Nuclear Magnetic Resonance and Magnetic Susceptibility of SmAl₃*

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The Knight shift of the Al^{27} NMR in $SmAl_3$ has been measured in the temperature region from 78 to 400°K, and the susceptibility of $SmAl_3$ has been measured up to 850°K. The part of the Knight shift arising from polarization of the conduction electrons through exchange with the $4f$ electrons reverses sign at (310 ± 20) °K, and the relation between the Knight shift and the susceptibility is not linear. This behavior results mainly from Van Vleck-type paramagnetism, and could adequately be calculated on the basis of free Sm^{3+} ions. The parameters used are the multiplet splitting constant $A/k = (410\pm20)$ °K, and the interionic exchange constant $\mathcal{J}_{ff}/k = -(15\pm5)$ °K, indicating antiferromagnetic ordering at low temperatures. The effective exchange constant between the conduction-electron spins and the $4f$-electron spins has been found to be $\mathcal{J}_{sf} = -0.21$ eV, equalling those derived for other RAl_3 compounds (R = rare earth). The nuclear quadrupole coupling has been measured to be $|e^2qQ|/h = (0.8\pm0.1)$ Mc/sec, and is discussed in terms of the point-charge model.

I. INTRODUCTION

DURING the last years there have been several investigations on the Knight shifts of rare-earth intermetallic compounds in relation to the susceptibilities, viz., the Knight shift of the Al nucleus in various RAl_2 [1,2] and RAl_3 [3] compounds, and the Knight shift of the Sn nucleus in RSn_3 [4,5] compounds. In interpreting the results it is assumed that the spin polarization of the conduction electrons is enhanced through an exchange interaction of the form

$$\mathcal{H} = -\mathcal{J}_{sf}\mathbf{S}\cdot\mathbf{s} \qquad (1)$$

between the localized $4f$-electron spins $\mathbf{S}$ of the rare-earth ions and the conduction electron spins $\mathbf{s}$. Then, if K_0 is the Knight shift due to Pauli paramagnetism, the total shift K is given by

$$K = K_0[1 - \mathcal{J}_{sf}\langle S_z\rangle/g_s\beta H], \qquad (2)$$

where $g_s(\approx 2)$ is the conduction electron g value. The expectation value $\langle S_z\rangle$ is usually taken to be proportional to the $4f$-electron susceptibility per rare-earth ion χ_f/N. That is,[1]

$$K = K_0[1 + \mathcal{J}_{sf}(g_f - 1)\chi_f/g_s g_f N\beta^2], \qquad (3)$$

where g_f is the $4f$-electron g value. By measuring both the Knight shift and the susceptibility as a function of the temperature, the linear relationship between K and χ_f, as expressed by Eq. (3), has been found for many members of the rare-earth series.[3-5] These measurements make it possible to determine the phenomenological exchange constant $\mathcal{J}_{sf}$. For RAl_2 compounds $\mathcal{J}_{sf}\approx -0.16$ eV has been found, for RAl_3 $\mathcal{J}_{sf}\approx -0.23$ eV, and for RSn_3 $\mathcal{J}_{sf}\approx -0.08$ eV.

For the linear relation between S_z and χ_f to be valid, only the ground multiplet level of the rare-earth ion should be involved. In the case of Sm^{3+}, however, the intervals between the lower multiplet levels are so narrow that temperature-independent Van Vleck terms,[6] associated with the second-order Zeeman effect, contribute appreciably to the Knight shift and the susceptibility. Considerable deviations from Eq. (3) are to be expected. White and Van Vleck[7] have already shown that, as a consequence of the second-order Zeeman effect, the part of the Knight shift due to the $4f$-electron spin reverses sign at a temperature of say 300°K. In addition, there are contributions arising from excited multiplet levels populated mainly at high temperatures.

