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Study of nuclear-magnetic and nuclear-quadrupolar relaxation in liquid Ga^{69}

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Calculations have been made of the nuclear magnetic and nuclear quadrupolar relaxation rate in liquid Ga^{69} at three temperatures 20, 50, and 150 °C. The pseudopotential perturbation theory was used for the former, and the model of neutral ion core interacting with the screened long-range potential was chosen for the latter. While the magnetic relaxation time decreased from 2.350 to 1.650 msec, the corresponding quadrupolar relaxation time increased from 1.045 to 3.045 msec in the above temperature interval. These results compare well with some of the recent experimental measurements and have been interpreted in terms of the possible effects such as, the electron-electron correlation, thermal and diffusive motions of the ions. The origin of the quadrupolar relaxation rate may be attributed to the translational, diffusive motion rather than the vibrational motion of the ions.

I. INTRODUCTION

The experimental nuclear-spin relaxation rate (T_1^{-1}) in solid and liquid Ga has been investigated by a number of workers.[1-4] From these studies it has been concluded that for both solid and liquid Ga^{69} that the nuclear-spin relaxation rate depends markedly on two parts: one is the magnetic relaxation part (T_{1m}^{-1}) that arises from the magnetic hyperfine interaction between the nuclear spin and the conduction electrons, including the contribution due to the spin-polarized core electrons and the conduction electrons; the second one is the electrical relaxation part which is the quadrupolar relaxation (T_{1q}^{-1}) arising from the coupling between the nuclear electric quadrupole moment and the electric field gradient.

The early work summarized by Faber[1] for liquid Ga^{69} reveals that the quadrupolar relaxation time T_{1q} increases with temperature, and T_{1q} is larger than T_{1m}. As for example, $T_{1q}=1.9$ msec compared to $T_{1m}=0.7$ msec for Ga^{69} at 19 °C. Later on, Cornell[3] studied the temperature dependence of the two relaxation processes in liquid Ga by isotopic separation method (i.e., utilizing Ga^{69} and Ga^{71} isotopes whose quadrupole moments differ by a factor of 1.5893) supporting some of the earlier conclusions of Faber.[1] Briefly, for Ga^{69}, Cornell[3] found a linear relationship with temperature for both T_{1m}^{-1} and T_{1q}^{-1} between 19 and 200 °C. These results were re-examined by a subsequent work of Rossini and Knight[4] which produced further evidence of the relative importance of one relaxation process over the other, and indicated that the rate of increase of T_{1m}^{-1} with temperature was much faster than that of T_{1q}^{-1}. However, the recent experimental investigation by Cartledge *et al.*[5] shows that the magnitude of T_{1m}^{-1} is about 2.5 times as that of T_{1q}^{-1}. Furthermore, they noted that both T_{1m}^{-1} and T_{1q}^{-1} increase with temperature in the range 27–227 °C. This work, therefore, contradicts all of the previous works including the usually acceptable view about the origin of the quadrupolar relaxation mechanism, which is the translational, diffusive motion of the ions in the liquid state. Instead, they conjecture that in liquid Ga the origin of T_{1q}^{-1} should be the vibrational motion of the ions. Then there is another experimental report on liquid Ga by Riegel *et al.*[6] based entirely on a different experimental arrangement, i.e., angular correlation measurement, which supports the earlier results of Cornell[3] and Rossini and Knight.[4] The temperature range studied in this work was much more extensive, 40–1050 °C, and great care was taken in the process of experimental measurement.

On theoretical side, we have demonstrated in our earlier works[7-10] that the pseudopotential perturbation technique is adequate for the magnetic relaxation process. We worked out theories pertinent to local[7] and nonlocal[6] character of the pseudopotential; three main types of hyperfine properties such as, the Knight shift, nuclear-spin relaxation rate and core-polarization effect were explained. A large number of liquid metals were studied, but the application of the theory to liquid Ga is still open.

The general theory for quadrupolar interactions in solids has been reviewed by Das and Hahn[11] and Abragam[12] and, more recently, by Lucken.[13] However, for liquids or more specifically for liquid metals, the progress has been relatively limited. Borsa and Rigamonti[14] made an attempt to calculate T_{1q}^{-1} in a number of liquid metals utilizing the Coulomb potential with appropriate screening and ionic antishielding factor,[15] but neglecting the contribution of the conduction electron to the electric field gradient. The neglect of the latter effect may be questioned in the light of the experimental results obtained by Rossini *et al.*[16] and Rossini and Knight.[4] However, Sholl[17] has developed a theory applicable to both solid and liquid metal incorporating the above effect and choosing a more appropriate form of the potential, screened interatomic type. Although Sholl[17] has discussed the calculation for two cases, liquid In at 175 °C and Ga at 19 °C, his results showed some disagreement with respective experiments. A complete exploitation of the theory for the study of the temperature dependence of quadrupolar relaxation rate in liquid metals has not yet been done.

