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Nuclear Quadrupolar Relaxation in Solid and Liquid $AuGa_2$, $Au_{0.95}Pd_{0.05}Ga_2$, and $AuIn_2$

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Nuclear quadrupolar relaxation rates have been measured in the solid and liquid states of $AuGa_2$, $Au_{0.95}Pd_{0.05}Ga_2$, and $AuIn_2$ in order to investigate the effect of melting on quadrupolar relaxation processes. The quadrupolar relaxation rates are found to increase by factors of 3 and 5, respectively, when $AuGa_2$ and $AuIn_2$ are heated through their melting points. For $Au_{0.95}Pd_{0.05}Ga_2$, the relaxation rate decreases by about 35%. The relaxation rates observed in the solids have been identified by their temperature dependences as arising from interactions between the nuclei and lattice vibrations. Comparison of these rates with the rates in the liquids suggests that vibrational motions may make appreciable contributions to quadrupolar relaxation above the melting point as well.

I. INTRODUCTION

Numerous experimental studies[1] of nuclear spin-lattice relaxation in liquid metals have shown that dynamic electric quadrupole interactions make important contributions to the observed relaxation rates $1/T_1$. In a few cases quadrupolar relaxation processes actually dominate competing magnetic processes.[2] Of the latter, the most important is the Korringa mechanism,[3] in which nuclear relaxation is accomplished through interactions between the nuclear magnetic dipole moments and fluctuating magnetic contact hyperfine fields produced by the conduction electrons. The quadrupolar mechanism, while it may also involve the conduction electrons, is important mainly because it is sensitive to the microscopic dynamics of ion cores in the liquid state.

In the past, attempts have been made to explain quadrupolar relaxation in liquid metals in terms of fluctuating electric field gradients produced by the diffusional motion of single ions.[4,5] While these efforts have been partially successful in predicting the order of magnitude of the relaxation rates, the diffusional theories predict incorrectly certain correlations between the temperature dependences of relaxation rates and macroscopic diffusion coefficients. A new theoretical investigation[6] of this problem suggests, however, that the difficulty may result from neglect of *vibrational* ionic motions in the earlier work. The presence of such motions in liquid metals has been established from inelastic neutron scattering studies[7] in which empirical fits of the observed spectra to various theoretical models indicate that the amplitudes and lifetimes of high-frequency collective modes are quite similar on both sides of the melting transition. Since quadrupolar relaxation due to vibrational motion (phonons) is the dominant mechanism in many nonmetallic solids at high temperatures,[8,9] one might expect to observe comparable vibrational contributions to quadrupolar relaxation on both sides of the melting point T_m.

The foregoing considerations suggest that an estimate of the magnitude of vibrational contributions in the liquid might be obtained by measuring the quadrupolar relaxation rate through the melting point of a simple metal and comparing the liquid rates with the vibrational rates just below T_m. Unfortunately, several criteria severely limit the choice of a suitable metal for such an experiment. In order to separate competing contributions of magnetic and quadrupolar relaxation processes, it is necessary to study a metal in which T_1 can be measured for two isotopes of the same atomic species.[10,11] At least one of these isotopes must have a nuclear quadrupole moment and, if both have quadrupole moments, either the dipole moments or quadrupole moments must differ sufficiently to permit accurate determination of the quadrupolar part of the relaxation rate. Moreover, previous experiments[2,10,12] have shown that quadrupolar relaxation is strongest (and thus most easily observed) in polyvalent metals. Presumably this is because the conduction-electron wave functions exhibit a large degree of p character and the electric field gradients are therefore larger than in monovalent metals (s electrons produce no electric field gradient). Finally, it is important that the crystal structure of the solid exhibit cubic symmetry. In noncubic structures the resonance spectra of nuclei possessing quadrupole moments are complicated and often severely broadened by static quadrupolar interactions. It is difficult to obtain accurate measurements of T_1 in the presence of such static interactions; this is particularly true at high temperatures where signal-to-noise ratios are generally poor.

