NUCLEAR MAGNETIC RESONANCE IN SCANDIUM AND LANTHANUM METAL

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(Received May 27, 1960)

We have observed the nuclear magnetic resonance (NMR) of Sc^{45} and La^{139} in hexagonal scandium and cubic and hexagonal lanthanum, respectively. The magnitudes of the Knight shift for these d^1 metals, when considered in comparison to the d^3 metals, are found to have an anomalous dependence on the number of d electrons which we suggest results from an enhanced polarization of the s electrons through the s-d exchange interaction. Both these metals exhibit an unexpectedly large temperature dependence of the Knight shift. Measurements were made in the range of temperatures 1.7°K to 300°K in fields extending to 14 koe using a Varian NMR spectrometer. The metals were spectroscopically pure.

The magnitude and temperature dependence of the observed Knight shifts (k) are shown in Fig. 1. The value of k for hexagonal and cubic La is the same at room temperature within the experimental error. Appropriate saturated nitrate solutions were used for establishing the unshifted resonance, at a given field, in each case.

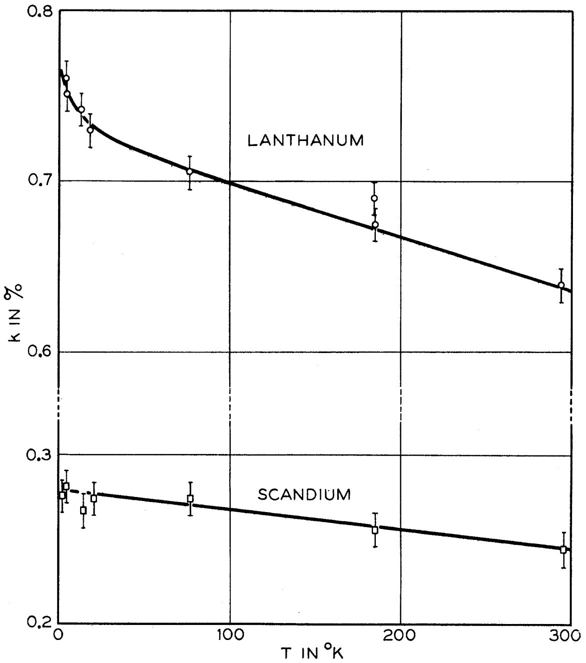

FIG. 1. The Knight shift (k) as a function of temperature for cubic La and hexagonal Sc metals. The indicated errors represent the absolute uncertainties in k, while the relative errors at different temperatures are smaller.

Both line shapes are symmetrical and Gaussian and have widths of 16 oe (Sc) and 13 oe (La) as measured between derivative extrema. The linewidths are independent of temperature and field strength. Although the symmetry of hexagonal Sc allows an electric field gradient, no quadrupole effects were observed. Perhaps this is in part due to the expected smallness of $Q(Sc^{45})$. Strain and self-annealing effects were observed in hexagonal La.

The longitudinal relaxation time (T_1) was measured by observing the degree of saturation as a function of the rf magnetic field strength. In the temperature ranges over which T_1 was measured (1.7°K to 20.2°K for La and 1.7°K to 295°K for Sc), T_1 varied as $1/T$. The product T_1T was 0.2 sec °K for La and 0.6 sec °K for Sc.

At 1.8°K the k for both Sc and La shows an increase of 15% over its value at 295°K. For any reasonable value of thermal expansion coefficients one would predict[1] a change in k of less than $\frac{1}{2}\%$ of its value in the above temperature range. The temperature dependence of the susceptibility of pure hexagonal La exhibits[2] a paramagnetism that increases with decreasing temperature while Sc, on the other hand, has a temperature-independent Pauli susceptibility.[3] It is worthwhile to point out that a paramagnetic impurity would not produce a temperature-dependent k but would only result in an increasing linewidth with decreasing temperature.[4]

The Knight shift[1] is thought to have its origin in the contact hyperfine interaction between the s conduction electron spin and the magnetic moment of the nucleus in question. Usually the conduction electron polarization is field induced alone via the Pauli susceptibility. For other than d or f group metals the magnitudes of the observed k have been in satisfactory agreement with the simple theory. Until now there has not been a sufficient number of measurements to attempt to correlate the magnitude of k with number of d electrons. In Table I we have arranged k in periodic table form.

