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NMR of SmMn$_2$Ge$_2$ at high pressure

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Abstract

The $^{147}$Sm, $^{149}$Sm and $^{57}$Mn NMR of SmMn$_2$Ge$_2$ has been observed at 4.2 K at pressures up to 6.5 kbar. The Sm resonance frequencies appear to be insensitive to pressure but the Mn frequency decreases under pressure. The Mn resonance has also been observed at 77 K at atmospheric pressure, but disappears under a pressure of 1.6 kbar in agreement with the phase boundary between FM and AFM proposed earlier.

1. Introduction

At atmospheric pressure SmMn$_2$Ge$_2$ is a re-entrant ferromagnet [1-5]. The phase diagram is shown in Fig. 1, taken from Ref. [3]. There are some discrepancies as to the values for the temperature and pressure of the phase transitions (see Ref. [4] for a review), but the general appearance of Fig. 1 is not in dispute.

The crystal structure of SmMn$_2$Ge$_2$ is of the body-centred tetragonal BaAl$_4$ type [6] with the two crystallographically inequivalent Al sites occupied by Mn and Ge atoms. The atoms of each type lie on planes perpendicular to the c-axis with the sequence Mn-Ge-Sm-Ge-Mn. The intralayer Mn or Sm distance is much smaller than the interlayer distance.

The change from ferromagnetism to antiferromagnetism of SmMn$_2$Ge$_2$ below 150 K at atmospheric pressure was attributed [1] to the Mn-Mn spacing dropping below a critical distance for ferromagnetic interactions. (The Sm magnetisation is not thought to be significant at 150 K.) This view is supported by the positive slope of $dT_N/dP$ [2,3], and the observation of a first order decrease in the lattice constant along the a-axis in the antiferromagnetic region [2]. The reversion of SmMn$_2$Ge$_2$ to the ferromagnetic state below 100 K was attributed [1] to ferromagnetic ordering of the Sm causing the Mn movements to align ferromag-

Fig. 1. The phase diagram for SmMn$_2$Ge$_2$, adapted from Ref. [3].

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Table 1
The NMR frequencies and effective fields for SmMn₂Ge₂

<table>
<thead>
<tr>
<th>Nucleus</th>
<th>T (K)</th>
<th>ν (MHz)</th>
<th>Bₑ (T)</th>
<th>(∂ ln ν / ∂ P) (Mbar⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>⁵⁵Mn</td>
<td>273</td>
<td>144.7</td>
<td>-13.7</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>77</td>
<td>189.0</td>
<td>-17.9</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>4.2</td>
<td>187.3</td>
<td>-17.7</td>
<td>-3.68(5)</td>
</tr>
<tr>
<td>¹⁴⁹Sm</td>
<td>4.2</td>
<td>475.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>¹⁴⁷Sm</td>
<td>4.2</td>
<td>576.6</td>
<td>330</td>
<td>0.00(3)</td>
</tr>
<tr>
<td>Sm free ion</td>
<td>338</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Footnote: *FM to AFM transition.*

The high pressure experiments were carried out in a new 10–1000 MHz phase coherent swept frequency spin echo spectrometer that will be described elsewhere. The spectra were recorded by integrating the spin echo at each frequency as described in Ref. [7]. The NMR frequencies are tabulated in Table 1. The Sm NMR frequencies were converted to an effective field allowing for a hyperfine anomaly as discussed in Ref. [8].

2. ⁵⁵Mn NMR

The ⁵⁵Mn NMR spectrum at atmospheric pressure and 4.2 K, shown in Fig. 2, consists of a single line some 3 MHz wide. There is no sign of quadrupole splitting (⁵⁵Mn, I = 5/2) of the NMR in the frequency swept spectrum, but the presence of an electric field gradient (EFG) is indicated by the modulation of the spin echo decay [9]. At 4.2 K the transverse relaxation time (T₂) is 400 μs and the modulation of the spin echo decay leads to a quadrupole splitting of 60 kHz, i.e. much less than the width of the inhomogeneously broadened line. At 77 K and above, the value of T₂ was so short, ~5 μs, that it was impossible to measure the modulation period of the echo.

Under pressure at 4.2 K the ⁵⁵Mn NMR frequency decreased (Table 1). Since the main contribution to the effective field at the ⁵⁵Mn nucleus arises from the contact interaction with the Mn moment, this suggests that the magnetisation of SmMn₂Ge₂ at 4.2 K decreases under pressure, supporting the view that wide spacing of the Mn atoms is essential for ferromagnetism in rare earth–Mn intermetallic compounds.

The ⁵⁵Mn NMR frequency at 77 K is higher than at 4.2 K although the magnetisation per formula unit has decreased from 3.8μₘ to 3.2μₘ. This would suggest that the Mn moment has hardly changed between 4.2 K and 77 K, T/Tₘ ~ 0.2, while the Sm moment, 0.7μₘ at 4.2 K, has largely collapsed. The proposal [1] that the Sm moment stabilises the ferromagnetic Mn interactions below 100 K may therefore be incorrect.
The $^{55}$Mn NMR could not be observed under pressure at 77 K; a pressure of less than 1.6 kbar was sufficient to destroy the signal.

The $^{55}$Mn NMR was also observed in the high temperature ferromagnetic phase at 273 K. The ratio of the $^{55}$Mn NMR frequency at 77 K and 273 K (Table 1) is equal to that of the magnetisation reported in Ref. [2], confirming that the Sm does not contribute significantly to the magnetisation in this range.

3. Sm NMR

The $^{147}$Sm and $^{149}$Sm NMR exhibit the seven line quadrupole split spectrum expected for nuclear spin $7/2$ (Fig. 2). The $^{149}$Sm quadrupole splitting was also observable as a modulation on the spin echo decay. It is unusual to be able to measure a quadrupole interaction by both methods in a given material.

The effective field at the Sm nucleus in SmMn$_2$Ge$_2$ is estimated to be 330 T, significantly less than the free Sm$^{3+}$ ion value of 338 T (see Ref. [8] for a discussion of the conversion of Sm NMR frequencies to effective fields). The largest contribution to the Sm effective field comes from the orbital motion of the 4f electrons of the parent atom which will induce a field parallel to the magnetisation. The 8T discrepancy between SmMn$_2$Ge$_2$ and the free Sm$^{3+}$ ion value presumably arises from a transferred effective field from the Mn moments. However, under pressures up to 6.5 kbar no change was observed in the frequency of the Sm central NMR line to an accuracy of ± 0.03 Mbar$^{-1}$ in $(\partial \ln \nu / \partial P)$. Since the Mn moment, assumed to be proportional to the $^{55}$Mn NMR frequency, has decreased by 2.4% by 6.5 kbar, a simple model would predict $\partial \ln \nu / \partial P \approx + 0.08$ Mbar$^{-1}$ for Sm. The decrease in the Mn moment under pressure must therefore be compensated by the decrease in the Mn–Sm distance.

The quadrupole splitting of the $^{147}$Sm ($^{149}$Sm) NMR at 4.2 K, 8.6 (2.4) MHz, is significantly less than the free ion values of 9.7 (2.8) MHz (see Ref. [8]), showing that the lattice contribution to the EFG has the opposite sign to the dominant 4f contribution. The value of $(\partial \ln \nu / \partial P)$ was estimated to be less than 0.3 Mbar$^{-1}$ which is consistent with our estimate of 0.1 Mbar$^{-1}$ if only the lattice contribution changes with pressure.

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