II. EXPERIMENTAL

A. Preparation

The samples of $SmAl_3$ were prepared by melting together the constituent metals in proper proportion on the copper hearth of an arc furnace with a thoriated tungsten rod as the nonconsumable electrode. The metals samarium and aluminum were 99.9% and 99.99%

[1] V. Jaccarino, B. Matthias, M. Peter, H. Suhl, and J. H. Wernick, Phys. Rev. Letters **5**, 251 (1960); V. Jaccarino, J. Appl. Phys. Suppl. **32**, 102 (1961).
[2] E. D. Jones and J. I. Budnick, J. Appl. Phys. **37**, 1250 (1966).
[3] A. M. van Diepen, H. W. de Wijn, and K. H. J. Buschow, J. Chem. Phys. **47**, 3489 (1967).
[4] R. G. Barnes, F. Borsa, and D. Peterson, J. Appl. Phys. **36**, 940 (1965).
[5] V. Udaya Shankar Rao and R. Vijayaraghavan, Phys. Letters **19**, 168 (1966).
[6] J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (Oxford University Press, Oxford, England, 1932), p. 233ff.
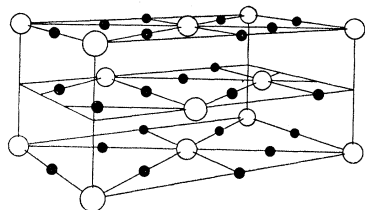[7] J. A. White and J. H. Van Vleck, Phys. Rev. Letters **6**, 412 (1961).

FIG. 1. Part of the lattice of SmAl₃. Larger white circles represent Sm^{3+} ions; smaller black circles Al^{3+} ions. The crystallographic structure (see Ref. 10) is the hexagonal Ni_3Sn structure, with space group $P6_3/mmc$. Dimensions of the unit cell are $a=6.380$ Å and $c=4.597$ Å. The Al ions, as well as the Sm ions, are at equivalent sites.

pure, respectively. After charging the furnace with the weighted amounts of the starting materials the furnace chamber was thoroughly evacuated before admitting argon gas. The argon was freed from oxygen and nitrogen by passing it over magnesium at 600°C. To ensure homogeneity the alloy buttons were turned and remelted several times.

The phase diagram[8] of the Sm-Al system, and the crystallographic structure[9] of SmAl₃ have been described earlier. While the structure of SmAl₂ is a cubic Laves phase, SmAl₃ crystallizes in the hexagonal Ni_3Sn structure (Fig. 1). It was shown by x-ray diffraction that after annealing in vacuum for two weeks at about 800°C in a sintered Al_2O_3 crucible the samples were
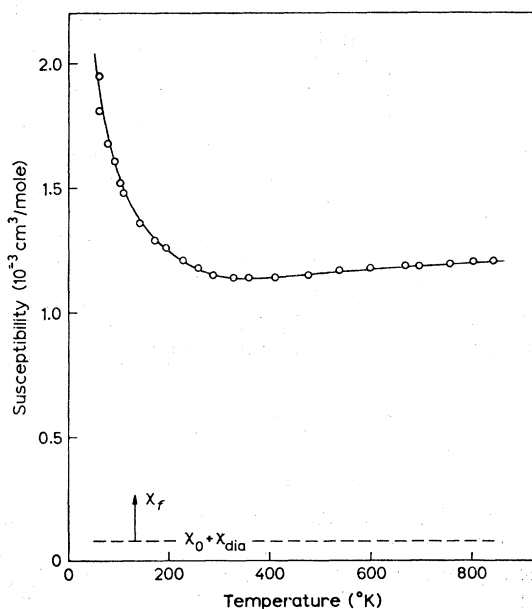

FIG. 2. The magnetic susceptibility of SmAl₃ as a function of the temperature.

[8] K. H. J. Buschow and J. H. N. van Vucht, Philips Res. Rept. **20**, 15 (1965); (to be published).
[9] J. H. N. van Vucht and K. H. J. Buschow, J. Less-Common Metals **10**, 98 (1965).

free of any second phase. The alloy buttons thus obtained were crushed to fine powder, and used for the NMR and susceptibility measurements.