As is clear from the above, there are some conflicting reports on liquid Ga^{69} especially with regard to its nuclear-quadrupole-resonance (NQR) properties, its investigation should be worthwhile and interesting. The purpose of this paper is twofold. One is to investigate the temperature dependence of the total relaxation rate itself, and second is to test the various theories for liquid metals developed recently from a quantitative point of view. Metal Ga^{69} is chosen because it is believed for this metal the magnetic relaxation is as strong as the quadrupolar relaxation and, on the other hand, its experimental measurements are confusing and uncertain. One of the prime aims of the present work is to clarify the experimental results, establishing unambiguously its correct temperature dependence. We shall first calculate the magnetic-relaxation part using the pseudopotential perturbation technique,[8] and then explore the Sholl[17] theory to extract information about the quadrupolar-relaxation part. Finally, we will combine the two effects to compare the result so obtained with the available experimental data. Thus, this maneuvering will enable us to understand the importance of one process over the other, and point out which of the mechanisms is more susceptible to change of temperature. The outline of this paper will be as follows. In Secs. II and III we will briefly describe the relevant theories for the magnetic and quadrupolar part, respectively In Sec. IV we will discuss the results. In Sec. V we will present our discussions and conclusions.

II. NUCLEAR-MAGNETIC RELAXATION RATES

For consideration of the magnetic relaxation rates, we go back to the interaction between the nuclear spin and the conduction electron. There are several possibilities by which the magnetic relaxation will occur. The most important one is the usual Fermi contact interaction. For interacting Bloch s electrons, the Fermi contact relaxation rate can be written[18]

$$W_{1m,s} = T^{-1}_{1m,s} = \tfrac{64}{9}\pi^3\hbar^3\gamma_e^2\gamma_n^2 g^2(E_F)k_BT \times (N\Omega_0 O^2_{k_F}P_F)^2 , \tag{2.1}$$

where γ_e and γ_n are respectively, the electron and nuclear gyromagnetic ratios; $g(E_F)$ is the electronic density of states at the Fermi level; N is the number of ions in the given volume; Ω_0 is the ionic volume; $O^2_{k_F}$ is the core enhancement factor; and P_F is the pseudospin density. The above equation, however, can be expressed in terms of the contact Knight shift K_s,

$$W_{1m,s} = \frac{4\pi k_BT}{\hbar}\left(\frac{\gamma_n}{\gamma_e}\right)^2 K_s^2K(\alpha) . \tag{2.2}$$

The term $K(\alpha)$ represents a correction factor due to the effects of electron-electron correlation and exchange interaction. In most metals, solid and liquid (for example, nontransition metals), $K(\alpha) = 0.75$, but it should be $K(\alpha) = 1$ for noninteracting electrons as in the Korringa relation.

The second term of our present interest is the exchange interaction between the spin polarized core electrons and the conduction electrons. This is usually called the exchange core polarization (ECP). The ECP has been investigated for solid metals[19] by using exchange perturbation and moment perturbation techniques. From these studies it has been concluded that such a contribution to the Knight shift is particularly important for alkali metals. We have previously developed[9] a theory for ECP contribution for liquid metals and shown that in liquid Mg and perhaps in liquid Be, this contribution should be rather important. Utilizing the moment perturbed method as in the solid state, we found that the ECP relaxation rate contains the s, p, and d terms

$$W_{cp} = W_{cp}(s) + W_{cp}(p) + W_{cp}(d) . \tag{2.3}$$

If only the s term of the ECP contribution is retained, and the contact term is included in it since it also arises from the s electrons, it follows easily that

$$W_{cp,s} = \tfrac{64}{9}\pi^3\hbar^3\gamma_e^2\gamma_n^2 k_BTg^2(E_F)\Omega_0^2\mathcal{S} , \tag{2.4}$$

where

$$\mathcal{S} = (S_s + S_{cp})^2 . \tag{2.5}$$

S_l in the above equation are the respective spin densities.

The third contribution to the magnetic relaxation process comes from the orbital and dipolar fields of the conduction electrons through their non-s states. Two theories are available for this effect—one is by Obata[20] for the electrons in the tight binding approximation and the other by Mitchell[21] for the Bloch electrons. From the Obata[20] theory one obtains for both p and d electrons

$$W_0^O = \left(\frac{4\pi k_BT}{\hbar}\right)\left(g(E_F)\left\langle\frac{1}{\gamma^3}\right\rangle\right)^2(\gamma_e\gamma_n\hbar^2)^2A(p,d), \tag{2.6}$$

where the function $A(p,d)$ is a dimensionless quantity and it is equal to 1 for p electrons, but 5 for d electrons. The average reciprocal cube of the distance between the electron and the nucleus is

$$\left\langle \frac{1}{r^3} \right\rangle = \int r^{-3} f_1^2(r)\, r^2\, dr \Big/ \int f_1^2(r)\, r^2\, dr\,, \qquad (2.7)$$

where $f_1(r)$ is the radial wave function of the atomic p and d wavefunctions. On the other hand, the Mitchell[21] theory gives

$$W_0^{\mathrm{M}} = \left(\frac{65}{9}\right)\left(\frac{\pi Z^2 m^{*2} B^2}{\hbar}\right) \gamma_e^2 \gamma_n^2 k_B T, \qquad (2.8)$$

where

$$B = \int \frac{\langle |f_1(r)|^2 \rangle}{r}\, dr \qquad (2.9)$$

and Z is the number of p or d electrons per atom. While Rossini and Knight[4] used the Obata equation, Warren and Clark[22] preferred the Mitchell[21] equation. The argument provided by the latter was that for free or nearly free electrons, as might be expected in liquid metals, the Mitchell[21] theory should be more pertinent.

