# SIGN OF KNIGHT SHIFT IN SAMARIUM INTERMETALLIC COMPOUNDS

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Measurements of the $Al^{27}$ nuclear resonance in rare-earth aluminum intermetallic compounds have shown that in these compounds the Knight shifts are large, temperature dependent, and may have either sign, depending on whether the spin polarization of the rare earth ions is parallel or antiparallel to the applied field.[1] These observations in general accord with the Zener-Ruderman-Kittel-Yosida mechanism[2] whereby conduction electrons are polarized by an exchange interaction between them and the rare earth ion spins, provided one assumes that this interaction has the opposite sign from that originally proposed by Zener. The samarium compound is unlike the others, however, in that the sign of the rare earth contribution to the Knight shift reverses in going from 77°K to room temperature.[3] It is the purpose of this note to show that this anomalous reversal in $SmAl_2$ is a consequence of theory when the second-order Zeeman effect is included.

We shall at first ignore the effect of the crystalline field, and assume that the exchange fields which the rare earth ions exert on each other, and on the conduction electrons which they polarize, are proportional to the expectation value of the spin of the samarium ion. If we neglect saturation, the formulas for the magnetic moment of the $Sm^{+++}$ and for this expectation value are

$$M_{\mathrm{Sm}} = aN\beta(H_0 - 5H_{\mathrm{ex}})T^{-1} + bN\beta(H_0 + 2H_{\mathrm{ex}}), \quad (1)$$

$$\langle S_z\rangle_{\mathrm{Sm}} = \tfrac{5}{2}a(H_0 - 5H_{\mathrm{ex}})T^{-1} - b(H_0 + 2H_{\mathrm{ex}}), \quad (2)$$

where

$$a = \beta g^2 J(J+1)/3k = 5\beta/21k, \quad b = 20\beta/7h\nu_{7/2,\,5/2}.$$

Note especially that the coefficients of $H_0$ and $H_{\mathrm{ex}}$ have the opposite sign in the $1/T$ term; this is because in $Sm^{+++}$ $g = 2/7$, and so $2(g-1)/g = -5$. The factor 2 in the second part of (1) or (2) has its origin in the fact that the matrix elements of $2S$ nondiagonal in $J$ are double those of $L+2S$ since $L+S$ is diagonal. The above formulas are obtained by adapting the standard expression[4] for the susceptibility of $Sm^{+++}$ to include an exchange field $H_{\mathrm{ex}}$ acting only on the spin in addition to the applied field $H_0$, in essentially the same fashion as was done by Wolf and Van Vleck for europium garnet.[5] In the case of $Sm^{+++}$, it is sufficient for our purposes to consider only the lowest multiplet component as inhabited, but it is essential to include the part of the susceptibility arising from the "temperature-independent paramagnetism," or second-order Zeeman effect, represented by the second part of (1) or (2).

The "crossover point," i.e., point of change in sign for the contribution of the $Sm^{+++}$ to the Knight shift, is that at which both $\langle S_z\rangle = 0$ and $H_{\mathrm{ex}} = 0$. It is consequently given by $T_{\mathrm{co}} = 5a/2b$. [The exchange field which polarizes the conduction electrons is not necessarily the same as that in (1) or (2) acting on the rare earth ions, but both are taken proportional to $\langle S_z\rangle$.] The interval $h\nu_{7/2,5/2}/k$ is about 1500°K, and so according to (2) the value of $T_{\mathrm{co}}$ is about 300°K. The predicted sign behavior is in accord with experiment; i.e., the $Sm^{+++}$ contribution to the Knight shift in $SmAl_2$ has at low and high temperatures, respectively, the opposite and the same sign as the $Gd^{+++}$ contribution to the Knight shift in $GdAl_2$. The observed value of $T_{\mathrm{co}}$ is about 150°K. However, $T_{\mathrm{co}}$ is hard to locate with precision, and also the above theory is a crude one which neglects such refinements as the crystalline field, and the effect of orbital orientation on exchange coupling.

Since the $Sm^{+++}$ ion is known to be at a site of cubic symmetry,[6] the effect of the crystalline field is to split the $J = 5/2$ level into a doublet and a quartet. Formulas (1) and (2) must then be modified by multiplying the $1/T$ terms by the factor[7]

$$f(T) = \frac{5/21 + (26/21)e^{-h\nu_c/kT} + (32\,kT/21h\nu_c)\left(1 - e^{-h\nu_c/kT}\right)}{1 + 2e^{-h\nu_c/kT}}, \quad (3)$$

where $h\nu_c$ is the splitting between the doublet and the quartet, and has a sign which is positive if the doublet lies lowest and negative if the quartet lies lowest. The temperature-independent terms in (1) and (2) will be little affected if crystalline splittings are small compared to the multiplet separation. It is seen from (3) that the effect of a crystalline field will, in general, be to reduce $T_{\rm co}$, thus giving improved agreement with experiment. The reduction will not be great, however, unless $h\nu_c \sim kT_{\rm co}$. Further discussion of this point must await a more accurate experimental value for $T_{\rm co}$.

At the crossover point, the susceptibility of the $Sm^{+++}$ ion in an applied field should not be influenced by the exchange couplings between $Sm^{+++}$ ions. This accords with measurements of Williams and Sherwood who find that at room temperature the susceptibility is[8] $\chi_M = 9.9 \times 10^{-4}$, in agreement with the theoretical value for free, uncoupled $Sm^{+++}$ ions.[4]

In closing we may note an interesting reciprocal relation between (1) and (2). The temperature at which an applied field generates no $\langle S_z \rangle$ is also the temperature at which an exchange field, acting alone, produces no magnetic moment. Hence in, say, samarium garnet, the exchange field from the ferric ion should induce no magnetic moment in the samarium in the vicinity of room temperatures. So it is experimentally. In fact, the difference between the magnetic moments of YIG and SmIG is found by Pauthenet to be practically zero throughout the range from 0°K to the Néel point.[9] The vanishing of the susceptibility in an exchange field at a particular temperature is not by itself enough to explain the magnetic inertness of the samarium in the garnet for all temperatures, and presumably at low temperatures the effect of the crystalline field should be included. Our attempts to obtain theoretically the requisite inertness have not yet met with quantitative success, and more complete experimental data on the magnetic behavior of the samarium garnets are highly desirable.

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