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Nuclear Spin-Lattice Relaxation in Liquid Nontransition Metals*

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We develop a broad interpretation for nuclear spin-lattice relaxation in liquid nontransition metals using our new data for Bi^{209} and previously reported data for $Ga^{69,71}$, $Rb^{85,87}$, $Sb^{121,123}$, Na^{23}, and In^{115}. Our work provides new insight into the relative importance of the various contributions to the NMR shift K and the nuclear spin-lattice relaxation rate R_1. The three potentially significant contributions to K are the hyperfine contact K_s, hyperfine orbital K_o, and core polarization K_{cp}. All other contributions to K are negligible. The sum of K_o and K_{cp} is small compared to K_s even in heavy elements. The first significant contribution to R_1 is the hyperfine contact rate R_{1s}, expressed by the Korringa relation, with $K(\alpha)$, the correction factor for electron-electron interactions, having a reasonable value of about 0.75 for all metals in our study. The second and last non-negligible contribution to R_1 is the nuclear quadrupole rate R_{1q} arising from the effect of ionic motion on the conduction electrons, whose magnitude decreases with an increase in temperature.

I. INTRODUCTION

In this paper, we develop a broad interpretation of nuclear spin-lattice relaxation in liquid nontransition metals based on recent experimental work. We discuss relevant contributions, both electric and magnetic, to the nuclear spin-lattice relaxation rate R_1, assess their importance, and treat their temperature dependence. A similar treatment of the contributions to the NMR shift K, provides a means of understanding the magnetic contributions to R_1. We analyze data for the isotopic pairs $Ga^{69,71}$, $Rb^{85,87}$, and $Sb^{121,123}$ and for the single isotopes Na^{23}, In^{115}, and Bi^{209}. The sources of data are shown in Table I.[1–9]

II. CONTRIBUTIONS TO R_1 AND K

A. Contributions to K

We expect the contact part K_s, which is always positive, to be the most significant contribution to the NMR shift.[10] The orbital contribution K_o, which may be positive or negative,[11] can be written in approximate form as[12]

$$K_o \approx 2\chi_o \langle 1/r^3 \rangle V_a , \tag{1}$$

with χ_o the orbital susceptibility and V_a the atomic volume. If we assume as a first approximation that $\chi_o \approx \chi_{p\ \text{free el}}$ and use the atomic values of $\langle 1/r^3 \rangle$ from the compilation of Barnes and Smith,[13] we find that K_o may be an appreciable fraction of K_s especially in Sb and Bi.

Core polarization may also contribute to K, but this contribution cannot be readily estimated in general. Calculations in some light metals give $|K_{cp}| \approx |0.1K_s|$.[14–16] The shifts due to the polarization of the core states by s, p, etc., electrons are calculated independently, and there may be cancellation among these terms. K_{cp} may be positive or negative.[11]

Any dipolar contribution to K must be averaged over all nuclear orientations and is therefore zero in the

Table I. Sources of R_1 and K data.

Element	R_1	K
Ga	D. A. Cornell[a] M. Hanabusa and N. Bloembergen[b]	D. A. Cornell[a]
Rb	D. F. Holcomb and R. E. Norberg[c]	B. R. McGarvey and H. S. Gutowsky[d,e]
Sb	W. W. Warren and W. G. Clark[f]	W. W. Warren and W. G. Clark[f]
Na	D. F. Holcomb and R. E. Norberg[c] M. Hanabusa and N. Bloembergen[b]	B. R. McGarvey and H. S. Gutowsky[d,e]
In	F. A. Rossini, *et al.*[g] W. W. Warren and W. G. Clark[f] G. Bonera, F. Borsa and A. Rigamonti[i]	W. W. Warren and W. G. Clark[f] F. A. Rossini[h]
Bi	F. A. Rossini[h]	F. A. Rossini[h]

[a] Reference 1. [d] Reference 4. [g] Reference 7.
[b] Reference 2. [e] Reference 5. [h] Reference 8.
[c] Reference 3. [f] Reference 6. [i] Reference 9.