Unfortunately, the criteria described above do not appear to be met simultaneously by any simple elemental metal.[13] They are, however, satisfied by the fluorite structure intermetallic compound $\mathrm{AuGa_2}$ and by alloys of the form $\mathrm{Au_{1-x}Pd_xGa_2}$. The gallium isotopes Ga^{69} and Ga^{71} have sufficiently different dipole and quadrupole moments that magnetic and quadrupolar processes of comparable magnitudes may be readily resolved. Moreover, band-structure calculations[14] indicate that the conduction-electron wave functions exhibit an appreciable amount of p character at the Ga site. Finally, in the cubic fluorite structure there is no static quadrupole splitting and, as it turns out, negligible quadrupolar broadening. These advantages are, of course, partially offset by additional complications introduced by the possible formation of molecular associations in the liquid state of an intermetallic compound.

In this paper we describe measurements of the quadrupolar contribution to spin-lattice relaxation in the solid and liquid states of pure $\mathrm{AuGa_2}$ and in $\mathrm{Au_{0.95}Pd_{0.05}Ga_2}$. We also include relaxation-rate data for In^{115} in the isomorphic system $\mathrm{AuIn_2}$. However, since only one indium isotope is available, determination of the quadrupolar relaxation component is not so direct as for the gallium isotopes. We shall be concerned only with quadrupolar relaxation in these metals; magnetic relaxation rates, Knight shifts, and magnetic susceptibilities will be described in a subsequent paper.

II. EXPERIMENTAL DETAILS AND RESULTS

The sample materials used for these experiments were prepared by induction melting stoichiometric proportions of the appropriate elements (99.9999+% purity) and were purified by zone melting (two passes) in quartz ampoules. The details of preparation and characterization of these materials have been described previously.[15] The composition of the $\mathrm{Au_{0.95}Pd_{0.05}Ga_2}$ sample was checked by powder x-ray diffraction and by measurement of the superconducting transition temperature T_c. Both the lattice constant and T_c were in agreement with values previously obtained[15] for this composition. All samples were powdered, sieved (325 mesh), and mixed in roughly equal proportions with powdered quartz. The quartz powder prevented sintering of the solid samples at high temperatures and provided a medium for dispersion of liquid droplets above T_m. The mixed powders were sealed under vacuum in quartz ampoules for experimental runs.

Nuclear spin-lattice relaxation times were measured with a coherent pulsed NMR spectrometer operating at a frequency of 16.0 MHz. A dual-channel boxcar integrator[16] was used to measure the amplitude of the free induction decay following the second pulse of an approximately $\pi-\frac{1}{2}\pi$ rf pulse sequence. For Ga^{69} and Ga^{71} the quadrupolar rates R_Q^{69} and R_Q^{71} were determined from the total rates R^{69} and R^{71} ($R \equiv 1/T_1$) by means of the formulas[2]

$$R_Q^{69} = (R^{69} - \alpha_M R^{71})/(1 - \alpha_M/\alpha_Q) \quad , \tag{1a}$$

$$R_Q^{71} = R_Q^{69}/\alpha_Q \quad , \tag{1b}$$

where $\alpha_M = (\gamma_{69}/\gamma_{71})^2$ and $\alpha_Q = (Q_{69}/Q_{71})^2$, and γ and Q are, respectively, the appropriate gyromagnetic ratios and quadrupole moments for the two isotopes.

In the case of the single isotope In^{115} in $\mathrm{AuIn_2}$, Eqs. (1a) and (1b) cannot be used and R_Q^{115} was determined from the relation

$$R_Q^{115} = R^{115} - (R_M^{115})_{\mathrm{KORR}} \quad . \tag{2}$$

The magnetic component $(R_M^{115})_{\mathrm{KORR}}$ was calculated from the observed Knight shift $\mathcal{K}$ by means of the Korringa relation[3,17]

$$(R_M^{115})_{\mathrm{KORR}} = \frac{4\pi k T}{\hbar}\left(\frac{\gamma_{115}}{\gamma_e}\right)^2 \mathcal{K}^2 K(\alpha) \quad , \tag{3}$$

in which k is Boltzmann's constant, γ_e is the electronic gyromagnetic ratio, and $K(\alpha)$ is a correction factor depending on the Stoner enhancement α for the electronic susceptibility.[18] We have used the value $K(\alpha) = 0.78$ determined from experimental values of R^{115} at temperatures sufficiently low ($T < 300$ K) that quadrupolar relaxation due to ionic motion is negligible. We have assumed $K(\alpha)$ to remain constant at this value over the temperature range studied in these experiments.