B. Susceptibility Measurements

Earlier measurements[10] of the susceptibility of SmAl₃ have been re-examined and extended to higher temperatures. The measurements were performed with a Curie balance and with a null-coil pendulum magnetometer. For the measurements from 300 to 850°K the SmAl₃ powder was sealed in an evacuated silica tube to prevent oxidation by air. Experimental values of the susceptibility are plotted versus the temperature in Fig. 2. At the temperature of liquid helium, SmAl₃ is antiferromagnetic. The Néel temperature is below 20°K.
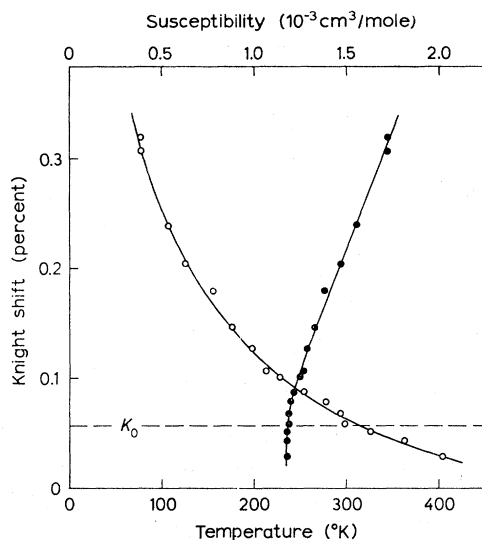

FIG. 3. The Knight shift of the Al^{27}NMR in SmAl₃ as a function of the temperature (open circles), and the Knight shift as a function of the susceptibility with the temperature as parameter (black circles).

C. NMR Measurements

The NMR of the Al^{27} nucleus $(I=\frac{5}{2})$ has been examined in the paramagnetic region of SmAl₃, from 400 to 78°K. The spectrometer used is a crossed-coil induction spectrometer, operating at a fixed frequency of 5 Mc/sec, followed by phase-sensitive detection. Magnetic-field measurements were made by the use of proton magnetic resonance, and the Al resonance of the diamagnetic nonmetallic solid $AlCl_3$ was taken as reference for the determination of the Knight shifts. The Knight shift K_0 arising from Pauli paramagnetism

[10] K. H. J. Buschow and J. F. Fast, Z. Physik. Chem. (Frankfurt) **50**, 1 (1966). The susceptibility data given in this paper for SmAl₃ were obtained with 99.0% pure samarium [see Ref. 8]. Re-examination with purer starting material revealed that these data are too high, probably because of the high impurity content.

has been measured in LaAl₃, isostructural with SmAl₃, and found to be temperature-independent,[3]

$$K_0 = +(0.056 \pm 0.010)\%.$$

In Fig. 3 the Knight shift has been plotted versus the temperature and the susceptibility. For SmAl₃, $K - K_0$ changes sign, in contrast with the other RAl₃ compounds; the crossover temperature is

$$T_{co} = (310 \pm 20)\,°K.$$

The curve obtained by plotting the Knight shift versus the susceptibility, although nearly linear in the temperature region, does not intersect the Knight shift axis in K_0. This clearly demonstrates that Eq. (3) does not apply to the case of Sm³⁺ ions in intermetallic compounds.

