

phase with zero anisotropy are in agreement with the Curie temperatures obtained for a ferromagnet of equal $|J|$, using the same approximations. This equality is in close agreement with the Padé predictions of Rushbrooke and Wood.⁴³ CD yields higher Néel temperatures than RPA and for the larger spin values is in better quantitative agreement with the results obtained by Rushbrooke and Wood.

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Self-Diffusion and Nuclear Quadrupolar Relaxation in fcc Lanthanum Metal*

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The nuclear magnetic-resonance spin-lattice (T_1) and spin-spin (T_2) relaxation times and the Knight shift of La^{139} in pure fcc lanthanum metal have been studied from 295 to 825°K. The relaxation times exhibit a temperature dependence which can be explained by vacancy diffusion and annealing effects that perturb the spin system via the nuclear electric-quadrupole interaction. At the highest temperatures, it is found that $T_1 = T_2 \propto \exp(E_a/kT)$ where $E_a = 15$ kcal/mole is found for the activation energy of vacancy formation and diffusion. The Knight shift is found to increase from 0.64% at 295°K to 0.72% at 825°K, which may be the result of an electron-phonon interaction.

I. INTRODUCTION

THE behavior of the nuclear spin-spin (T_2) and spin-lattice (T_1) relaxation times of La^{139} in pure fcc lanthanum metal has been studied from 25 to 550°C. The major part of their temperature dependence can be interpreted on the basis of vacancy diffusion and formation, on a competition between the two stable crystal structure forms, hcp and fcc, and annealing effects, all of which affect the nuclear-spin system via the electric-quadrupole interaction.

X-ray studies¹ have shown that hcp La metal begins to transform to an fcc structure at 200°C which is then stable even below 200°C. Cold working below 200°C restores the hcp phase. However, even in the fcc phase, a small amount of hcp phase remains.¹ The fact that the c/a ratio $(c/a)_{\text{La}} = 1.61$ of hcp La is not ideal, and that La^{139} possesses a moderate quadrupole moment, leads to a quadrupole interaction which has the effect of broadening the resonance linewidth, or alternatively of shortening T_2 , while at the same time reducing the intensity of the resonance by removing the satellite transitions from the central resonance. The central resonance ($m = \frac{1}{2} \rightarrow m = -\frac{1}{2}$) and the two inner satellites

($m = |\frac{1}{2}| \leftrightarrow |\frac{3}{2}|$) have been observed² in hcp La which was annealed for several days at a temperature just below the phase-transition temperature. Another source for a quadrupole interaction in hcp La, which will manifest itself whenever the local symmetry is noncubic, is strains and stacking faults which are difficult to anneal away since annealing must be done below 200°C to preserve the hcp phase.

The fcc phase of La should ideally show no evidence of a static quadrupole interaction. However, any deviation from cubic symmetry such as a small amount of the hcp phase will produce an observable effect. On the other hand, even in a pure fcc phase rapidly time varying or momentary deviations from cubic symmetry as may be produced by diffusing vacancies or other defects will be observable in a T_1 (spin-lattice relaxation-time) measurement, where T_1 is considerably shortened via the quadrupolar-relaxation mechanism.

A study of the La linewidth, with some direct T_1 measurements, from 25 to 550°C reveals the effect of both a static and a time varying quadrupole interaction. Quantitative results of vacancy formation and diffusion and annealing effects are deduced and are discussed in Sec. III. A Knight shift, increasing with temperature, is also observed and is qualitatively discussed.

II. EXPERIMENTAL

In order to avoid skin-depth-effect problems, the samples were prepared in the form of a powder by using

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¹ W. T. Ziegler, R. A. Young, and A. L. Floyd, *J. Am. Chem. Soc.* **75**, 1215 (1953).

² D. Torgeson, D. Peterson, and R. G. Barnes, *Bull. Am. Phys. Soc.* **8**, 529 (1963).