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liquid.[17] The Landau diamagnetic contribution to K[18] turns out to be insignificant for these metals when the free-electron approximation, an appropriate first approximation for liquid metals, is used.

We divide K into two parts

$$K=K_s+K', \tag{2}$$

where K' is composed of K_o and K_{cp} which cannot be distinguished experimentally.

The temperature dependence of K is sufficiently small that its effect on R_1 is no greater than the experimental error in R_1 and it is therefore neglected.

B. Magnetic Contributions to R_1

The principal magnetic contribution to R_1 derives from the contact interaction. An expression for this rate for noninteracting electrons was derived by Korringa.[19] Electron-electron corrections were made by Pines[20] and Silverstein.[21,22] A more complete model for these corrections was proposed by Moriya[23] and corrected and extended by Narath and Weaver[24] who use the following expression for R_{1s}:

$$R_{1s}=(4\pi k_BT/\hbar)K_s^2(\gamma_n/\gamma_e)^2K(\alpha), \tag{3}$$

in which $K(\alpha)$, the electron-electron correction factor, is necessarily less than or equal to 1.00.

Mitchell[25] has calculated the orbital relaxation rate for Bloch electrons and Obata[26] for electrons in solid cubic metals in the tight binding approximation. Both results give the same order of magnitude. We will use Obata's more tractable expression for p-like conduction electrons in our estimates

$$R_{1o}\approx(4\pi/\hbar)(\gamma_e\gamma_n\hbar^2)^2k_BT\rho^2(E_f)\langle 1/r^3\rangle. \tag{4}$$

We use the atomic $\langle 1/r^3\rangle$ and the free electron $\rho(E_f)$. R_{1o} is then within the experimental error for Bi, where it should be the largest. The spin-dipole rate turns out from Obata's work to be 0.3 R_{1o} and hence is also insignificant in the present treatment.

For a metal with p-like conduction electrons the expression for core polarization relaxation is [27]

$$R_{1cp}=(4\pi k_BT/3\hbar)(\gamma_n/\gamma_e)^2K_{cp}^2. \tag{5}$$

The temperature dependence of K_{cp} has never been calculated. We do not know K_{cp} directly for any of our metals, but if $|K_{cp}|\approx|0.25K_s|$, $R_{1cp}\approx 0.02R_{1s}$ or smaller than the typical experimental error. We will therefore neglect R_{1cp} and see this neglect justified as we continue.

The dipole-dipole,[28] pseudodipolar[29] and indirect exchange[30] interactions are motionally narrowed[28,29] in the liquid. Using the expression[31] $R_1\approx(\delta\omega)^2\tau_c$ with $\tau_c\approx 10^{-13}$ sec,[7] we find these contributions to be much less than 1 cps.

C. Electric Quadrupole Contributions to R_1

The work of Cornell[1] and Warren and Clark[6] have shown that for metals with $I>\frac{1}{2}$ there is a significant relaxation rate which is directly attributable to the electric quadrupole interaction.

The general expression for quadrupole relaxation in a liquid due to atomic motion is[32]

$$R_{1q}=\frac{3}{80}\frac{2I+3}{I^2(2I-1)}\left(\frac{e^2Q}{\hbar}\right)^2J(0), \tag{6}$$

where J is the spectral density of the correlation function.

Using the correlation time approximation, $J(0)\propto q^2\tau_c$, Rossini *et al.*[7] estimated q, the electric field gradient (efg), for liquid indium. They found that q had its largest contribution from the effect of ionic motion on the p-conduction electrons which were assumed to bond covalently. They obtained the correlation time τ_c from the expression for jump diffusion, $D=\langle r^2\rangle_{\mathrm{av}}/6\tau_c$. This model is crude but nevertheless physically plausible.

Borsa and Rigamonti[33] calculated R_{1q} in a number of liquid metals using a screened Coulomb potential. This calculation neglected the conduction-electron contributions to the efg which Rossini *et al.* found so important. Borsa and Rigamonti used the ionic antishielding factor [34]$(1-\gamma_\infty)$ to account for the effect of the ions on the core electrons.