Since the point symmetry of the Al site is noncubic, nuclear quadrupole interaction is allowed. To first order, the $m = +\frac{1}{2} \leftrightarrow -\frac{1}{2}$ transition remains unshifted, whereas in the case of axial symmetry the other four $\Delta m = \pm 1$ transitions are shifted by amounts

$$\pm [3e^2qQ/4I(2I-1)](3\cos^2\theta - 1),$$
$$\pm [6e^2qQ/4I(2I-1)](3\cos^2\theta - 1). \quad (4)$$

Here q is the electric field gradient, Q is the quadrupole moment of the Al²⁷ nucleus, and θ is the angle between the applied magnetic field and the axis of the field gradient. In a powdered sample, the orientations of the field gradient axis are random, so that θ takes on all values between 0 and π, the contributions to the line intensity being proportional to $\sin\theta$. At $\theta = \pi/2$ the intensity has a maximum, and in the spectrum four satellites of the central $m = +\frac{1}{2} \leftrightarrow -\frac{1}{2}$ transition are observed. From the spacings between the satellites e^2qQ has been derived to be

$$| e^2qQ |/h = (0.8 \pm 0.1)\ \text{Mc/sec}.$$

The quadrupole coupling affects the resonance field of the central transition to second order, and this effect should be discussed in order to derive the Knight shift, which is of pure magnetic origin.[11] The second-order shift of the resonance field is

$$\frac{9}{64} \frac{2I+3}{4I^2(2I-1)} \frac{(e^2qQ)^2}{\gamma^2\hbar^2 H_0} (1-9\cos^2\theta)(1-\cos^2\theta), \quad (5)$$

where γ is the gyromagnetic ratio of the Al nucleus. The shift of the center of the quadrupole broadened $m = +\frac{1}{2} \leftrightarrow -\frac{1}{2}$ transition can now be calculated to be $\approx\frac{1}{4}$ G. This shift is a few times smaller than the experimental error in the determination of the resonance field and the Knight shift K. In the *differential* shift $K - K_0$, the second-order shifts of SmAl₃ and LaAl₃ cancel, and consequently quadrupole effects do not interfere in the determination of T_{co}.

III. DISCUSSION

A. 4f-Electron Magnetism

The exchange fields which the Sm³⁺ ions exert on each other are through the Ruderman-Kittel-Kasuya-Yosida[12] mechanism operative in a metal, rather than through direct exchange coupling encountered in nonconducting magnetic materials. In a molecular field approximation the exchange field is given by

$$\beta H_{ex} = -\mathcal{J}_{ff}\langle S_z \rangle_{av}, \quad (6)$$

where "av" denotes Boltzmann averaging over the J multiplet levels, split by the spin-orbit coupling $A\mathbf{L}\cdot\mathbf{S}$.

The Knight shift, which results from the exchange interaction between the conduction electrons and the 4f-electrons, is proportional to $\langle S_z \rangle_{av}$. The susceptibility associated with 4f electrons is proportional to $\langle L_z + 2S_z \rangle_{av}$. In calculating these quantities for a Sm³⁺ ion perturbed by the external field H, which acts on $L_z + 2S_z$, and the exchange field H_{ex}, which acts on S_z, we proceed along the lines pointed out in Van Vleck's book.[6] Both S_z and $L_z + 2S_z$ have matrix elements which are nondiagonal in J because $\mathbf{S}$ and $\mathbf{L}+2\mathbf{S}$, unlike $\mathbf{J}=\mathbf{L}+\mathbf{S}$, are not constants of the motion, and the fields therefore mix the different J states. Second-order perturbation theory results in the following expressions:

$$\frac{\langle S_z \rangle_{av}}{H} = -\left\{\sum_J p(J)\left[\frac{(g_f-1)a}{g_fT}+b\right]\right\}\left\{1-\frac{2\mathcal{J}_{ff}}{\beta}\sum_J p(J)\left[\frac{(g_f-1)^2a}{g_f^2T}+b\right]\right\}^{-1}, \quad (7)$$

$$\frac{\langle L_z+2S_z \rangle_{av}}{H} = -\sum_J p(J)\left[\frac{a}{T}+b\right]-\frac{2\mathcal{J}_{ff}}{\beta}\left\{\sum_J p(J)\left[\frac{(g_f-1)a}{g_fT}+b\right]\right\}^2\left\{1-\frac{2\mathcal{J}_{ff}}{\beta}\sum_J p(J)\left[\frac{(g_f-1)^2a}{g_f^2T}+b\right]\right\}^{-1}, \quad (8)$$

[11] A. C. Gossard, V. Jaccarino, and J. H. Wernick, Phys. Rev. **128**, 1038 (1962); W. H. Jones, T. P. Graham, and R. G. Barnes, *ibid.* **132**, 1898 (1963).