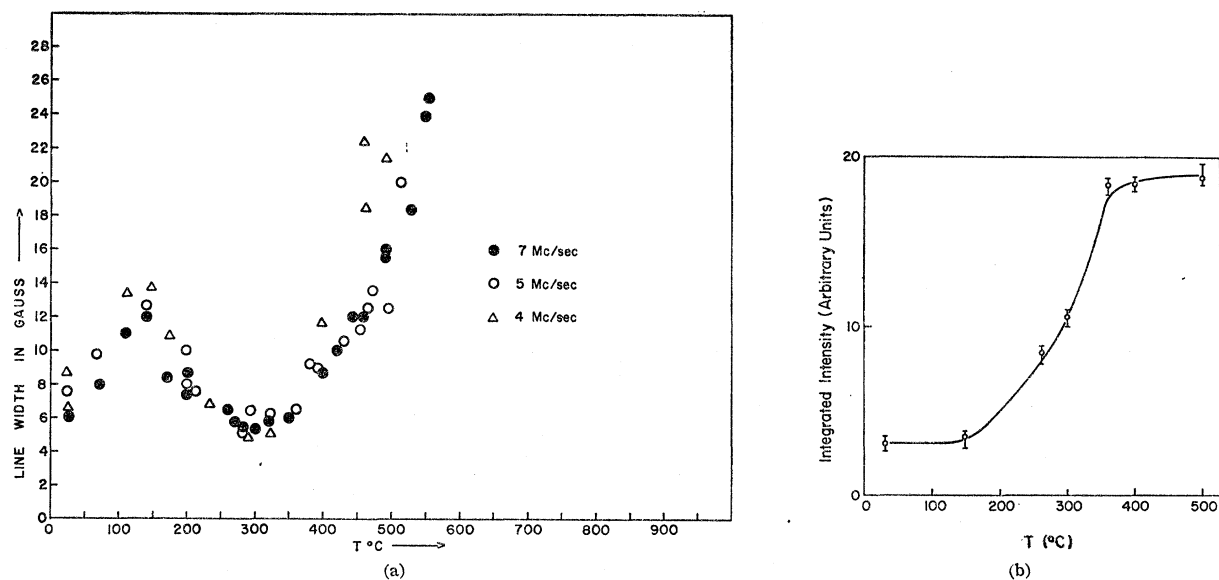


FIG. 1. (a) La linewidth as a function of temperature for three different magnetic fields, 11.7, 8.3, and 6.6 kG. (b) Integrated intensity of La absorption as a function of temperature, corrected for the Boltzman factor temperature dependence.

two distinct methods of preparation. One was the conventional method of filing and sieving to retain only the smaller particles. These were then annealed at or above 400°C to obtain the fcc structure from the initially cold-worked hcp phase. This structure was confirmed by an x-ray analysis. The second method consisted of heating the metal ingot in the presence of hydrogen and hydriding the metal to a composition of about LaH_2 . Lanthanum dihydride is very brittle and was easily crushed in a mortar under an inert atmosphere to a fine powder which was then mixed with La_2O_3 so that when the mixture was heated to about 500°C and pumped under a 5×10^{-6} mm Hg vacuum to extract the hydrogen, the resulting small particles of pure La metal did not sinter together. To ascertain that the samples prepared in the second way, thereafter called hydride-dehydride, were free of any residual hydrogen, they were examined for a hydride lanthanum resonance³ and a proton resonance, neither of which was observed. It is interesting to observe that fcc samples prepared by the hydride-dehydride method had low-temperature linewidths narrower by a factor of 2 than those produced by filing as previously reported.⁴ The experimental detection equipment, both c.w. and pulsed, and the high-temperature setup are described elsewhere.³

III. RESULTS AND DISCUSSION

Figure 1(a) shows the linewidth behavior of hydride-dehydride fcc La from 25 to 550°C for 3 different magnetic fields. The line shape is asymmetric up to 300°C,

becoming symmetric and nearly Lorentzian with long tails above this temperature. The relative integrated intensity of the resonance is plotted as a function of temperature in Fig. 1(b). Results similar to those shown in Figs. 1(a) and 1(b), but showing only an already broadened linewidth at 25°C which narrowed at 280°C, were found⁵ for small particles of fcc La prepared by filing and annealing, though they were not carried to as high a temperature. The resonance with a Knight shift of 0.21% given in Ref. 5 is that of La^{139} in LaH_2 . Both the fcc and hcp phases of La have nearly identical Knight shifts.

We shall divide our discussion of the linewidth behavior for fcc hydride-dehydride La into three parts corresponding to the 3 distinct temperature ranges (1) 25 to 150°C, (2) 150 to 300°C, and (3) 300 to 550°C.