In a more basic calculation of R_{1q} for liquid In and Ga, Sholl[35] used the spectral-density formalism and included conduction-electron effects. He used the asymptotic form of a screened interatomic potential of amplitude A

$$V(r)\rightarrow\cos 2k_Fr/(2k_Fr)^3 \tag{7}$$

to calculate $J(0)$, which he multiplied by the anti-

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shielding factor for an almost neutral ion, $(1-\gamma_\infty)_{\rm an}$. He calculated $A(1-\gamma_\infty)_{\rm an}$ by using the potential to calculate the efg in the solid by a lattice sum which came out $q=Aq_0(1-\gamma_\infty)_{\rm an}$, where $(1-\gamma_\infty)_{\rm an}$ appears as an enhancement factor to the purely ionic field gradient Aq_0. He compared his q with the measured quadrupole coupling in the solid, e^2qQ/h. Since q_0 is a number, a numerical value of $AQ(1-\gamma_\infty)_{\rm an}$ may be derived. The value of A may be calculated if the unscreened potential is assumed to be Coulomb-like. Thus, with Q known, the value of $(1-\gamma_\infty)_{\rm an}$ may be obtained.

Sholl's result for R_{1q} is

$$R_{1q}=\frac{2I+3}{I^2(2I-1)}\left[\frac{A(1-\gamma_\infty)_{\rm an}Q}{h}\right]^2\frac{\pi\rho I_1}{75D}, \tag{8}$$

where ρ is the number of atoms per unit volume. I_1 is given by

$$I_1=\int_0^\infty f(r_0)G(r_0)dr_0, \tag{9}$$

where $f(r_0)$ is defined by

$$f(r_0)=\frac{1}{A}r\frac{d}{dr}\left[\frac{1}{r}\frac{dV(r)}{dr}\right]\bigg|_{r=r0}=(2k_F)^2\frac{7(2k_Fr_0)^2\sin(2k_Fr_0)+[15-(2k_Fr_0)^2]\cos(2k_Fr_0)}{(2k_Fr_0)^5}, \tag{10}$$

and $G(r_0)$ is

$$G(r_0)=\frac{g^{\frac{1}{2}}(r_0)}{r_0}\left[\int_0^{r0} f(r_1)g^{\frac{1}{2}}(r_1)r_1{}^4dr_1+r_0{}^5\int_{r0}^\infty\frac{f(r_1)}{r_1}g^{\frac{1}{2}}(r_1)dr_1,\right. \tag{11}$$

with the g the x-ray radial distribution function (rdf).

The temperature dependence of Eq. (8) arises from ρ, I_1, and D. The density ρ varies typically a few percent over a wide temperature range. I_1 depends on $g(r)$ and k_F which are only slightly temperature-dependent. The diffusion coefficient D for a liquid metal typically varies with temperature as $e^{-(1500°{\rm K})/T}$ which is much stronger than any of the other temperature-dependent quantities in Eq. (8). Thus, our estimates for R_{1q} from Sholl's expression will vary in temperature approximately as D.

Physically, Sholl's model and the simpler model of Rossini *et al.* can account for the most significant part of the efg as arising from the conduction electrons near the nucleus due to ionic motion. Sholl calculates the efg at the nucleus due to ionic motion and then includes the effect of the conduction electrons as a screening cloud sensitive to ionic motion. Rossini *et al.* begin with the free atom and then add the effect of the other atoms by treating the p-conduction electrons as directional covalent bonds sensitive to ionic motion. As is to be expected the two models give comparable results with R_{1q} contributing a significant part of the observed R_1.