Besides the above three sources, there are several other, but much smaller, contributions which we shall not discuss here, since they are unimportant to the case of liquid Ga. Even the second and the third type of contributions just mentioned above, as we shall see later, might be easily dropped.

III. NUCLEAR-QUADRUPOLAR RELAXATION RATE

The quadrupolar effect is important in metals with spin $I > \frac{1}{2}$ and it originates, as stated before, from the interaction between the nuclear quadrupole moment and the electric field gradient. Metal Ga has $I = \frac{3}{2}$, and there is sufficient experimental evidence for this metal to warrant a calculation for the relaxation rate. It should, however, be noted that the nuclear-quadrupolar resonance shift is associated with solids only, as it averages out to zero for liquids due to rapid fluctuations and thermal motions of the ions.

There are two different mechanisms by which the electric field gradient at the nucleus (or the distortion of the nuclear charge distribution) will occur, leading to two types of quadrupolar relaxation rates. The first one is a thermal process which originates from the ionic motions due to translation, rotation, vibration, and diffusion. The second one is a scattering process directly resulting from the interaction between the nuclear charge and the conduction electrons. The latter is analogous to the magnetic relaxation process as mentioned in Sec. II.

We will first elaborate on the scattering-type field gradient. While there is some theoretical work for solids, there is no report of such work for liquids. For solids, the early theory by Mitchell[21] and the latter work by Obata[23] should be mentioned. For Bloch electrons, according to the Mitchell[21] theory, the quadrupolar relaxation rate is

$$W_{1q} = \frac{1}{50}\left(\frac{\pi e^4 Z^2 m^{*2}}{\hbar^5}\right) B^2 Q^2 f(I)\, k_B T\,, \qquad (3.1)$$

where B is the same as defined in Sec. II, Q is the quadrupole moment, and the function $f(I)$ is given by

$$f(I) = (2I+3)/[I^2(2I-1)]\,. \qquad (3.2)$$

This equation was arrived at by assuming the scattering of the conduction electrons at the Fermi surface and it is believed to be of any value when the thermal and diffusion processes are negligible as in the low-temperature limit. We then immediately see that this effect in liquid metals should be unimportant due to large kinetic energy associated with the conduction electrons.

To study the major term of the quadrupolar relaxation rate one has to consider two different quantities. The first one is to study the structural change, which can be quantitatively represented by the actual radial distribution function, and the second one is to include the temperature dependence of the self-diffusion constant. The initial theory of Borsa and Rigamonti[14] using the screened Coulomb potential is an attempt along this direction. The subsequent theory by Sholl[17] is an improvement over the previous theory because it incorporated the long-range effect of the conduction electrons. In this theory the interacting potential is a screened oscillatory potential of the form

$$v(r) \sim \cos(2k_F r)/(2k_F r)^3 \qquad (3.3)$$

and the positions of the ions are described by a three-body correlation function

$$\rho^3(r_0, r_2) = \rho^3 g(r_0) g(r_2) g(r_{02})\,, \qquad (3.4)$$

where ρ is the average density of the solid or liquid and g's are the pair probability functions which we will elaborate in the next section. We will briefly outline the Sholl[17] theory, here, because it forms the basis of our calculation for the quadrupolar relaxation rate.

The quadrupolar relaxation-rate expression is shown to be

$$W_{1q} = f(I)\left(\frac{A(1-\gamma_\infty)eQ}{\hbar}\right)^2 F(D)(I_1 + 2\pi\rho I_2), \qquad (3.5)$$

where $(1-\gamma_\infty)$ is the Sternheimer antishielding factor, and A is the potential parameter defined by

$$A = 2Z me^3/\pi \hbar^2 k_F^2 \epsilon^2(2k_F). \qquad (3.6)$$

Furthermore,

$$F(D) = \pi\rho/75\, D\,, \qquad (3.7)$$

where ϵ is the dielectric constant and D is coefficient of diffusion. The symbols I_1 and I_2 represent two integrals of the type

$$I_1 = \int_0^\infty f(r_0)\, G(r_0)\, dr_0 \tag{3.8}$$

and

$$I_2 = \int_0^\infty f(r_0)\, g(r_0) r_0^2\, dr_0 \int_0^\infty G(r_2)\, dr_2 \times \int_{-1}^{1} [g(r_{02}) - 1]\, P_2(Z)\, dZ, \tag{3.9}$$

where

$$f(r_0) = (2k_F)^2\, \frac{7(2k_F r_0)\sin(2k_F r_0) + [15 - (2k_F r_0)^2]\cos(2k_F r_0)}{(2k_F r_0)^5}\,, \tag{3.10}$$

and

$$G(r_0) = \frac{g^{1/2}(r_0)}{r_0}\left(\int_0^{r_0} f(r_1)\, g^{1/2}(r_1)\, r_1^4\, dr_1 + r_0^5 \int_{r_0}^\infty \frac{f(r_1)}{r_1}\, g^{1/2}(r_1)\, dr_1\right). \tag{3.11}$$