(1) At 25°C, x-ray diffractions measurements showed the sample to be of the fcc phase, although there was some evidence for a very small amount of the hcp phase of stacking faults. Others¹ have also reported that regardless of the annealing and quenching procedures, some hcp phase tends to persist. The nuclear magnetic resonance of La^{139} is sensitive (via the quadrupole interaction) to the presence of a noncubic structure resulting from stacking faults, strains, or some hcp phase. The fact that the integrated intensity of the resonance is much reduced over that obtained at higher temperatures shows that local order is not purely cubic. In fact, the intensity reduction of about a factor of 5 is just what one would expect for a spin $I = \frac{7}{2}$ nucleus if the local quadrupole interactions were just large enough to wipe out the satellite transitions leaving the central transition unperturbed.

³ D. S. Schreiber and R. M. Cotts, Phys. Rev. **131**, 1118 (1963).

⁴ W. E. Blumberg, J. Eisinger, V. Jaccarino, and B. T. Matthias, Phys. Rev. Letters **5**, 52 (1960).

⁵ D. S. Schreiber and R. M. Cotts, Bull. Am. Soc. **6**, 224 (1961).

Upon heating, the local strains increase out of a competition between the hcp and the fcc phase, the former tending to be more energetically favorable and in its maximum amount in what is predominately an fcc structure at 150°C. Similar behavior was found in the case of Co metal.⁶ The above behavior would account for the broadening of the linewidth with increasing temperature in range (1). It is also known that the most strain-free hcp phase, is obtained by annealing a filed or cold-worked sample for a long period at temperatures up to 200°C.²

In range (2), above 150°C the transformation to the fcc phase starts.¹ The local distortion decreases, the nuclei see a more nearly cubic environment, and as a result the linewidth narrows and its integrated intensity increases. Above 300°C, in range (3), T_1 is short enough to cause lifetime broadening. The linewidth can be expressed as $\Delta H = (\alpha/\gamma)(1/T_1 + 1/T_2)$ where γ is the nuclear magnetogyric ratio and α is some constant, the order of unity depending on the exact line shape which in our case is neither exactly Gaussian or Lorentzian. At 300°C, a direct measurement of T_1 using pulsed techniques gives a $T_1 \cong 300 \mu\text{sec}$ or a $\Delta H_{T_1} \cong 1.0\text{G}$. Hence the observed ΔH of 6 G at 300°C is predominately dipolar in origin [$\Delta H_{T_2} = (\alpha/\gamma)(1/T_2) = 6\text{G}$], but at higher temperature the T_1 contribution dominates so that a plot of $\ln[1/(\Delta H - 6)]$ (which is proportional to T_1) versus $1/T$, should yield a straight line if T_1 results from a thermally activated process. This is seen to be the case in range (3) as shown in the plot of Fig. 2. The source of this thermally activated contribution to

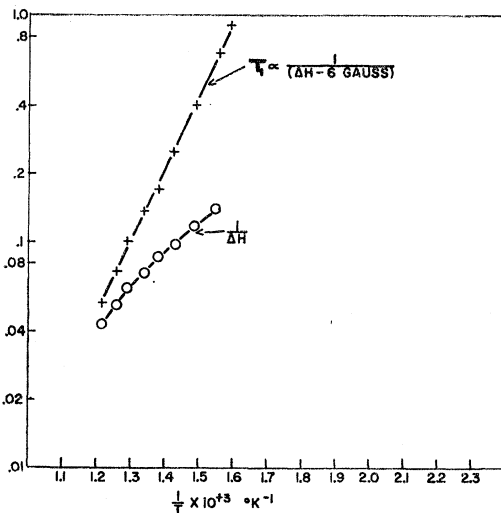


FIG. 2. Semilogarithmic plot of the measured reciprocal La linewidth as a function of (absolute temperature)⁻¹. Note that after subtracting off the dipolar contribution of 6G to the observed linewidth, the remaining lifetime broadened linewidth gives rise to a straight line on this semilog plot, showing the thermally activated origin of T_1 . The vertical ordinate may be read as (G)⁻¹ or some constant \times (sec).

⁶ C. Houska, V. Averbach, and M. Cohen, *Acta Met.* **8**, 82 (1960).