Another mechanism for quadrupole relaxation is the scattering of conduction electrons at the Fermi surface similar to the magnetic hyperfine interaction. Such calculations have been made by Mitchell[36] for Bloch electrons and by Obata[37] for electrons in the tight binding approximation. Hanabusa[17] has expressed the Mitchell result as

$$R_{1q'}=\frac{9\pi}{50}\frac{m^2}{\hbar^5}\frac{2I+1}{I^2(2I-1)}\frac{e^4Q^2}{k_F{}^4}\left\langle\frac{1}{r^3}\right\rangle^2k_BT. \tag{12}$$

Although it has no where been considered previously, the appropriate antishielding factor for $R_{1q'}$ should be the conduction-electron antishielding factor $(1-R_Q)$[38,39] and not $(1-\gamma_\infty)$. The former quantity is approximately unity for the metals under consideration.[38,39] As calculated from Eq. (12) $R_{1q'}$ is much less than 1% of the experimentally known quadrupole coupling in Ga and Sb. It is also very small in the other cases of interest.

Thus, R_1 may be divided in two significant parts,

$$R_1=R_{1s}+R_{1q}, \tag{13}$$

where in the cases of interest to us the other magnetic and quadrupole contributions are negligible.

III. ANALYSIS

For elements with two magnetic isotopes, we may uniquely solve for the magnetic and quadrupolar rates by using two simultaneous equations for R_1. Since this is not possible for elements with one magnetic isotope, we will study them later in the light of what we learned from the isotopic pairs.

Before we turn to the data, three points should be noted. First, Narath and Weaver[24] find $K(\alpha)$ to be nearly the same for all of the solid alkali metals. Since these are the most free-electron-like of solid metals and furthermore since all liquid metals are nearly free-electron-like,[40] we assume that $K(\alpha)$ does not differ greatly among liquid metals. This assumption is in fact validated by the experimental results. The parameters in the calculation for $K(\alpha)$ have a temperature dependence which is insignificant. In the separation of R_{1s} and R_{1q} from the experimental R_1 for elements of

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two magnetic isotopes, the percentage error in $K(\alpha)$ turns out to be about twice the percentage error in R_1 making difficult a check on possible temperature dependence. Second, the limited information available on K_o and K_{cp} indicates that in general they should not be as large as K_s. Because of cancellation, K' might be smaller in absolute value than either of its components. Third, the only quadrupole relaxation mechanism of sufficient size to cause the observed rate is that due to the effects of ionic motion on the conduction electrons. Theory predicts a decreasing temperature dependence for this rate. Theoretical estimates for R_{1q} are not known precisely as will be seen because of the difficulty in applying the complicated Sholl formalism to specific cases.

We now estmiate R_{1q} from the Sholl formalism. The nuclear-moment values used in our estimates are taken from the compilation of Fuller and Cohen.[41] Densities are from the *Liquid Metals Handbook*.[42] Diffusion data for Ga, In, and Na are listed in Nachtrieb's review article.[43] The diffusion coefficient for Bi was estimated from the viscosity data by Ofte and Wittenberg.[44] For Rb and Sb, D was obtained from the viscosity data following the method of Saxton and Sherby.[45] We will use the A which Sholl calculated for an unscreened Coulomb potential $A \approx 0.121$ cgs. Sholl's calculation of $(1-\gamma_\infty)_{\rm an}$ turned out about three times the calculated ionic value of $(1-\gamma_\infty)$ in Ga and In. We use the same ratio in estimating $(1-\gamma_\infty)_{\rm an}$. There is no easy way of estimating I_1 short of doing the difficult integrals. Sholl found I_1 to be 30% smaller for In than Ga, which is quite close considering the imprecision of our estimates. As a first approximation we may look at the values of $f(r_1)$ and $f(r_2)$ corresponding to the first two peaks of the x-ray rdf and compare them for different elements. We then appeal to Paskin's "law of corresponding states[46]" by which the structure factors of a pair of liquid metals with the wave vectors scaled by the ratio of the cube root of the atomic volume are nearly the same implying similar rdfs. Paskin has shown this for In, Rb, and Na among others. We extend this result to Ga, Sb, and Bi. If f is relatively large at the rdf peaks, we expect a relatively large I_1 and conversely. Using the calculated values of I_1 in Ga and In for comparison, we will roughly estimate I_1 for the others. Typical errors for D are between 10 and 20%. We arbitrarily set our error for the rough estimate of R_{1q} at ±50% of its largest value. This is reasonable in view of the previously mentioned uncertainties and since the R_{1q} value is not expected to be exact. Typical experimental errors for R_1 are about 5%. Table II shows values for I, I_1, $(1-\gamma_\infty)_{\rm an}$, and our estimates for R_{1q}.

