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High-field Knight shifts of impurity nuclei in ferromagnets using NMRON

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Abstract. Following an earlier proposal that meaningful Knight shift values for dilute impurities in ferromagnets may only be deduced from NMRON field shift measurements performed in large applied magnetic fields ($B_{\mathrm{app}} > 1$ T), an extensive literature search has been undertaken, to assess the effects of this proposal on over twenty years of field shift NMRON studies. This literature search ultimately reveals only four systems ($< 8\%$ of studies) satisfying the above prerequisite. The associated systems are ^{60}CoFe and $^{103\mathrm{m}}$RhFe, with non-zero Knight shift values of $K = +1.5(0.4)\%$ and $K = -5.6(1.7)\%$ respectively; and ^{54}MnNi and ^{125}SbFe with effectively zero Knight shifts. From these results, suggestions for further studies are proposed.

1. Introduction

Positive Knight shifts in the elemental (i.e. host-like NMR probe) ferromagnetic 3d transition metals ^{59}CoCo (HCP) (Fekete *et al* 1976), ^{57}FeFe (Oppelt *et al* 1980) and ^{61}NiNi (Kropp *et al* 1982) have long been established using conventional nuclear magnetic resonance (NMR). It is therefore disconcerting that despite over two decades of field shift studies of dilute impurities in iron, cobalt and nickel hosts using NMR on oriented nuclei (NMRON), no clear systematic trends have emerged with respect to signs (let alone magnitudes) of Knight shifts of the radioactive probe impurities. Indeed, there have been substantial variations in quoted Knight shifts reported in the NMRON literature for nominally identical (i.e. specific impurity–ferromagnetic host) systems (e.g. Leuthold *et al* (1980), cf Eder *et al* (1985a) on ^{97}RhFe and Eder *et al* (1985a); cf Nishimura *et al* (1986) on $^{101\mathrm{m}}$RhFe). This inability to derive sensible systematics with respect to impurity Knight shifts points to problems symptomatic of the NMRON technique, or procedures different to those employed in the conventional NMR studies of the pure elements.

In a recent publication (Yazidjoglou *et al* 1992), we proposed that it was necessary to perform NMRON field shift measurements in fields significantly greater than 1 T in order to obtain meaningful values for the Knight shift. This proposal was based on experimental results obtained for well aligned, bulk single-crystal ^{54}MnNi and ^{125}SbFe with B_{app} parallel to principal crystal axes. The results in that study showed

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a significant discrepancy in deduced impurity Knight shifts depending on whether low- ($0.3\ \mathrm{T} \leqslant B_{\mathrm{app}} \leqslant 0.8\ \mathrm{T}$) or high-field ($1.0\ \mathrm{T} \leqslant B_{\mathrm{app}} < 8.0\ \mathrm{T}$) data sets were considered.

In this communication, we look at the consequences of this proposal on the previous 20 years of NMRON field shift studies on impurity nuclei. The subsequent rationalization of the very large number of field shift studies (as indicated below) leads to a much smaller, though more coherent picture, wherein a non-zero impurity Knight shift is far less prevalent.

2. Results and discussion

From 1974 to the present, over sixty field shift studies of dilute impurities in ferromagnets using NMRON have been reported in which a Knight shift could, in principle, be extracted. This Knight shift would be based on existing excited state moments at somewhat lesser, but still acceptable precision, compared to the ground state moments used for the Knight shift determination of the elemental ferromagnets. A further approximate twenty studies have provided current best estimates of the excited state nuclear magnetic dipole moments on the basis of assuming the Knight shift, K, to be zero. The impurity mass range extends from ^{48}VFe (Bures *et al* 1980) through to ^{198}AuFe (Hagn and Eska 1974) for Fe hosts, and ^{52}MnNi (Hagn *et al* 1982, Eder *et al* 1985b) through to ^{198}AuNi (Hagn and Zech 1984) for Ni hosts.