[12] M. A. Ruderman and C. Kittel, Phys. Rev. **96**, 99 (1954); T. Kasuya, Progr. Theoret. Phys. (Kyoto) **16**, 45 (1956); K. Yosida, Phys. Rev. **106**, 893 (1957).
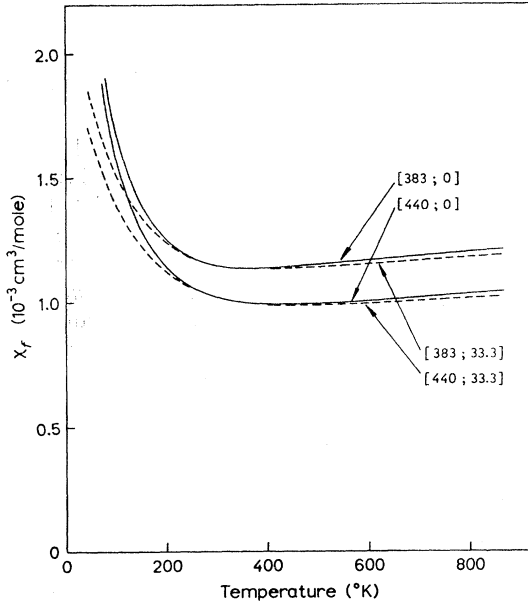
FIG. 4. The theoretical $4f$-electron susceptibility χ_f versus the temperature. Numbers in brackets denote A/k and $-\mathcal{J}_{ff}/k$ in °K, respectively.

in which $p(J)$ are the Boltzmann factors of the multiplet levels, and

$$a = \beta g_f{}^2 J(J+1)/3k, \quad (9)$$

$$b = \frac{-\beta}{6(2J+1)}\left[\frac{F(J+1)}{E_J{}^{(0)}-E_{J+1}{}^{(0)}}+\frac{F(J)}{E_J{}^{(0)}-E_{J-1}{}^{(0)}}\right], \quad (10)$$

with

$$F(J) = [(S+L+1)^2 - J^2][J^2-(J-L)^2]/J. \quad (11)$$

At low temperatures, where all Sm^{3+} ions are in the $^6H_{5/2}$ ground level, Eqs. (7) and (8) reduce to forms that can be made identical with the expressions given by White and Van Vleck.[7] If the multiplet splitting is very large, excited levels are negligibly populated and Van Vleck terms vanish. In this case Eqs. (7) and (8) reduce to the Curie-Weiss forms

$$\langle S_z\rangle_{\mathrm{av}}/H = -(g_f-1)a/g_f(T-T_\theta), \quad (12)$$

$$\langle L_z+2S_z\rangle_{\mathrm{av}}/H = -a/(T-T_\theta), \quad (13)$$

in which the paramagnetic Curie temperature T_θ is given by

$$T_\theta = 2\mathcal{J}_{ff}(g_f-1)^2a/\beta g_f{}^2. \quad (14)$$

Elimination of the temperature now leads to a linear relation, Eq. (3), between the Knight shift and the susceptibility, independent of the exchange constant $\mathcal{J}_{ff}$.