In analyzing the data, we begin by assuming $K=K_s$. Figures 1–4 show this case for R_{1s} in Ga^{69}, Rb^{85}, Sb^{121}, and Na^{23}. In each case, $K(\alpha)$ of about 0.75 fits the data well. Data for R_{1q} in Ga^{69}, Rb^{85}, and Sb^{121} are shown in Figs. 5–7. The qualitative features of the data are similar for both isotopes of Ga, Rb, and Sb. Cornell's Ga data were used since only he studied both isotopes. Estimates for R_{1q} in Na^{23} give a value of about 1% of the experimental R_1. The consistency of the magnetic data for $K=K_s$ and $K(\alpha)\approx 0.75$ lead us to conclude that $K(\alpha)$ is in the neighborhood of 0.75 for liquid metals and that K' is probably small. In Ga and Rb, R_{1q} is not known over large temperature ranges. On inspection of the data in Figs. 5 and 6 we feel that R_{1q} appears to be constant in temperature. However, the Hanabusa data for Ga predicts a decreasing temperature dependence for R_{1q}. Figure 7 shows clearly a decreasing temperature dependence of R_{1q} in Sb.

The cases of In^{115} and Bi^{209} are more complicated because we are dealing with single magnetic isotopes and a very significant contribution from R_{1q}. If we assume that $K=K_s$ and $K(\alpha)\approx 0.75$ for In, Fig. 8 shows an unaccounted for relaxation rate which is approximately linear. Since $R_{1q'}/T \approx 2.5\times 10^{-3}$ from Eq. (12), this rate must be magnetic. This means a finite K'. If $K(\alpha)\approx 0.75$, $K'\approx -0.1\,K_s$ is reasonable in view of calculations for K_{cp} in light metals.[14–16] The slope of R_1 versus T flattens as T decreases to the melting point.[8] A clearer indication of this point may be found in the measurements by Styles[47] of the In^{115} linewidth in 50% In–50% Bi alloys which extend lower into the supercooled region. This flattening indicates a quadrupole relaxation rate decreasing with temperature and smaller than our estimates in Table II.

The minimum of R_1 in Bi^{209} is obvious from the data of Rossini[8] shown in Fig. 9 and is confirmed in the work of Styles,[47] since R_1 is proportional to the linewidth in the liquid. The estimate in Table II for R_{1q} appears to

TABLE II. Estimates for R_{1q}.

Isotope	I	$(1-\gamma_\infty)_{\rm an}$	I_1	R_{1q}[a,b]
Ga^{69}	$\frac{3}{2}$	28 [c]	3.30×10^{-11} [c]	73.5 $e^{564/T}$
Ga^{71}	$\frac{3}{2}$			29.3 $e^{564/T}$
Rb^{85}	$\frac{5}{2}$	150 [d]	2.37×10^{-11} [a]	2.87 $e^{938/T}$
Rb^{87}	$\frac{3}{2}$			
Sb^{121}	$\frac{5}{2}$	30 [a]	3.90×10^{-11} [a]	250 $e^{2490/T}$
Sb^{123}	$\frac{7}{2}$			154 $e^{2490/T}$
Na^{23}	$\frac{3}{2}$	17 [d]	2.37×10^{-11} [a]	0.041 $e^{1220/T}$
In^{115}	$\frac{9}{2}$	77 [c]	2.37×10^{-11} [c]	158 $e^{1250/T}$
Bi^{209}	$\frac{9}{2}$	150 [a]	3.90×10^{-11} [a]	46.4 $e^{1520/T}$

[a] Our estimate.
[b] T in °K.
[c] Sholl calculation.
[d] $3\times(1-\gamma\ )_{\rm ionic}$ from literature.