Our observed values of R_Q^{69} and R_Q^{115} for solid and liquid $\mathrm{AuGa_2}$, $\mathrm{Au_{0.95}Pd_{0.05}Ga_2}$, and $\mathrm{AuIn_2}$ are shown in Figs. 1 and 2. The experimental uncertainties in R_Q are larger than those of the raw T_1 data (± 2.5–5.0%) because of the accumulation of errors

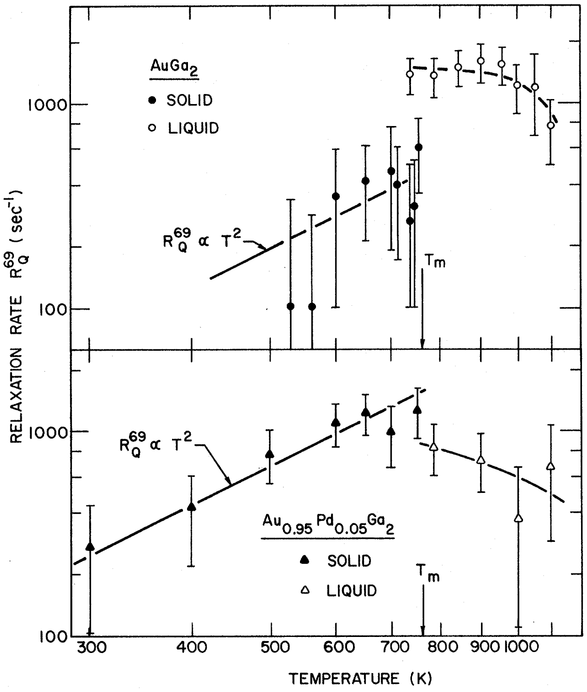

FIG. 1. Log-log plot of the nuclear quadrupolar relaxation rate R_Q^{69} vs temperature for Ga^{69} in $AuGa_2$ and $Au_{0.95}Pd_{0.05}Ga_2$. Solid data (closed points) are compared with the T^2 temperature dependence expected for relaxation due to lattice vibrations. The point shown below T_m for liquid $AuGa_2$ was taken in the supercooled liquid.

resulting from the use of Eqs. (1a) and (2). In each case, the experimental error overwhelms the calculated rate at a sufficiently low temperature and the quadrupolar rate cannot then be resolved.

The main features of the data may be summarized as follows. The values of R_Q^{69} in $Au_{0.95}Pd_{0.05}Ga_2$ are roughly three times greater than in pure $AuGa_2$. However, the temperature dependence of R_Q^{69} in each case is consistent with R_Q^{69} proportional to T^2. At T_m, R_Q^{69} increases by about a factor of 3 in $AuGa_2$ while it *decreases* to roughly 65% of the solid value in liquid $Au_{0.95}Pd_{0.05}Ga_2$. In the liquid state, R_Q^{69} in $AuGa_2$ is almost twice as great as in $Au_{0.95}Pd_{0.05}Ga_2$, and in both systems, R_Q^{69} tends to decrease slowly with increasing temperature.

The value of R_Q^{115} for solid $AuIn_2$ increases somewhat more rapidly than T^2. This result is, however, somewhat inconclusive owing to the assumptions underlying Eq. (2). The increase of a factor of 5 upon melting is greater than for pure $AuGa_2$; the decrease of R_Q^{115} at higher temperatures is similar to the observations in $AuGa_2$ and $Au_{0.95}Pd_{0.05}Ga_2$.

III. DISCUSSION

The experimental results described above support the idea that vibrational modes of ionic motion make a nonnegligible contribution to quadrupolar relaxation in liquid metals. In this section, we elaborate on our reasons for believing this to be true.