As expected, there is an increase in k as one goes from $3d^1$ to $5d^1$ or $3d^3$ to $5d^3$ since the hyperfine interaction increases with Z. How-

Table I. The room temperature values of k for the d^1 and d^3 metals in percent.[a,b]

	d^1	d^2	d^3
$n=3$	$_{21}$Sc: 0.24		$_{23}$V: 0.58
$n=4$			$_{41}$Nb: 0.87
$n=5$	$_{57}$La: 0.63		$_{73}$Ta: 1.1

[a] W. D. Knight, reference 1.

[b] L. H. Bennett and J. I. Budnick, Bull. Am. Phys. Soc. 5, 242 (1960).

ever, the large increase as one proceeds from $3d^1$ to $3d^3$ or $5d^1$ to $5d^3$ is not expected.[5] We suggest that this results from the enhanced s-electron polarization produced by the s-d exchange interaction.

It is noteworthy that the linewidths of Sc, V, Nb, and La are all considerably larger than the direct nuclear dipole-dipole interaction would allow. Since all these elements have single isotopes of overwhelming abundance any indirect exchange interaction would not produce line broadening.[6] The field independence of the linewidth and the line shapes exclude both quadrupolar and anisotropic magnetic contributions. These facts, combined with the Gaussian shape and the temperature independence of the linewidth, indicate a pseudodipolar origin for the observed line shapes.

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[1] C. H. Townes, C. Herring, and W. D. Knight, Phys. Rev. 77, 852 (1950), W. D. Knight, Solid State Physics, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1956), Vol II, p. 93.

[2] J. M. Lock, Proc. Phys. Soc. (London) B70, 566 (1957). This author reports a Curie-Weiss behavior with the Curie constant indicating an effective magnetic moment of one-half of a Bohr magneton.

[3] R. M. Bozorth (private communication).

[4] K. Yosida, Phys. Rev. 106, 893 (1957).

[5] One must of course allow for the fact that all of the $4f$ elements occur between La and Ta.

[6] M. A. Ruderman and C. Kittel, Phys. Rev. 96, 99 (1954).

NUCLEAR MAGNETIC RESONANCE IN α AND β MANGANESE

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(Received May 27, 1960)

The properties of the nuclear magnetic resonance (NMR) of Mn^{55} in α and β Mn have been investigated as a function of field and temperature.[1] A very broad asymmetric NMR ($\delta H \sim 250$ oe) was observed in αMn at 295°K. The center of gravity of the resonance corresponds to a negative Knight shift (k) (see Table I). Since there are four magnetically inequivalent sites,[2] it was first thought that the line shape was the result of superposition of several resonances. However, a negligible field dependence was observed for the shape of the line. The α phase is known to have an antiferromagnetic transition at 95°K.[3] Correspondingly, no resonance was visible at 77°K and 20.2°K in the randomly oriented powdered sample.

In βMn only a single resonance line was found, although there occur two physically inequivalent sites. The value of k observed as a function of

Table I. The temperature dependence of the Knight shift in βMn as observed at 14.245 Mc/sec. An error of ± 0.02% exists in each of the values given. k was determined with respect to the Mn^{55} NMR in a saturated solution of $LiMnO_4$ and in $KMnO_4$. The field for resonance in the two solutions is identical to one part in 10^5. No chemical shifts have been reported for Mn^{55} in the literature.

T (°K)	k (%)
1.8	-0.11
4.2	-0.11
20.2	-0.12
77	-0.13
190	-0.13
295	-0.13