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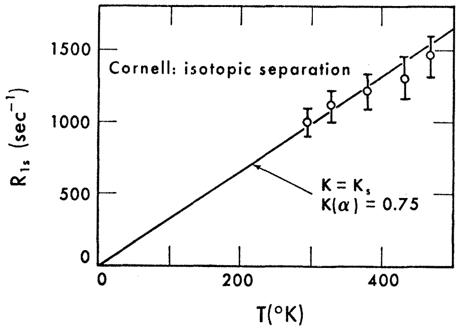

FIG. 1. R_{1s} versus T in liquid Ga^{69}.

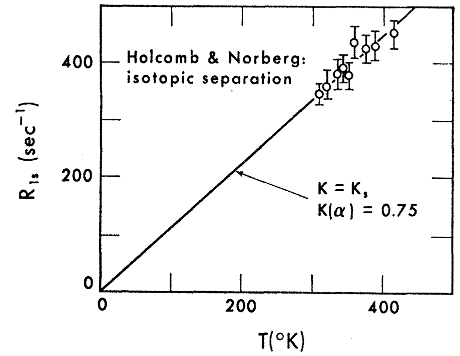

FIG. 2. R_{1s} versus T in liquid Rb^{85}.

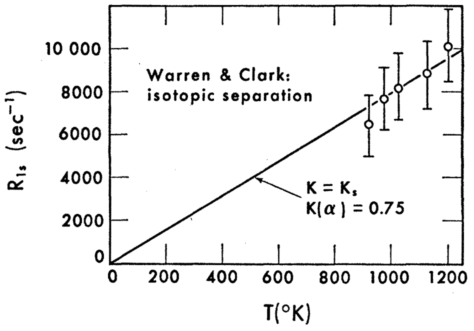

FIG. 3. R_{1s} versus T in liquid Sb^{121}.

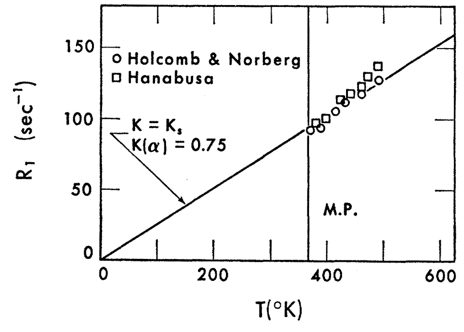

FIG. 4. $R_{1s} \approx R_1$ versus T in liquid Na^{23}.

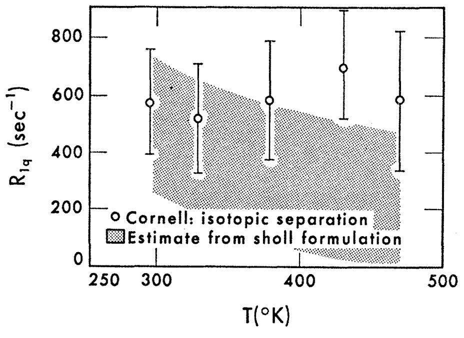

FIG. 5. R_{1q} versus T in liquid Ga^{69}.

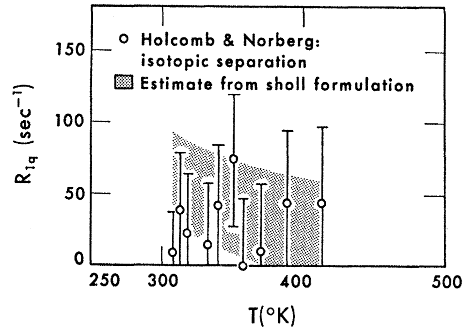

FIG. 6. R_{1q} versus T in liquid Rb^{85}.