As can be seen from Eqs. (3.10) and (3.11) there are several symbols which need some further explanations. Here g's are the pair probability functions as before, $P_2(z)$ is the second-order Legendre polynomial and

$$r_{02}^2 = r_0^2 + r_2^2 - 2r_0 r_2 z\,, \tag{3.12}$$

in which z is the cosine of the angle between the position vectors $\vec{r}_0$ and $\vec{r}_2$. In the literature g's were used under the name of radial distribution function. Unfortunately, the three pair probability functions involved here are not known. We shall overcome this difficulty by making some approximation and defer any discussion on this until Sec. IV.

Now one may argue that the form of the function $f(r)$ depends on the form of the atomic potential as in Eq. (3.3), because by definition

$$f(r) = r\, \frac{d}{dr}\left(\frac{1}{r}\, \frac{dV(r)}{dr}\right). \tag{3.13}$$

A more exact selection of the potential, such as

$$V(x) = \sin x/x - \cos x/x^3\,, \tag{3.14}$$

where $x = (2k_F r)$, leads to a rather complicated form

$$f(r) = [(24 - x^2)\cos x + 8x \sin x]/x^5 - 24 \sin x/x^6. \tag{3.15}$$

We have utilized both the Eqs. (3.10) and (3.15) for computation, but found very little difference in the final results. Because of the asymptotic nature of the potential and because the pair probability function $g(r)$ is zero in the region of small r, which we shall see later in Sec. IV C, the small difference that is observed does not noticeably change the values of integrals I_1 and I_2. Unfortunately, however, in Sholl's original paper[17] Eq. (3.10) is in error [see, for example, Ref. 17, Eqs. (3.6) and (4.27)], which is quite serious. This error can produce some unrealistic and misleading conclusions.

We clearly see that the above integrals are not simple, but nonetheless their numerical evaluation is possible. It is one of the major points in this investigation to evaluate these integrals for the first time as exactly as feasible within the limits of high-speed computers. For the sake of convenience and to bring $f(r)$ in line with the actual potential derivatives, we rewrite our Eq. (3.5) as

$$W_{1q} = f(I)\,[(1 - \gamma_\infty)\, e\, Q/\hbar]^2\, F(D)(I_1 + 2\pi\rho I_2)\,, \tag{3.16}$$

where

$$f(r_0) = A(2k_F)^2\, \frac{7(2k_F r_0)\sin(2k_F r_0) + [15 - (2k_F r_0)^2]\cos(2k_F r_0)}{(2k_F r_0)^5} \tag{3.17}$$

Introduction of A, as in Eq. (3.17), will change the value of $G(r)$ in Eq. (3.11) and, therefore, the quantity $(I_1 + 2\pi\rho I_2)$. In this respect, our results will differ from those of Sholl as will be seen later in Sec. IV C.

IV. RESULTS AND DISCUSSIONS

A. Knight-shift calculation

In order to study the temperature dependence of the magnetic relaxation rate, we have first evaluated the pseudospin density P_F as a function of temperature. We used the local pseudopotential of the Animalu and Heine type[24] and the experimental interference functions of Narten[25] for Ga at 20 °C, and

TABLE I. Input NMR data for Ga^{69}.

Temp. (°C)	k_F (a.u.)	Ω (a.u.)^3	χ_s (cgs vol units)	$O^2_{k_F}$	N_{k_F}	P_F
20	0.8863	127.59	1.2×10^{-6}	331.54	0.9163	0.7795
50	0.8844	128.42	1.19	331.98	0.9169	0.7782
150	0.8807	130.03	1.19	332.81	0.9189	0.7708

of Ascarelli[26] for Ga at 50 and 150 °C. These data are believed to be reliable and have been found to yield[27] good results in the study of other electronic properties of liquid Ga.

We have directly used the interference functions $I(q)$ to obtain our results. The appropriate theoretical steps and procedure are described in our previous publications.[7,8] Two more quantities are needed before we can get to T_{1m}. One is the Pauli-spin paramagnetic susceptibility χ_s and the other the core enhancement factor O^2_{kF}. In absence of the exact value for χ_s, we have introduced the free-electron value, which is related to the corrected value by the relation

$$\chi_s = \chi_s^{\text{free}}(m^*/m)\ \eta_s\,, \qquad (4.1)$$

where the factor m^*/m comes from the crystal potential and the factor η_s comes from the electron-electron interaction. For the calculation of O^2_{kF} we needed to carry out the algebra

$$O^2_{k_F} = \frac{1}{N_{k_F}}\left(1 - \sum_{ns} b_{ns}(\vec{k}_F)\Theta_{ns}(0)\right)^2 \qquad (4.2)$$

where N_{k_F} is the normalization constant, $\Theta_{ns}(0)$ represents the core function ns at the origin, and the function b_{ns} is the orthogonalization parameter defined by

$$b_{ns}(\vec{k}) = \langle\Theta_{ns}(\vec{r})\,|\,e^{i\vec{k}\cdot\vec{r}}\rangle\ . \qquad (4.3)$$

Under some simple approximation that b_{ns} is a slowly varying function of k over the atomic core, we evaluated the above summation utilizing the Mann core wave functions. As pointed out previously,[10] if one were to use the wave functions of the Herman-Skillman type, the core enhancement factors would be a little different.

