually the form factor must weigh preferentially in the range below the first maximum of S_{NN}. This fact draws the attention to the behavior of the partial structure factors in the hydrodynamical

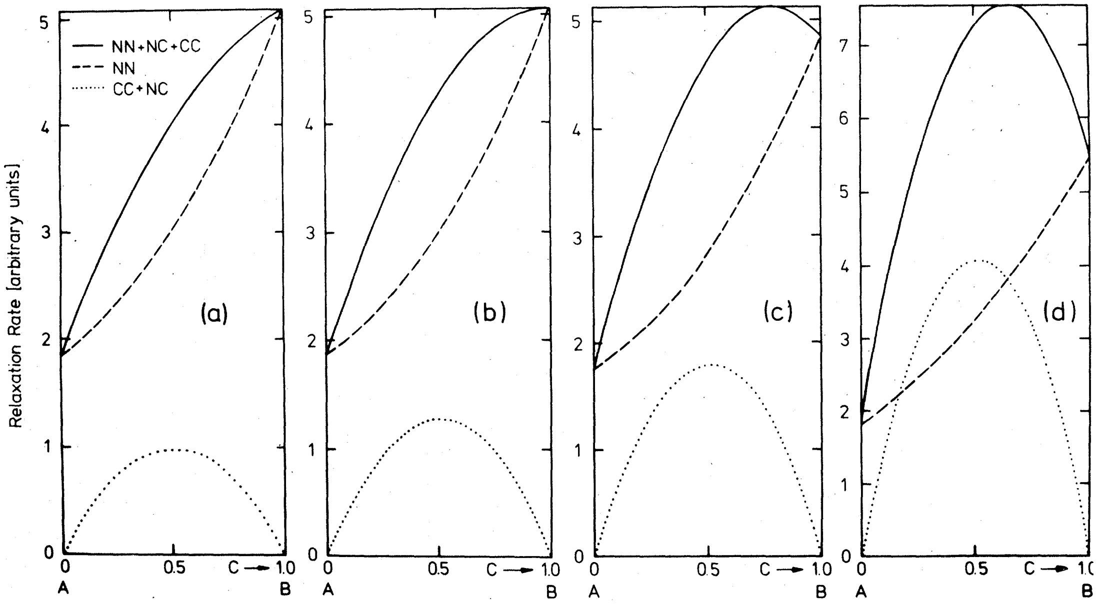

FIG. 5. Composition dependence of R_Q using a hard-sphere model for the partial-static structure factors. The parameters for the diameter ratio and the valence difference are chosen so that A corresponds to In and B corresponds to Sb. Full line: total rate; dashed line: density fluctuation contribution; dotted line: the sum of the concentration fluctuation and the mixed concentration density fluctuation contribution. (a) $\sigma/r=0.82$, (b) $\sigma/r=0.65$, (c) $\sigma/r=0.5$, and (d) $\sigma/r=0.3$.

TABLE III. Alloy enhancement calculated according to Eq. (14).[a]

Alloy Partner	R_D (Å)	α	Enhancement $\sigma/r=0.5$	Enhancement $\sigma/r=0.3$	Observed rate (sec^{-1})
Cu	1.41	0.77	1.33	2.52	2450
Ag	1.60	0.87	1.29	2.31	750
Au	1.60	0.87	1.29	2.30	2310
Zn	1.54	0.84	1.12	2.08	230
Cd	1.73	0.94	1.07	1.65	200
Hg	1.80	0.98	1.14	1.78	2850
Ga	1.66	0.90	1.36	2.18	120
In	1.84	...	...	...	...
Tl	1.90	1.03	1.03	1.10	400
Ge	1.76	0.96	1.86	2.53	460
Sn	1.80	0.98	1.73	2.19	750
Pb	1.93	1.08	1.57	1.90	400
As	1.73	0.94	3.65	6.15	3250
Sb	1.94	1.08	2.62	3.60	5850
Bi	2.04	1.11	2.60	3.99	6650

[a] The results quoted in columns 3 and 4 are the quantities $R_Q(\mathrm{In}_{0.5}X_{0.5})/R_Q(\mathrm{In})$. R_D is the radius of the partner element as derived from the density and we have $\alpha=R_D(X)/R_D(\mathrm{In})$. Column 5 gives the measured rates $R_Q(\mathrm{In}_{0.5}X_{0.5})$ at the melting temperature taken from Table II.

range which the hard-sphere model fails to reproduce reliably.[17] Experimental data show that the $k\rightarrow 0$ limit of $S_{NN}(k)$, i.e., the macroscopic compressibility of liquid metals, is systematically smaller by a factor 3–5 than expected from the hard-sphere model.[52] This means that the above calculations probably overestimate S_{NN} in the whole region below the main peak, leading to the erroneous predominance of the density fluctuation term.