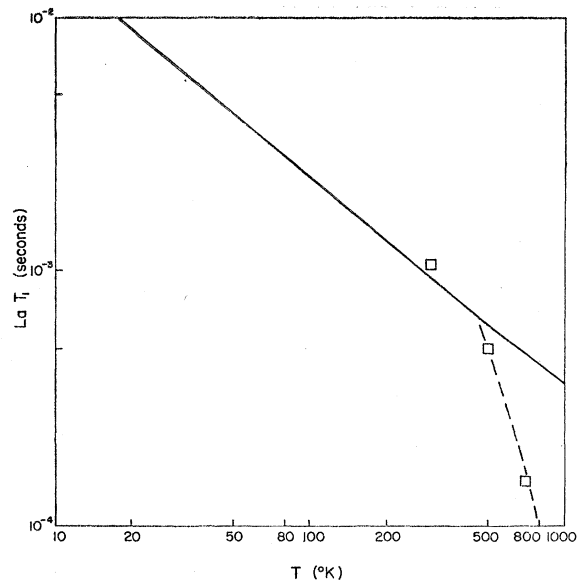


FIG. 3. Log-log plot of La spin-lattice relaxation time T_1 versus temperature T . The solid straight line portion is $T_1 T = 0.2^\circ\text{K}^{-1}\text{-sec}$ as obtained at low temperatures by Blumberg *et al.* (Ref. 4). The points \square are direct pulse measurements from the present work and show the onset of an additional T_1 mechanism.

T_1 can be shown to arise from diffusing vacancies which provide a time varying electric field gradient, and hence a fluctuating quadrupole interaction. If the spectral density of these fluctuations is appreciable at frequencies ω_0 or $2\omega_0$ where $\omega_0 = \gamma H_0$ is the resonance frequency in a field H_0 , spin transitions are induced and thus T_1 is shortened.

The theory of defect diffusion induced spin-lattice relaxation is based on ideas first developed by Bloembergen, Purcell, and Pound⁷ and modified for quadrupolar coupling by Cohen and Reif.⁸ The treatment here of La is similar to that used in Ref. 3, Sec. B-3, except that the number of diffusing protons per unit cell is replaced by n , the atomic fraction of diffusing vacancies. The modified equation is then (for $\nu_c \ll \omega_0$, since there is no deviation from a straight line in Fig. 2)

$$(1/T_1) = (8\pi/245)(n/a_0^6)[B(Ze)^2Q/\hbar]^2 \nu_c / \omega_0^2, \quad (1)$$

where the antishielding factor $B = 50$, $Q = 0.3 \times 10^{-24} \text{cm}^2$, $a_0 = 5.3 \times 10^{-8} \text{cm}$, $\omega_0 = 2\pi \times 7 \times 10^6 \text{sec}^{-1}$, ν_c is the vacancy-jump frequency, and $Z = 3$, the effective charge of a vacancy in a metal with a +3 valence. After substituting these values, we have $(1/T_1)_e \cong 2.5n\nu_c \text{sec}^{-1}$.

There is also a contribution to the measured relaxation time $(T_1)_{\text{meas}}$ from the conduction-electron hyperfine interaction which is inversely proportional to temperature. At low temperatures (where this is the main mechanism for relaxation) we have⁴ $(T_1)_e = 0.2/T^\circ\text{K}^{-1}\text{-sec}$, and it can be seen from Fig. 3, a plot of pulsed

⁷ N. Bloembergen, E. Purcell, and R. Pound, *Phys. Rev.* **73**, 679 (1948).

⁸ M. H. Cohen and F. Reif, *Solid State Phys.* **5**, 321 (1957).

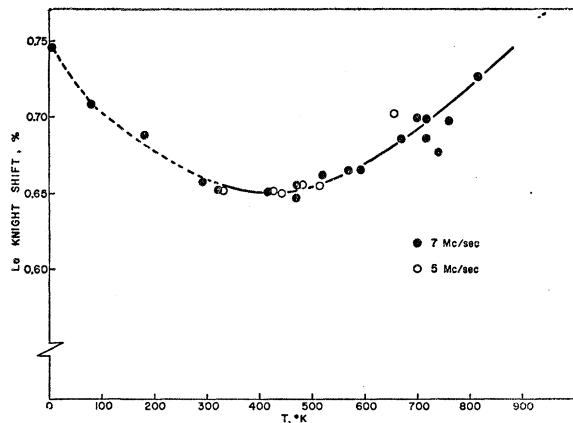


FIG. 4. The La Knight shift as a function of temperature. The dashed line (below room temperature) indicates the data of Bloomberg *et al.* (Ref. 4).