However, in contrast to the NMR experiments on the elemental ferromagnets where the *smallest* applied magnetic field employed for field shift measurements was 2.0 T (Oppelt *et al* 1980), only twelve NMRON field shifted studies approach or better this magnitude of field. Of the sixty or so systems where a zero Knight shift was not assumed, > 80% of the NMRON field shift data are reported with *maximum* fields of the order of 1 T.

In view of the discrepancies between low- and high-field data sets, and the sensible nature of the Knight shifts determined from the high-field data as presented in Yazidjoglou *et al* (1992), some doubt must be cast on Knight shifts quoted from low-applied-field data. Possible sources for the intrinsic distortion of low-field data result from processes such that

$$\mathrm{d}M/\mathrm{d}B_{\mathrm{app}} \neq 0.$$

These processes include the various ferromagnetic anisotropies, such as strain anisotropy, shape anisotropy and magnetocrystalline anisotropy, which have the tendency to misalign, in low fields, the host magnetization M with respect to the applied field, and are thus potential sources of non-linearity in the field shift data. In addition there may also be a local impurity hardness. This non-linearity has also recently been observed on well aligned, single-crystal ^{125}SbNi $\langle 111 \rangle$ (to be presented at a later date), where preliminary results indicate $\simeq 3\%$ discrepancy in the Knight shift between low- and high-field data sets with $K = +1.2(1.5)\%$ at high fields (2 T to 7.5 T). These mechanisms are the subject of a parallel study, to be published elsewhere. The purpose of this communication is to pursue the sensibility of the systematics that emerge when only high-field data are considered.

There are three systems in the above-mentioned high-field studies, with potentially large spin–orbit electric quadrupole interactions (EQIS) ($A_{\rm impurity} \geqslant 150$); specifically, ^{192}IrFe (Daly *et al* 1976), ^{192}IrNi (Daly *et al* 1976) and ^{183}TaFe (Murray 1982). In these investigations the deduction of a centre resonance frequency, ν_0, was determined by the inclusion of the sign and magnitude of the EQI in the line-fitting analysis of the resonance lineshapes. However, the as-yet unexplained magnetic field dependence of the amplitudes of the individual quadrupolar subresonances (see Hagn *et al* (1981b) and Hagn *et al* (1980)), places a severe uncertainty on any ν_0 and hence K-value determined. For this reason alone, these three systems are eliminated from the high-field data set to yield the list of studies presented in table 1. Of the remaining nine high-field impurity studies, embracing five systems (MnNi, CoFe, RhFe, InFe and SbFe), there are only four high-field *non-zero* Knight shift studies determined to date by NMRON techniques. These are, ^{56}CoFe (Back *et al* 1985), ^{60}CoFe (Foster *et al* 1981), $^{103\rm m}$RhFe (Kempter and Klein 1977) and $^{114\rm m}$InFe (Lattimer and Stone 1979).

On initial inspection, the existence of a significant Knight shift for $^{114\rm m}$InFe (negative hyperfine field) is puzzling, in that In is unlikely to have a local moment in Fe. However, this result was obtained by comparison of $d\nu_0/dB_{\rm app}$ with the nuclear moment deduced from the *same* NMRON data set, linearly extrapolated back to zero field. This can lead to incorrect deductions (see, e.g., Chaplin and Hutchison 1992). In the case of linear extrapolation for a negative hyperfine field, too high a moment is always deduced (see Kempter and Klein 1977); the degree of error depending on, *inter alia*, the extent of the effective demagnetizing fields in the ferromagnetic sample. As a consequence it is possible to deduce an apparent negative Knight shift even if the correct hyperfine field is known. In contrast the $^{103\rm m}$RhFe result follows from a zero field intercept, obtained by following the low-field curvature back to (almost) zero field, and can therefore be considered as more reliable. (The large value of $-5.6(1.7)\%$ is unlikely to be reduced to below the uncertainty in the result, even with a better method of determining the moment.)