These results ask for a modification of the earlier view[3,4,53,54] that the structure factor weighs most heavily the region around $2k_F$, i.e., the region around or above the main peak of $S(k)$. According to the work of Sholl[4] and Warren[3] this fact rested on the selection of the asymptotic form of a screened Coulombic potential for the calculation of the EFG form factor. The difficulties to justify this special assumption have been emphasized previously.[3] Although the function Eq. (23) for the EFG form factor used here is the result of a more sophisticated treatment of the EFG problem in liquid metals,[5] it seems likewise to overestimate the contributions from large k values. We believe the present experiments to prove that if indeed the atomic motions control R_Q according to the theory of Sholl and Warren, we are forced to modify the current expressions for the radial dependence of the EFG functions in a sense, that the large k region of the structure factor becomes less heavily weighed relative to the hydrodynamical range.

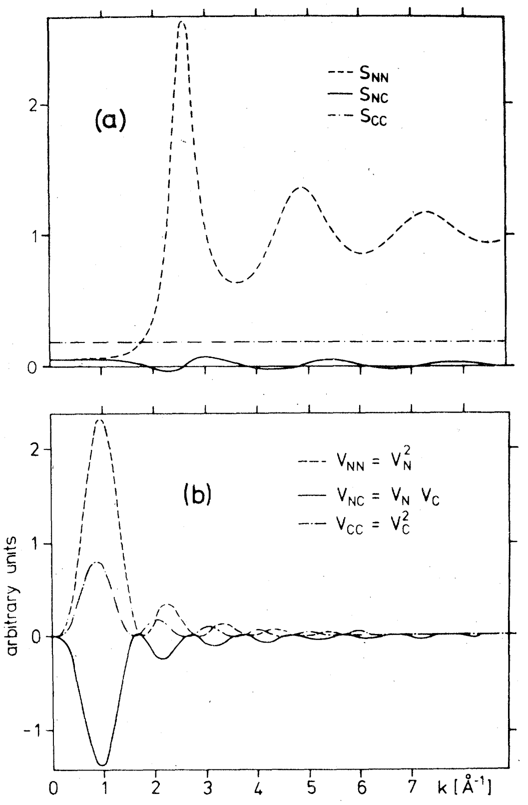

FIG. 6. Hard-sphere partial structure factors (a) and EFG form factors (b) according to Eq. (23). We have $V_{NN} = (C_A V_A + C_B V_B)^2$, $V_{NC} = (C_A V_A + C_B V_B)(V_A - V_B)$, and $V_{CC} = (V_A - V_B)^2$. The curves correspond to an $\mathrm{In}_C\mathrm{Sb}_{1-C}$ alloy for $C = 0.75$. The hard-sphere to EFG diameter ratio is chosen at $\sigma/r = 0.82$.

In a recent discussion[53,54] a predominance of the contributions from large k values to the integral for R_Q has been postulated explicitly, however it is based on other reasoning. Marsden *et al.*[53,54] focus on the temperature dependence of R_Q in pure metals which is weaker than expected from the reciprocal diffusion constant. The expression they quote for R_Q contains $S_s(k,\omega)$ only, instead of both $S_s(k,\omega)$ and $S(k,\omega)$. Since $S_s(k,\omega)$ at k values above about $2k_F$ has a weak temperature dependence ("ideal-gas behavior") while at low k values the strong temperature dependence originating from diffusion dominates, they conclude that the shape of the EFG form factor must be such as to weigh $S_s(k,\omega)$ at those high k values which correspond to distances considerably smaller than atomic diameters.

Because quite generally partial structure factors at $k \approx 0$ are determined by thermodynamical properties of the liquid,[17] we will include these in a forthcoming analysis of data for R_Q in alloys.[18]

ACKNOWLEDGMENTS

This work was supported by the Deutsche Forschungsgemeinschaft through Sfb 161. We are obliged to the Kernforschungszentrum Karlsruhe for machine time and acknowledge greatly the help of the cyclotron staff. We thank Dr. W. Schirmacher for valuable discussions. One of us (J.R.) is supported by the Hahn-Meitner-Institut, Berlin.