Tables I and II show our results for liquid Ga^{69} for contact shifts. The Knight shifts decrease from $K_s = 0.259\%$ at 20 °C to $K_s = 0.256\%$ at 150 °C. The change is very small, but in agreement with the experimental trend of the plot published by Cornell.[3] However, quantitatively there is substantial disagreement in that the experimental results range from 0.449 to 0.445% in the above temperature interval. As has been noted in the investigation of other liquid metals there could be several reasons for such a disagreement. The contributions to Knight shift from other sources such as, core polarization, orbital, and dipolar fields are not included here. These calculations are rather complicated and are of secondary importance to the present investigation. Consequently, we should fall back to the primary causes; we may then attribute the disagreement to the neglect of electron-electron interaction, the uncertainty in the calculated local pseudopotential and perhaps to some extent, the errors in the measurement of the interference functions. We will elaborate on these points in the following discussion.

B. Magnetic-relaxation part

We see from Table II that the calculated T_{1m} decreases from 2.35 msec at 20 °C to 1.65 msec at 150 °C, but the corresponding experimental values fall from 1.034 to 0.716 msec. Experimentally, for the magnetic relaxation, Cornell[3] suggested a linear relationship with temperature

$$T_{1m}^{-1} = 3.3\,T\ . \qquad (4.4)$$

In the present study it turns out that

$$T_{1m}^{-1} = 1.443\,T\ . \qquad (4.5)$$

As is clear, numerically there is a difference between the experimental and the calculated T_{1m},

TABLE II. NMR results for Ga^{69}. Units are K_s in %, T_{1m} in msec, and W_{1m} in (msec)$^{-1}$.

Temp. (° C)	Calc. K_s	Calc. T_{1m}	Calc. W_{1m}	Expt. K_s	Expt. T_{1m}	Expt. W_{1m}
20	.259	2.35	0.426	0.449	1.034	0.967
50	.257	2.14	0.467	0.448	0.938	1.066
150	.256	1.65	0.606	0.445	0.716	1.397

TABLE III. Input NQR data for Ga^{69}.

Z	I	Q (b)	Q_E (kcal/ mole)	D_0 (cm^2 sec^{-1})	γ_∞	Å (dyn$^{1/2}$)
3	3/2	0.180	1.12	1.1×10^{-4}	-10.5	0.1205

but the temperature dependence is in agreement for the temperature range under consideration.

Let us now attempt to analyze the present results in the light of the existing theoretical arguments. We shall now consider the various exchange enhancement factors. The uniform exchange enhancement factors η_s can be obtained empirically as well as theoretically. In the present investigation we obtained the empirical value by a curve fitting procedure, or more conveniently from the ratio of the two Knight shifts near the melting temperature, i.e.,

$$\eta_s^{\text{emp}} = K_s^{\text{expt}}/K_s^{\text{theo}} = 1.73 \, . \qquad (4.6)$$

The appropriate values of K_s are shown in Table II, in which the experimental K_s are taken from Cornell.[3] We then compare this ratio with the corresponding theoretical value which can be calculated from the two values of the Pauli-spin paramagnetic susceptibility. One is the usual free electron susceptibility χ_s^{free} and the other is the uniform susceptibility $\chi_s(q=0,\ \omega=0)=\chi_s^{\text{band}}$ obtained from computation as in Silverstein.[28] Therefore,

$$\eta_s^{\text{theo}} = \chi_s^{\text{free}}/\chi_s^{\text{band}} = 1.26. \qquad (4.7)$$

These η_s are not expected to change with temperature. However, some difference may occur between these two values, since the number in Eq. (4.6) was derived from the K_s data, whereas that in Eq. (4.7) was obtained from the susceptibility data. In a similar manner we may also find the values of the nonuniform exchange enhancement factors η_m from the relaxation rates. The empirical value, in this case, is the ratio between the two relaxation rates near the melting temperature

$$\eta_m^{\text{emp}} = (T_{1m}^{\text{expt}}T)^{-1}/(T_{1m}^{\text{theo}}T)^{-1} = 2.30. \qquad (4.8)$$

The pertinent relaxation rates are also given in Table II. To find the theoretical value of η_m, we use the corrected Moriya[29] theory as suggested by Narath and Weaver.[30] However, our method of calculation is the same as in our previous publications.[7,8] This value is then

$$\eta_m^{\text{theo}} = 2.45. \qquad (4.9)$$

Despite the fact that there are various complexities in the problem and the approximations involved in their consideration, the agreement between the two η_s and that between the two η_m are quite good.