B. Susceptibility

The total susceptibility at a temperature T is given by

$$\chi(T) = \chi_f(T) + \chi_0 + \chi_{\mathrm{dia}}. \quad (15)$$

The Pauli susceptibility χ_0 and the diamagnetic susceptibility χ_{dia} are small relative to the $4f$-electron susceptibility χ_f. They have been estimated by measuring the susceptibility of the nonmagnetic compound $LaAl_3$:

$$\chi_0+\chi_{\mathrm{dia}} = +0.08\times10^{-3} \text{ cm}^3/\text{mole}.$$

The $4f$-electron susceptibility has been calculated on the basis of Eq. (8) and the relation

$$\chi_f = -N\beta\langle L_z+2S_z\rangle_{\mathrm{av}}/H. \quad (16)$$

The results of these calculations are plotted in Fig. 4 for various combinations of the multiplet splitting constant A and the exchange constant $\mathcal{J}_{ff}$. It is noted that at the higher temperatures the population of the first excited multiplet level contributes by about one third to the susceptibility. The best fit of the theoretical curves to the experimental points (Fig. 2) is obtained for

$$A/k = (410\pm20)°K,$$

$$\mathcal{J}_{ff}/k = -(15\pm5)°K.$$

This value of A equals the values obtained for Sm^{3+} ions in nonconducting compounds,[6] such as the oxide, and corresponds to a screening number σ of the Sm^{3+} ion between 33 and 34. The negative exchange constant $\mathcal{J}_{ff}$ indicates that at low temperatures $SmAl_3$ becomes antiferromagnetic, which has been found experimentally. The paramagnetic Curie temperature, as approximated by Eq. (14), is about $-45°K$.
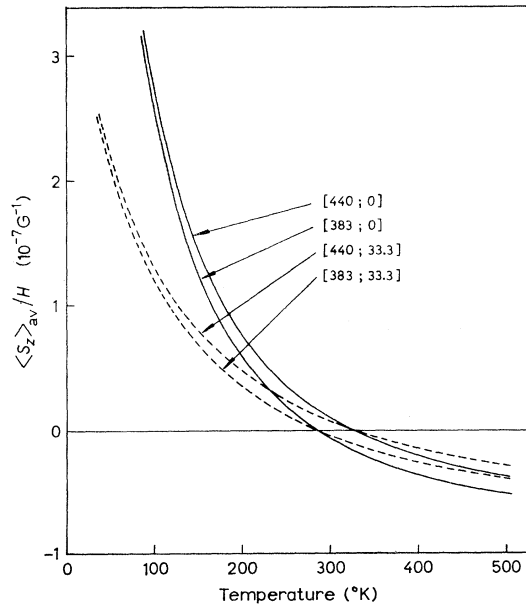

FIG. 5. The theoretical $4f$-electron spin polarization per unit field strength $\langle S_z\rangle_{\mathrm{av}}/H$ versus the temperature, as calculated from Eq. (7). Numbers in brackets denote A/k and $-\mathcal{J}_{ff}/k$ in °K, respectively.

C. Knight Shift

We express the Knight shift as a function of the temperature as

$$K(T) = K_f(T) + K_0 + \delta K_{\text{dia}}. \tag{17}$$

Because $K(T)$ has been measured with reference to the Al resonance in $AlCl_3$, only the differential diamagnetic shift enters into Eq. (17). This differential shift is negligible relative to the other shifts. The Knight shift due to $4f$-electron polarization K_f is related to $\langle S_z \rangle_{\text{av}}$ through [cf. Eq. (2)]

$$K_f(T) = -K_0 \mathcal{J}_{sf} \langle S_z \rangle_{\text{av}} / g_s \beta H. \tag{18}$$

Since K_f is proportional to $\mathcal{J}_{sf}$, which is to be determined, it cannot be calculated from Eq. (7) in the way χ_f has been calculated from Eq. (8).