APPENDIX

We note the following relations between the S_{CC} terms in Eqs. (14) – (16) which apply to the region of small k and small ω. There $S_s(k,\omega)$ is represented correctly by the free diffusion approximation[55]

$$S_s(k,\omega) = (Dk^2/\pi)/[\omega^2 + (Dk^2)^2] \ , \tag{A1}$$

where D is the coefficient for self-diffusion.[56] In the same limit the hydrodynamical model for $S_{CC}(k,\omega)$ will be a reasonable approximation. We start from the hydrodynamical formula for $S_{CC}(k,\omega)$, which in the notation of Bhatia *et al.*[35] is given by

$$S_{CC}(k,\omega) = \frac{Nk_B T}{2\pi Z}\left(\frac{2A_7 X k^2}{\omega^2 + X^2 k^4} + \frac{2A_8 Y k^2}{\omega^2 + Y k^4}\right) , \tag{A2}$$

with

$$2X = (\chi + \underline{\mathfrak{D}}) + [(\chi + \underline{\mathfrak{D}})^2 - 4\chi\underline{\mathfrak{D}}]^{1/2}$$

and

$$2Y = (\chi + \underline{\mathfrak{D}}) - [(\chi + \underline{\mathfrak{D}})^2 - 4\chi\underline{\mathfrak{D}}]^{1/2} \ ;$$

$$\underline{\mathfrak{D}} = D^+(1 + k_T^2 Z/TC_p) \ . \tag{A3}$$

Here D^+ is the constant of interdiffusion. If we now suppose the thermal diffusion ratio k_T to be small, i.e.,

$$k_T^2 << Z/TC_P \tag{A4}$$

we obtain immediately

$$D^+ \approx \underline{\mathfrak{D}} \ . \tag{A5}$$

Thus, we arrive at

$$S_{CC} \approx (Nk_B T/\pi Z) D^+ k^2/[\omega^2 + (D^+ k^2)^2] \ . \tag{A6}$$

This leads to the following explicit forms for the S_{CC} term: in Eq. (14)

$$\begin{aligned}\tfrac{1}{2} S_{CC}(k) S_s(k, \tfrac{1}{2}\omega) &= \frac{Nk_B T}{2Z} \frac{Dk^2/\pi}{(\omega/2)^2 + (Dk^2)^2} \\ &= \frac{Nk_B T}{Z} \frac{1}{2\pi Dk^2} \quad \text{for } \omega \to 0 \ .\end{aligned} \tag{A7}$$

Here we inserted for $S_{CC}(k)$, the frequency integral of $S_{CC}(k,\omega)$, as given by Eq. (A2). Similarly Eq.

(15) contains the right-hand side of Eq. (A7), however, with D replaced by the interdiffusion constant D^{+}. From the convolution in Eq. (16) we obtain the right-hand side of Eq. (A7) again, where D is now replaced by arithmetic mean value $\frac{1}{2}(D+D^{+})$. Thus, apart from the fact that different diffusion coefficients occur, Eqs. (14) – (16) result in the same form for the temperature dependence. In the spirit of the Sholl and Warren model, the expression which contains the averaged diffusion coefficient $\frac{1}{2}(D+D^{+})$, describes the dynamics of $S_{CC}(k,\omega)$ best. Because the composition C is contained in the stability function Z, the dependence on C is the same in all three expressions.

---

[1] E. F. W. Seymour and G. A. Styles, Proc. Phys. Soc. 87, 473 (1966).

[2] F. Borsa and A. Rigamonti, Nuovo Cimento 488, 144 (1967).

[3] W. W. Warren, Jr. and W. G. Clark, Phys. Rev. 177, 600 (1969).

[4] C. A. Sholl, Proc. Phys. Soc. London 91, 130 (1967).

[5] W. Schirmacher, thesis (Freie Universität Berlin, 1977) (unpublished).

[6] C. A. Sholl, J. Phys. F 4, 1556 (1974).

[7] W. W. Warren, Jr., Phys. Rev. A 10, 657 (1974).

[8] J. M. Titman and R. I. Jolly, Phys. Lett. A 39, 213 (1972).

[9] H. Gabriel, Phys. Status Solidi B 64, K63 (1974).

[10] M. v. Hartrott, K. Nishiyama, J. Rossbach, E. Weihreter, and D. Quitmann, J. Phys. F 7, 713 (1977).

[11] E. Claridge, D. S. Moore, E. F. W. Seymour, and C. A. Sholl, J. Phys. F 2, 1162 (1972).

[12] M. v. Hartrott, J. Höhne, D. Quitmann, J. Rossbach, E. Weihreter, and F. Willeke, *Proceedings of the Fourth International Conference on Hyperfine Interactions*, edited by R. S. Raghavan and D. E. Murnick (North-Holland, Amsterdam, 1978), p. 816.

[13] J. Heighway and E. F. W. Seymour, J. Phys. F 1, 138 (1971).

[14] T. E. Faber and J. M. Ziman, Philos. Mag. 11, 153 (1965).

[15] N. W. Ashcroft and D. C. Langreth, Phys. Rev. 156, 685 (1967).

[16] A. B. Bhatia and D. E. Thornton, Phys. Rev. B 2, 3004 (1970).

[17] A. B. Bhatia, *Liquid Metals*, edited by R. Evans and D. A. Greenwood (Institute of Physics and Physical Society, London, 1977) p. 21.