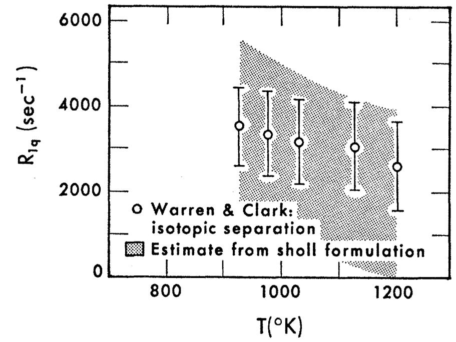

FIG. 7. R_{1q} versus T in liquid Sb^{121}.

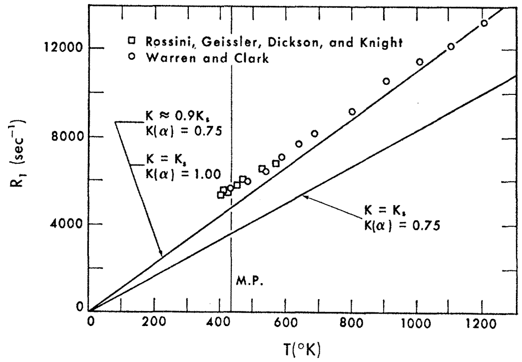

FIG. 8. R_1 versus T in liquid In^{115}.

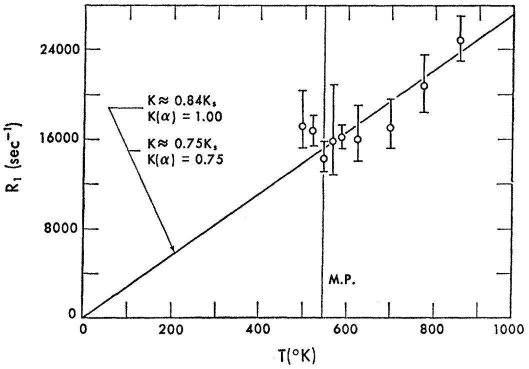

FIG. 9. R_1 versus T in liquid Bi^{209}—data of Rossini (Ref. 8).

be small. If we take $K(\alpha)\approx 0.75$, $K'\approx -0.25\ K_s$. Again this is reasonable as bismuth's large $\langle 1/r^3\rangle$ might lead to a significant K_o and since K_{cp} is unknown. It is interesting to note that where R_{1q} appears to be temperature-dependent it decreases with temperature. Only in the alkalis, where R_{1q} is relatively less important, does this not appear clearly.

IV. CONCLUSIONS

We have developed a broad interpretation for nuclear spin-lattice relaxation in liquid nontransition metals in terms of all known interactions of the nuclear magnetic dipole and electric quadrupole moments with the lattice. Data for R_1 and K in $Ga^{69,71}$, $Rb^{85,87}$, $Sb^{121,123}$, Na^{23}, In^{115}, and Bi^{209} have been examined within this framework. Four conclusions may be drawn:

(1) The potentially significant contributions to K are hyperfine contact K_s, hyperfine orbital, and core polarization. (The sum of the last two is referred to as K'.)

(2) K' is small compared to K_s even in heavy elements.

(3) The potentially significant contributions to R_1 are the hyperfine contact R_{1s} expressed by the modified Korringa relation and the nuclear quadrupolar contribution arising from the effect of ionic motion on the conduction electrons R_{1q}, which decreases with temperature.

(4) Reasonable values of $K(\alpha)$ are close to 0.75 for all liquid metals examined.

The presence of significant magnetic relaxation mechanisms other than hyperfine contact, such as orbital core polarization, which were considered possible especially for heavy elements, is discounted. The temperature dependence of R_{1q} expected from a model where the efg follows the diffusive motion of the ions is shown to be reasonable. The experimental data are explained without requiring $K(\alpha)$ to have a temperature dependence. K_s dominates K even in heavy elements with K' turning out to be at most about 0.25 K_s. It is of some significance that this method of analysis places small upper limits for noncontact magnetic interactions which have heretofore not been evaluated by any direct experimental method. The available data fit very well into this framework for nuclear spin-lattice relaxation in liquid nontransition metals.

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