In Fig. 5, values of $\langle S_z \rangle_{\text{av}}/H$, calculated with use of Eq. (7), have been plotted for various combinations of A and $\mathcal{J}_{ff}$. The crossover temperature, i.e., the temperature of change of sign of $K_f(T)$, is given by

$$T_{\text{co}} = -\sum_J p(J) \frac{(g_f-1)a}{g_f} \Big/ \sum_J p(J)b. \tag{19}$$

T_{co} depends on A through b, but is independent of the exchange constant $\mathcal{J}_{ff}$. If only the lowest multiplet level is populated, Eq. (19) reduces to

$$T_{\text{co}} = -(g_f-1)a/g_f b = 5a/2b$$

for Sm^{3+} (cf. Ref. 7).

For $A/k = 410°K$, the value derived from the susceptibility data, we have from Eq. (19) the theoretical value $T_{\text{co}} = 304°K$. This number is in agreement with the experimental value $T_{\text{co}} = (310 \pm 20)°K$. Best fitting of the theoretical curves of $\langle S_z \rangle_{\text{av}}/H$ versus T to the experimental graph of K versus T is obtained for

$$\mathcal{J}_{sf} = -0.21 \text{ eV.}$$

D. Nuclear Quadrupole Coupling

The nuclear quadrupole coupling constant e^2qQ of the Al^{27} nucleus in $SmAl_3$ will be compared to the value in $SmAl_2$, for which we have measured $|e^2qQ|/h = 4.4$ Mc/sec. Both for $SmAl_3$ and $SmAl_2$ the electric field gradient q at the site of the Al nucleus has been calculated on the basis of the point-charge model. Rare-

earth and aluminum ions being considered to be trivalent positive, the symmetry at the Al nucleus is axial in both compounds. The electric field gradient operator $(3\cos^2\varphi_i - 1)/r^3$ has been summed over all lattice positions within a sphere with radius of 20 Å. The ratio of the calculated quadrupole couplings in $SmAl_3$ and $SmAl_2$ is 0.214, which is in good agreement with the experimental ratio 0.18. The magnitude of $|e^2qQ|$, as derived from the summations with $Q = 0.149 \times 10^{-24}$ cm² and the theoretical antishielding factor $\gamma_\infty = -2.36$,[13] is 1.37 Mc/sec in $SmAl_3$, and 6.44 Mc/sec in $SmAl_2$. Comparison with experiment suggests that the trivalent point charges are screened in part by the conduction-electron charge distribution.

IV. CONCLUDING REMARKS

The anomalous behavior of the Knight shift and the susceptibility in $SmAl_3$ as a function of the temperature can adequately be described in terms of the model of free Sm^{3+} ions. The reason for this is that crystalline fields are weak, and do not substantially influence the Knight shift and susceptibility in the temperature region above say 70°K. The Sm^{3+} ions being at a site of hexagonal symmetry, the $^6H_{5/2}$ ground multiplet level splits into three Kramers doublets. In the Laves phase RAl_2, where the crystalline field at the rare-earth site is of cubic symmetry, the splitting is of the order of a few hundred degrees Kelvin.[14] Numerical calculations using point charges at the lattice positions show that the crystalline field parameters of a Sm^{3+} ion in RAl_3 are smaller by an order of magnitude compared to those in RAl_2.

Experiment and theory have shown that the linear relation between the Knight shift and the susceptibility expressed by Eq. (3) is broken down because of appreciable contributions of Van Vleck-type paramagnetism. Nevertheless, it is possible to determine the phenomenological exchange constant $\mathcal{J}_{sf}$. The value of $\mathcal{J}_{sf}$ derived for $SmAl_3$ equals those derived for other members of the RAl_3 series within the experimental error. It is not unlikely that also for other samarium intermetallic compounds, such as $SmAl_2$, a $\mathcal{J}_{sf}$ can be found, which is consistent with the $\mathcal{J}_{sf}$ of the isostructural compounds of other rare-earth ions.

[13] R. M. Sternheimer, Phys. Rev. **146**, 140 (1966).

[14] J. A. White, H. J. Williams, J. H. Wernick, and R. C. Sherwood, Phys. Rev. **131**, 1039 (1962).