[18] E. Weihreter, M. v. Hartrott, J. Höhne, D. Quitmann, J. Rossbach, and F. Willeke, Phys. Lett. A 67, 394 (1978).

[19] J. Rossbach, thesis (Freie Universität Berlin, 1978) (unpublished).

[20] E. Weihreter, thesis (Freie Universität Berlin, 1978) (unpublished).

[21] M. v. Hartrott, J. Hadijuana, K. Nishiyama, D. Quitmann, D. Riegel, and H. Schweickert, Z. Phys. A 278, 303 (1976).

[22] W. D. Fromm, H. F. Brinckmann, F. Dönau, C. Heiser, F. R. May, V. V. Pashkevich, and H. Rotter, Nucl. Phys. A 243, 9 (1975).

[23] E. Weihreter, M. v. Hartrott, J. Höhne, D. Quitmann, and J. Rossbach, *Proceedings of the Fourth International Conference on Hyperfine Interactions,* edited by R. S. Raghavan and D. E. Murnick (North-Holland, Amsterdam, 1978), p. 926.

[24] G. C. Carter, L. H. Bennett, and D. H. Kahan, *Metallic Shifts in NMR* (Pergamon, Oxford, 1977).

[25] A. L. Kerlin and W. G. Clark, Phys. Rev. B 12, 3533 (1975).

[26] M. v. Hartrott, K. Nishiyama, J. Rossbach, E. Weihreter, and D. Quitmann, in Ref. 17, p. 460.

[27] A. Abragam and R. V. Pound, Phys. Rev. 92, 943 (1953).

[28] L. van Hove, Phys. Rev. 95, 249 (1954).

[29] K. Nishiyama and D. Riegel, Hyperfine Interactions 2, 276 (1976).

[30] G. A. Styles, Adv. Phys. 16, 275 (1967).

[31] G. Bonera, F. Borsa and A. Rigamonti in *Magnetic Resonance and Radiofrequency Spectroscopy,* edited by P. Averbuch (North-Holland, Amsterdam, 1969), p. 359.

[32] R. I. Jolly and J. M. Titmann, J. Phys. C 5, 1284 (1972).

[33] G. Cartledge, R. L. Havill, and J. M. Titman, J. Phys. F. 6, 639 (1976).

[34] C. N. J. Wagner, in Ref. 17, p. 258.

[35] A. B. Bhatia, D. E. Thornton, and N. H. March, Phys. Chem. Liq. 4, 97 (1974).

[36] D. N. Lee and B. D. Lichter, in Ref. 17, p. 130.

[37] G. V. Samsonov, *Handbook of the Physicochemical Properties of the Elements* (Plenum, New York), p. 98.

[38] G. Cartledge, R. L. Havill, and J. M. Titman, Phys. Status Solidi 20, K131 (1973).

[39] F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry* (Interscience, New York, 1967), p. 103.

[40] W. Gordy and W. J. O. Thomas, J. Chem. Phys. 24, 439 (1956).

[41] F. D. Feiock and W. R. Johnson, Phys. Rev. 187, 37 (1969).

[42] E. Watson, A. C. Gossard, and Y. Yafet, Phys. Rev. 140, A 375 (1965).

[43] G. Cartledge, R. L. Havill, and J. M. Titman, J. Phys. F 3, 213 (1972).

[44] R. L. Havill, J. Marsden, and J. M. Titman, Phys. Status Solidi 80, K141 (1977).

[45] F. D. Richardson, *Physical Chemistry of Melts in Metallurgy* (Academic, London, 1974), p. 8.

[46] W. W. Warren, Jr., Phys. Rev. B 3, 3708 (1971).

[47] R. Brandenburg, B. Kokavecz, and K. D. Kramer, J. Phys. F 6, 1 (1977).

[48] P. Lamparter and S. Steeb, Z. Naturforsch. 32a, 1015 (1977).

[49] J. E. Enderby and D. M. North, Phys. Chem. Liq. 1, 1 (1968).

[50] N. W. Ashcroft and J. Lekner, Phys. Rev. 145, 83 (1966).

[51] T. E. Faber, *Introduction to the Theory of Liquid Metals* (Cambridge University, 1972), p. 131.

[52] R. Evans and W. Schirmacher, J. Phys. C (to be published).

[53] R. L. Havill, J. Marsden and J. M. Titman, J. Phys. F 7, 2357 (1977).

[54] J. Marsden, R. L. Havill, and J. M. Titman, J. Phys. F 8, 1321 (1978).

[55] N. H. March and M. P. Tosi, *Atomic Dynamics in Liquids* (MacMillan, London, 1976), p. 52.

[56] N. H. Nachtrieb, in *The Properties of Liquid Metals,* edited by S. Takeuchi (Taylor and Francis, London, 1973), p. 521.