The first point to be recognized is that the temperature dependence of R_Q in the solids indicates that lattice vibrations provide the dominant quadrupolar relaxation mechanism below T_m. The theory of this type of relaxation process has been developed extensively[19-21] and although quantitative prediction of the magnitude of R_Q has proved difficult, there is general agreement that for $T > \Theta_D$ (Θ_D is the Debye temperature) the temperature dependence is given by

$$R_Q \propto T^2 \text{ (phonons)} . \tag{4}$$

This behavior has been verified experimentally for both compounds[8,9,22] and elements.[23,24] The only probable alternative processes are those in which the fluctuating electric field gradients result from self-diffusion or diffusion of defects. For these mechanisms the temperature dependence is described by[25,26]

$$R_Q \propto e^{-E_A/RT} \text{ (diffusion)} , \tag{5}$$

where E_A is an appropriate activation energy.

The data shown in Fig. 1 for $AuGa_2$ and $Au_{0.95}Pd_{0.05}Ga_2$ are, on the one hand, consistent with Eq. (4), while, on the other hand, it does not appear reasonable to describe them by a temperature dependence of the form given in Eq. (5). For example, if we attempt to fit the data for $Au_{0.95}Pd_{0.05}Ga_2$ to Eq. (5) we obtain a value $E_A = 185 \pm 85$ cal/mole for the activation energy. This value is two orders of magnitude smaller than

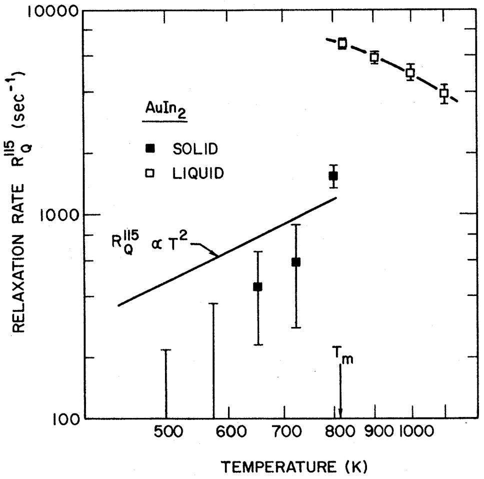

FIG. 2. Log-log plot of the nuclear quadrupolar relaxation rate R_Q^{115} vs temperature for In^{115} in $AuIn_2$. Solid data (closed squares) are compared with the T^2 temperature dependence expected for relaxation due to lattice vibrations.

values typically found for self-diffusion in fcc metals[27] and it effectively rules out diffusional motion as a source of quadrupolar relaxation in this metal. For $AuGa_2$ and $AuIn_2$, the maximum values of E_A consistent with the data are 545 and 1250 cal/mole, respectively. While these values are somewhat larger than found for $Au_{0.95}Pd_{0.05}Ga_2$, they remain much too small to be ascribed to a diffusion mechanism. As further evidence of the weakness of diffusion-related processes, we cite the fact that no motional narrowing[25] of the resonance line was observed in any of the materials studied. Thus, it may safely be concluded that lattice vibrations are primarily responsible for the observed relaxation in solid $AuGa_2$ and $Au_{0.95}Pd_{0.05}Ga_2$. The enhanced *magnitude* of R_Q in the Pd-doped material is probably a consequence of increased local electric field gradients produced by charge density oscillations near the impurities.

The data for $AuIn_2$ do not appear to fit Eq. (4). However, this may simply reflect the ambiguity in the determination of R_Q^{115} which inevitably results from the use of Eq. (2). It should be noted that one need only invoke a 4% reduction of $K(\alpha)$ at high temperatures in order to bring the temperature dependence of R_Q^{115} into agreement with Eq. (4). Variations of $K(\alpha)$ of this magnitude are not unusual and we consider it extremely probable that lattice vibrations also produce the observed quadrupolar relaxation in $AuIn_2$.

We turn now to a discussion of the quadrupolar relaxation rates above T_m. The contribution of single-particle diffusional modes to quadrupolar relaxation in liquids has been considered by Sholl[4] and by Borsa and Rigamonti.[5] These authors have shown that the temperature dependence of R_Q for this mechanism is given approximately by

$$R_Q \propto \rho(T)/D(T) \quad \text{(single-particle diffusion)}, \qquad (6)$$

where ρ is the density and D is the macroscopic diffusion coefficient. Since ρ normally decreases with increasing temperature while D increases, Eq. (6) predicts a fairly rapid decrease of R_Q with increasing temperature. In fact, in such liquid metals as indium,[1,2] antimony,[2] and gallium,[10] and in liquid xenon,[23] R_Q does not decrease as rapidly as predicted by Eq. (6). These observations suggest that a simple diffusion model does not adequately describe the microscopic dynamics responsible for quadrupolar relaxation in simple liquids.