C. Structural and thermodynamic functions

The input data for the evaluation of the quadrupolar relaxation are shown in Table III. In this case we took the interference functions and Fourier transformed them to obtain the pair probability function

$$g(r) = 1 + \frac{1}{2\pi^2 \rho r} \int_0^\infty q\,[I(q)-1]\sin qr\, dq \qquad (4.10)$$

We have no way of ascertaining[31] the individual pair probability functions $g(r_0)$, $g(r_2)$, and $g(r_{02})$. Since we intend to deal with the time average quantity $g(r)$ of these functions, the average value to be obtained from any good x-ray experiment would be adequate approximation. The behavior of such functions is described in Figs. 1(a) and 1(b). The effect of temperature on $g(r)$ is distinctly visible in Fig. 1(b). The first peak height falls with temperature accompanied by some slight increase in the value of the first nearing neighbor distance. In the long-wavelength limit, of course, the oscillations in $g(r)$ gradually diminish and the curve approaches unity within a few atomic diameters.

The potential function $f(r)$ is plotted in Fig. 2. It should be noted that the function $f(r)$ has been multiplied by the constant A as in Eq. (3.6) for the sake of convenience. The function $f(r)$ is infinitely sharp in the region of small r, but it has a strong peak at $r = 2.5$ Å. Above $r = 10$ Å this function practically merges with zero. However, the critical region which contributes most to the quadrupolar relaxation for Ga is found to be $2.5 < r < 5$ Å. The function $g(r)$ becomes zero below $r = 2.5$ Å and so the meaning of the function $f(r)$ in this region becomes irrelevant. The function $G(r)$ can now be obtained from Eq. (3.11). A typical plot of $G(r)$ for Ga at 20 °C is shown in Fig. 3. This is a slowly varying function whose behavior is determined by the nature of the function $f(r)$. The limits of the integrals in Eq. (3.11) were critically defined by the modulations and the extent of the functions $f(r)$ and $g(r)$. In our study the upper limit of the second integral was found to be satisfactory at $r_0 \geq 50$ Å. These integrals were evaluated with sufficient accuracy by the usual Simpson rule with an error control.

The value of the integral I_1 in Eq. (3.8) then followed from the above two functions $f(r)$ and $G(r)$. In this case we tried several upper limits for the

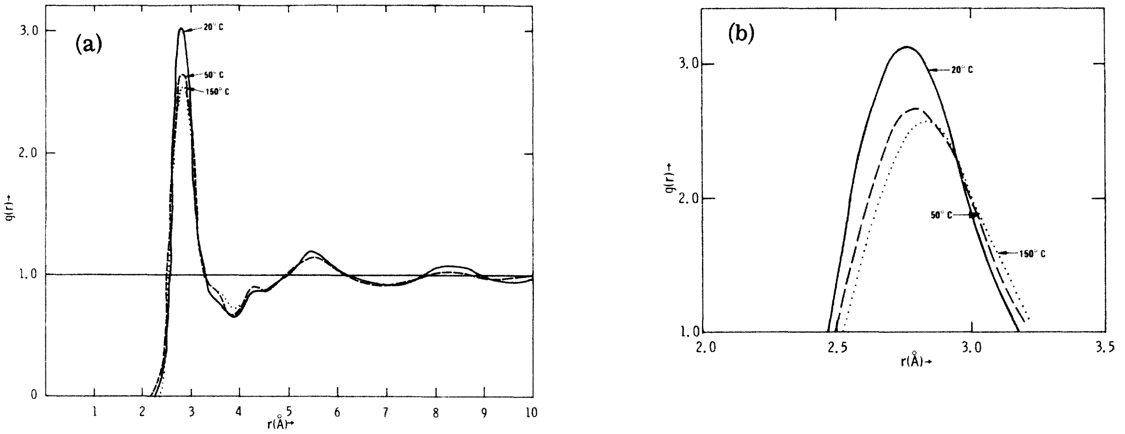

FIG. 1. (a) Plots of pair-probability function $g(r)$ for liquid Ga at three different temperatures. (b) Plots of the first peak maximum of $g(r)$ showing marked changes with temperature.

integration and finally stopped when no change was observed in the integral after adding some further increment to the previous value of the limit. However, I_2 in Eq. (3.9) was more time consuming and it needed additional precautions. The third integral in Eq. (3.9) was analytically carried out. Essentially, we expressed this integral as

$$\int_{-1}^{1}[g(r)-1]\,P_2(z)\,dz$$

$$=\frac{1}{4r_0^3r_2^3}\left[(3a^2-b^2)F_1-6aF_3+3F_5\right], \qquad (4.11)$$

where

$$a=r_0^2+r_2^2, \quad b=2r_0r_2 \,,$$

and

$$F_l=\int_{|r_0-r_2|}^{r_0+r_2}[g(r)-1]\,r^l\,dr. \qquad (4.12)$$

Table IV lists the results of these calculations. It should be noted that both the values of I_1 and I_2 decrease with temperature. As these results suggest, $(2\pi\rho I_2)$ is not negligible compared to I_1. It is about the same order of magnitude as I_1, and I_2 has the same sign as I_1. The self-diffusion coefficient D in liquid metals is a strong function of temperature.[32] It has been measured[33] for liquid Ga. Although there are some questions as to the exact nature of the temperature dependence, the relation