resonance measurements, that T_1 at high temperatures deviates sharply from this low-temperature dependence showing the onset of the diffusion quadrupolar mechanism. To obtain the contribution of this latter part from $(1/T_1)_{\text{meas}}$, we can simply subtract the electronic rate $(1/T_1)_e$. Thus, $(1/T_1)_v = (1/T_1)_{\text{meas}} - (1/T_1)_e$. At 550°C we have $(1/T_1)_v = 2.5 \nu_c = 7 \times 10^4 \text{ sec}^{-1}$, $\nu_c = 2.8 \times 10^3 \text{ sec}^{-1}$. An upper limit on ν_c for $T = 550^\circ\text{C}$ is given by $\nu_c \ll \omega_0$ or $\nu_c \approx 5 \times 10^{16} \text{ sec}^{-1}$, so that $n \gtrsim 6 \times 10^{-4}$ at 550°C , which is a reasonable value. From the slope of $\ln T_1$ versus $1/T$ in Fig. 2, we can obtain the activation energy for La self-diffusion E_a which is the sum of the activation energies for vacancy formation and diffusion, E_f and E_d , respectively, which is $E_a = E_f + E_d = 15 \text{ kcal}$.

In this experiment there is no clear way of assigning values to E_f and E_d separately since n and ν_c enter in the same way in the expression for T_1 , ($n \propto \exp(-E_f/kT)$, $\nu_c \propto \exp(-E_d/kT)$, $n\nu_c \propto \exp(-E_a/kT)$). If measurements could have been carried to higher temperatures were $\nu_c \gg \omega_0$, then the dependence of T_1 upon ν_c becomes $1/T_1 \propto 1/\nu_c$ instead of $1/T_1 \propto \nu_c$, and the plot of $\ln T_1$ versus $1/T$ would show a minimum or at least a departure from a straight line so that E_f and E_d might have been identified separately.

It should also be pointed out that while we have considered only the diffusion of vacancies, the magnitude of the contributions to T_1 of other defects such as some

residual diffusing hydrogen ions or protons should be considered. For the case that only protons are considered, the Z in Eq. (1) is set equal to 1 and $(1/T_1) = 0.03 n\nu_c \approx 1.7 \times 10^4 \text{ sec}^{-1}$, which yields $n \gtrsim 0.1$. Concentrations of this much hydrogen would give readily observable resonance signals so that vacancies can reasonably be considered to be the effective diffusing agents.

In Fig. 4 we show the variation of the La Knight shift with temperature. The low-temperature data is that of Blumberg *et al.*⁴ It is probable that in this range the temperature dependence can be interpreted in terms of the temperature-dependent spin susceptibility of the d electrons. The d electrons can contribute to the Knight shift in two ways: (a) by polarizing the core s electrons, (b) through orbital paramagnetism.^{9,10} At high temperatures, however, we would like to point out that the change in the Knight shift might be of a different origin. The main mechanism could be the phonon-electron interaction first suggested for the alkali metals by Benedek and Kushida.¹¹ They have shown that the temperature dependence of the Knight shift can be written in the form $(\partial \ln K/\partial T)_p = (\partial \ln K/\partial T)_T + (\partial \ln V/\partial T)_p + (\partial \ln K/\partial T)_v$. The quantity on the left-hand side is what is observed experimentally. The first term on the right-hand side is the thermal expansion effect and could be estimated by measuring the pressure dependence of the Knight shift. The last term arises from the electron-phonon interaction. Muto *et al.*¹² have calculated this effect in detail for the alkali metals, and it depends on the elastic properties of the metal. Lanthanum is a relatively soft metal with a low Debye temperature, $\theta_D \approx 150^\circ\text{K}$, and we expect this effect to be large. It can only be measured directly by finding the Knight-shift pressure dependence.

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We would like to thank Professor R. M. Cotts and Professor W. W. Webb for several helpful discussions.

⁹ Y. Masuda, J. Phys. Soc. Japan **19**, 239 (1964).

¹⁰ A. M. Clogston, V. Jaccarino, and Y. Yafet, Phys. Rev. **134**, A650 (1964).

¹¹ G. B. Benedek and T. Kushida, Phys. Chem. Solids **5**, 241 (1958).

¹² T. Muto, S. Kobayasi, M. Watanabe, and H. Kaizima, Phys. Chem. Solids **23**, 1303 (1962).