The ^{60}CoFe Knight shift result, however, is referred to an excited state moment obtained from a non-magnetic host (Niesen and Huiskamp 1972), as is also the case for ^{54}MnNi (Niesen and Huiskamp 1970). The ^{56}CoFe Knight shift result is obtained from a ^{56}Co moment determined by a direct comparison of resonant frequencies with co-diffused ^{60}Co, thereby obviating difficulties due to differences in demagnetizing fields. The ^{125}Sb reference moment is traceable to an experiment with resonance precision on a non-magnetic host (^{122}SbSi; Pipkin 1958). It should be noted that the ^{122}Sb and ^{125}Sb moment values which appear ostensibly as 'bare' magnetic dipole moment values in Lederer and Shirley (1978) are in fact diamagnetically uncorrected values, and are hence the correct values to use in impurity-doped ferromagnetic NMRON Knight shift studies.

3. Conclusion

To date, only two impurity systems, CoFe and MnNi, have been investigated to sufficiently high magnetic fields to approach potentially a meaningful Knight shift measurement, *and* have well determined nuclear moments from non-magnetic hosts

Table 1. Field shift studies where sufficiently large applied magnetic fields have been used to determine Knight shifts. Also included are NMR elemental Knight shift studies.

Sample	Deduced Knight Shift	Max. Field	Reference
HIGH FIELD NMRON IMPURITY KNIGHT SHIFT STUDIES			
^{54}MnNi <100>	0.0(0.2)% #	7.8T	Yazidjoglou *et al* 1992
^{54}MnNi <111>	-0.2(0.2)% #	5.0T	Pax 1985
^{56}CoFe	+2.3(1.5)%	3.0T	Back *et al* 1985
^{60}CoFe	+1.5(0.4)%	8.05T	Foster *et al* 1981
^{103m}RhFe	-5.6(1.7)% *	1.4T	Kempter and Klein 1977
^{114m}InFe	-2.4(0.6)%	1.5T	Lattimer and Stone 1979
^{125}SbFe <110>	+0.2(1.4)% #	8.0T	Yazidjoglou *et al* 1992
^{125}SbFe <112>	+0.5(1.4)% #	8.0T	Yazidjoglou *et al* 1988
^{125}SbFe <100>	+0.6(1.4)% #	8.0T	Yazidjoglou *et al* 1988
HIGH FIELD NMR ELEMENTAL KNIGHT SHIFT STUDIES			
^{57}FeFe	+ 0.78(0.10)%	2.0T	Oppelt *et al* 1980
^{59}CoCo(hcp)	+ 1.94(0.25)%	6.5T	Fekete *et al* 1976
^{61}NiNi	+ 0.90(0.27)%	2.7T	Kropp *et al* 1982

Knight shifts which can be considered as zero within experimental accuracy.
* As interpreted by Eder *et al* (1985a) and Hagn *et al* (1981a). Not as stated by Kempter and Klein (1977).

at a level of precision comparable with that of the stable probes used in the elemental studies. The absence of a measurable Knight shift for ^{54}MnNi is significant, being in contrast to the non-zero positive Knight shifts obtained for ^{57}FeFe, ^{59}CoCo and ^{61}NiNi. The +1.5(0.4)% Knight shift obtained for ^{60}CoFe is consistent with the earlier observations that the Co impurity provides a relatively host-independent Knight shift due to Van Vleck orbital paramagnetism at the impurity site (NMR on Co compounds, Walstedt *et al* 1967).

To a lesser degree of precision, a non-zero Knight shift, $K = -5.6(1.7)\%$, and zero Knight shift, is deduced for the RhFe and SbFe systems respectively. The zero Knight shifts of MnNi and SbFe offer no evidence for van Vleck orbital paramagnetism, which is to be expected due to the lack of any orbital angular momentum associated with the Mn and Sb wavefunctions. Conversely, the CoFe and RhFe results, whose impurity elements both appear in the same group in the Periodic Table, suggest that genuine non-zero impurity Knight shifts reflect predominantly the degree of unquenched orbital angular momentum at the impurity site. The need to expand this data base (as defined by table 1) using large magnetic fields ($\gg 1$) on other systems with nuclear moments of requisite precision is necessary. To this end studies on MnFe, RhFe and IrFe would be particularly informative.

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