The quadrupolar relaxation rates in liquid $AuGa_2$ and $AuIn_2$ are enhanced by factors of roughly 3 and 5, respectively, compared to the values observed just below T_m. The rates in these liquid compounds also exceed, by roughly the same factors, those observed for the same nuclei in the pure liquid metals.[1,2,10] This suggests the existence in the liquid compounds of molecular associations whose diffusional and rotational motions provide increased relaxation rates.[28] The observed decrease of R_Q at higher temperatures is consistent with this picture since molecular groups should tend to dissociate and become more mobile with increasing T. One can, on this basis, also understand the reduction of R_Q^{69} in liquid $AuGa_2$ on alloying Pd. Since $PdGa_2$ does not exist as a stable compound,[29] substitution of Pd for Au should lead to dissociation or formation of some other complex based on, say, PdGa or Pd_2Ga. In either case, generation of free Ga ions and reduction of R_Q^{69} would result.

The approximate strength of vibrational contributions to R_Q in the liquid compounds may be estimated from the observed rates just below T_m. It has been clearly established in theoretical discussions of vibrational relaxation in crystals[19,21] that the major contribution to R_Q results from scattering of high-frequency phonons ($\omega \sim k\Theta_D/\hbar$). This is just the frequency range in which collective modes have been observed above T_m in simple metals such as Pb by inelastic neutron scattering.[7] If we postulate the existence of such modes in the liquid AuX_2 compounds, it follows that the vibrational contributions to R_Q above T_m in these liquids should be approximately equal to the observed values of R_Q just below T_m. On this basis, we estimate that vibrational modes contribute roughly 30% of the total quadrupolar relaxation in liquid $AuGa_2$ and 20% in $AuIn_2$. In $Au_{0.95}Pd_{0.05}Ga_2$, R_Q^{69} actually decreases slightly at T_m. We must then conclude either that diffusional and rotational relaxation are negligible in this liquid or that changes in electronic structure reduce the Pd-induced enhancement of R_Q^{69} above T_m. However, even if the enhancement is removed completely so that the vibrational contribution to R_Q^{69} is the same as in $AuGa_2$, one still finds a vibrational contribution of about 50% in $Au_{0.95}Pd_{0.05}Ga_2$.

IV. SUMMARY

Nuclear quadrupolar relaxation rates R_Q have been measured for Ga^{69} and In^{115} in solid and liquid $AuGa_2$, $Au_{0.95}Pd_{0.05}Ga_2$, and $AuIn_2$. The temperature dependences of R_Q in the solids are in satisfactory agreement with the expected T^2 dependence for relaxation via lattice vibrations, whereas the data do not fit the exponential temperature dependence expected of diffusion-related processes with reasonable values of the activation energy. Therefore, it is concluded that quadrupolar relaxation below T_m is dominated by interactions with vibrational modes in the crystal. We have argued that the relatively small changes in R_Q at T_m suggest that vibrational modes continue to be of importance (though not dominant) in the liquid state. Using the simple assumption that the vibrational contributions are unchanged at the melting point, we estimate that the vibrational contributions vary from about 20% ($AuIn_2$) to more than 50% ($Au_{0.95}Pd_{0.05}Ga_2$) of the observed quadrupolar relaxation rate in the liquids.

We caution that these results do not in any sense demonstrate the *existence* of vibrational modes in the liquid state. We conclude merely that if such modes are general features of classical liquids, as is suggested by the neutron experiments, then it is likely that they make significant contributions to electric quadrupolar relaxation. In pure monatomic liquids such modes may play a dominant role since the probability of atomic associations is greatly reduced in those cases. It is clear, in any event, that a successful theory of quadrupolar relaxation in simple liquids must take into proper account the effects of this type of atomic or ionic motion.

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