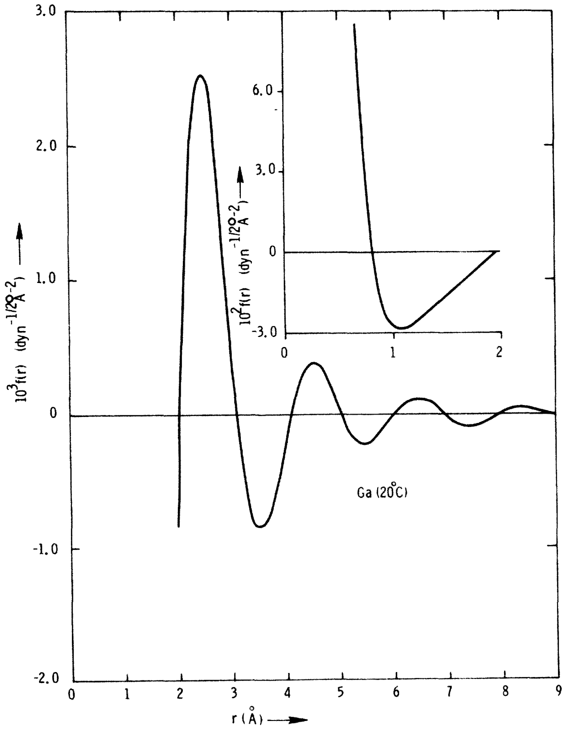

FIG. 2. Plot of the potential function $f(r)$ for Ga at 20 °C as defined in Eq. (3.17).

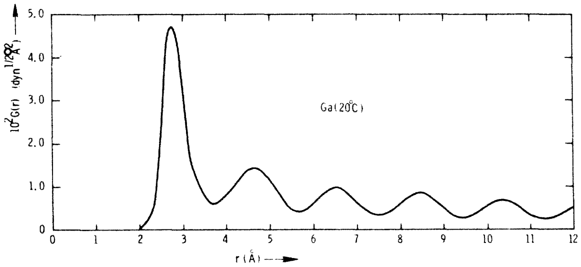

FIG. 3. Plot of the function $G(r)$ for Ga at 20 °C. The function $f(r)$ in Fig. 2 was used to compute this function.

$$D = D_0 e^{-Q_E/RT} \tag{4.13}$$

is fairly satisfactory to the majority of liquid metals. In the above equation D_0 is a constant of the diffusion equation not affected by temperature, Q_E is the activation energy, and R is the universal gas constant. All these quantities are displayed in Tables III and IV.

The evaluation of the integrals both in the magnetic part and quadrupolar part was accomplished with sufficient accuracy within less than 1% error. While it is not quite clear from the paper by Sholl,[17] and also from the subsequent paper by Titman and Jolly,[34] how these calculations were made, our results for I_1 and I_2 are sufficiently detailed. Sholl[17] used the data of radial distribution function (RDF) measured by Orton,[35] but we selected the latest data of Narten[25] and Ascarelli.[26] From the present study we are convinced that the position r_1 of the first peak maximum in $g(r)$ in Fig. 1(b), which is equivalent to the average interatomic spacing, is very critical. A slight shift in r_1 would change the value of I_1 and I_2 quite drastically. As for example, we have estimated that a 2% error in r_1 would give about 15% error in I_1 and about 41% error in I_2 at 20 °C. Obviously, I_2 is more sensitive to the position r_1 than I_1. Again, we know that r_1 changes slightly with temperature. One must, therefore, exercise great caution in selecting these RDF, determining their first peak position, and computing the above integrals. The asymptotic form of the potential function $f(r)$ in the small r limit does not pose any problem, because all other functions, such as, $g(r)$ and $G(r)$ are zero in this region. On the other hand, the oscillatory nature of $f(r)$ is in agreement with the predicted short-range interatomic interaction.

D. Quadrupolar-relaxation part

The calculated temperature relaxation time T_{1q} are shown in Table IV along with the experimentally estimated values. From these results two important conclusions can be drawn: first is that the magnitude of the calculated T_{1q} is of right order, and second is that it increases with temperature. The latter is very significant because it is opposite to what is observed in the case of the magnetic relaxation time T_{1m}. The total relaxation time

$$1/T_1 = 1/T_{1m} + 1/T_{1q} \tag{4.14}$$

therefore, depends on the competition between these two terms, provided all other contributions are trivial as in the case of Ga. At any rate this effect may create a situation in some liquid metals where the increase in T_{1m} may be neutralized by the equivalent decrease in T_{1q} resulting in nonobservable change in the total relaxation time T_1. The temperature dependence of T_{1q} is not solely governed by the temperature dependence of the self-diffusion coefficient D as has been previously thought to be the case. The tendency of D is to increase T_{1q}, but that of $g(r)$ is to decrease T_{1q} with temperature. D being a relatively stronger function than $g(r)$, the over-all picture emerges out in favor of D. If we were to neglect the temperature dependence of $g(r)$ as noticed in Fig. 1(b), the presently calculated results would become out of proportion and large error would be introduced into the relaxation time. Titman and Jolly,[34] and Jolly and Titman[36] have recently criticized the Sholl[17] theory on the ground that this theory overestimates the quadrupolar relaxation rate due to ionic motion. However, they emphaized the importance of the three-particle or two-particle (pair) probability functions. Furthermore, they argued that the first Sholl integral I_1 is rather large and it represents the sum of the effects of all the ions. Since the liquid metal, to a good approximation, is spherically symmetric, there should be some cancellation of the various electric field gradients of the ions. They suggested that this sort of cancellation would make the translational, diffusive contribution to W_{1q} totally unimportant. Therefore, the vibrational mode of the ions would be important and it would take over the translational mode to guide the effective temperature dependence of W_{1q}. To the knowledge of this author, this conclusion is based on the preliminary work reported by Sholl.[17] There are no extensive data either on I_1 or I_2 on any metal prior to the present study. Our careful investigation, however, shows that I_2 is not negligible and it is positive rather than negative. Therefore, the question of cancellation of the elec-

TABLE IV. NQR results for Ga^{69}. The integrals I_1 and I_2 contain the factor A^2 through the function $f(r)$ as in Eq. (3.17).

Temp. (°C)	D ($cm^2\ sec^{-1}$)	I_1 (Å dyn)	$(2\pi\rho I_2)$ (Å dyn)	Calc. T_{1q} (msec)	Calc. W_{1q} $(msec)^{-1}$	Expt. T_{1q} (msec)	Expt. W_{1q} $(msec)^{-1}$
20	1.60×10^{-5}	0.3931×10^{-4}	0.5904×10^{-4}	1.045	0.9566	1.656	0.604
50	1.92	0.3260	0.4128	1.678	0.5957	1.712	0.584
150	2.90	0.2880	0.3358	3.045	0.3284	1.934	0.517

tric field gradient due to the angular correlation part of the ions does not seem to arise. We might then like to suggest some explanations for the observed negative I_2 in Ref. 17. While it is difficult to find the correct answer to the above question, our experience indicates that the inadvertent error, as pointed out earlier, in Eq. (3.6) of Ref. 17 coupled with probably an inadequate determination of the difficult integrations, might give such an erroneous sign. It is found that the magnitude and sign of I_2 are very sensitive to the function $f(r)$ and $G(r)$ which are essentially derived from the potential $V(r)$ and the pair probability function $g(r)$.

The relaxation rates calculated here seem to agree reasonably well with experimental results of Cornell[3] and Riegel *et al.*,[6] but disagree with those reported by Cartledge *et al.*[5] The relation between the atomic structure and the two relaxation processes are reasonably well described by the x-ray interference functions or the pair probability functions. Three-body probability functions are not known and, perhaps, it is impossible to measure them experimentally. The pair probability functions are sufficient as evidenced from the present calculation. Exact temperature dependence of the pair-probability function is hard to predict analytically, nonetheless that of the self diffusion is somewhat stronger and it goes as in Eq. (4.3). Claridge *et al.*[37] have recently extended the Sholl[17] theory to the case of liquid alloys. Again, for lack of structural data, no firm conclusion could be reached as to the nature of the origin of the quadrupolar relaxation in liquid alloys. Most likely, as in the pure liquid metal case, the chief source of the quadrupolar relaxation in liquid alloys could be the self-diffusion mechanism. Certainly, these sort of studies are very complicated and must, therefore, be done with great caution under the present limitations of the theory and experiment.

It appears from the above that the present theory of neutral ion core situated in a screened oscillatory potential works for the case of Ga^{69} and it should be enthusiastically pursued further. In view of this, one might be tempted to extract relevant informations about the origin of the quadrupolar relaxation, such as, whether it is due to translational, or vibrational, or quadrupolar hyperfine coupling to conduction electrons, or some combination of these.

V. CONCLUSIONS

The temperature dependence of the nuclear-magnetic relaxation and the nuclear-quadrupolar relaxation rate for liquid-metal Ga^{69} have been investigated. To calculate the magnetic part, we have used the pseudopotential perturbation technique to first order to obtain the spin density at the nucleus. However, for the quadrupolar part we used the recent theory proposed by Sholl.[17] These calculations are meant to be more exact and quantitative than the results hitherto published.

The results of our investigation at three temperatures are found to be in good agreement with the experimental measurements of Cornell.[3] The significance and importance of these results follow: (i) T_{1m} arises mostly from the hyperfine contact interaction between the nuclear spin and the conduction electron, and the potentially significant T_{1q} arises from the coupling between the nuclear quadrupolar moment and the electric field gradient brought about by the structural change and diffusive motion of the ions. (ii) The magnitude of T_{1m} is about the same order of magnitude as T_{1q} near the melting temperature. (iii) While T_{1m} decreases with temperature, T_{1q} increases with temperature.

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