Quadrupole coupling at ^{193}Ir nuclei in iron[*]

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Mössbauer-source experiments on Fe(^{193}Os) alloys with less than 0.1-at.% osmium show that quadrupole coupling persists in domains at high dilution, thereby confirming and extending the earlier NMR results of Aiga and Itoh on wall resonances and the Mössbauer results of Wagner and Potzel on a more concentrated alloy. Arguments are presented to show that a Mössbauer spectrum on a more concentrated alloy can yield a reasonably accurate value of e^2qQ, including its sign, even in the presence of substantial solute-solute-induced magnetic and quadrupole perturbations. For the ground state of ^{193}Ir in iron, this work yielded $e^2qQ/2h = -2.05(25)$ MHz, $\nu_0 = 119.6(3)$ MHz, and $H_{hf} = 1481(4)$ kOe.

I. INTRODUCTION

Hyperfine magnetic fields at nuclei of solute atoms occupying substitutional sites in ferromagnetic lattices are well known. Quadrupole hyperfine structure may also be present in such solutes, even in a cubic host lattice such as iron. Quadrupole interactions could arise from solute-solute effects, lattice distrotion at the impurity site, spin-orbit interactions in combination with nonzero $\langle S_z \rangle$, or perhaps from effects peculiar to domain walls. Recently two values have been reported for the quadrupole splitting of ^{193}Ir in iron. Aiga and Itoh[1] observed clearly resolved satellites at $\Delta\nu(=|e^2qQ/2h|)$ = 2.5 MHz above and below the main line in the spin-echo NMR spectrum of $Ir_{0.003}Fe_{0.997}$. Wagner and Potzel[2] analyzed the ^{193}Ir Mössbauer spectrum of and $Ir_{0.03}Fe_{0.97}$ alloy to yield $e^2qQ/2h = 1.6 \pm 0.3$ MHz. Here h is Planck's constant. The disagreement between these two values leaves the situation regarding induced quadrupole structure at solutes in ferromagnets in a rather unsatisfactory state, because Fe(Ir) is an important prototype for such systems. In an attempt to resolve this discrepancy, we have studied a very dilute alloy by Mössbauer spectroscopy. The experiments are described in Sec. II and compared with the earlier results in Sec. III.

II. EXPERIMENTAL

Mössbauer-*source* experiments were performed, in order to study Fe(Ir) systems sufficiently dilute that solute-solute interactions could be neglected. It has become increasingly clear in recent years that even a 1-at.% solution in a ferromagnetic host cannot be regarded as dilute in the above sense. In fact for the Fe(Ir) system, the quadrupole structure is not even resolved in the NMR spectrum at 1-at.% concentration.[3] Our source alloys were made up by co-melting neutron-irradiated ^{192}Os with 99.99% pure iron in an argon arc furnace, thereafter pressed into thin discs and annealed in a

hydrogen atmosphere. The compositions of these alloys were ≤ 0.1-at.% osmium. An upper limit is given because there was some loss of osmium in the melting procedure. If solute-solute interactions are truly negligible at this concentration, it should of course be irrelevant whether the solute is mostly osmium or iridium.

The absorbers for the 73.1-keV γ ray of ^{193}Ir were 90-mg/cm^2 iridium foils of 99.99% purity. Since iridium has an fcc structure, the absorption spectrum directly replicates the emission spectrum from the source alloy. All measurements were made at 4.2 K in zero magnetic field.

The Mössbauer-absorption spectrum from one sample is shown in Fig. 1. The resolution of the eight components is considerably better than that obtained by Wagner and Potzel, suggesting that the spectrum of their 3-at.% alloy was seriously affected by inhomogeneous broadening. Our spectra were analyzed using the hyperfine spin Hamiltonian

$$\mathcal{H} = -g\mu_N H_{hf} I_z + \frac{e^2qQ}{4I(2I-1)}[3I_z^2 - I(I+1)] \quad , \quad (1)$$

to yield the parameters given in Table I. Here we have assumed the quadrupole interaction to be cylindrically symmetric. In this analysis we used the fixed g-factor ratio $g(\frac{1}{2})/g(\frac{3}{2}) = 8.874(13)$ for the ground and 73.2-keV states of ^{193}Ir given by Wagner and Potzel, to facilitate comparison with their results (the derived value of this ratio should be insensitive to inhomogeneous broadening). The ground-state magnetic moment was taken as $\mu(\frac{3}{2}) = +0.10591(6)\mu_N$ for the purpose of deriving H_{hf}, which was found to have a value of 1481(4) kOe.

III. DISCUSSION

In making comparisons of our data with the earlier results, also set out in Table I, it is important to bear in mind the differences among the three experiments. The NMR measurements detected ^{193}Ir nuclei in domain walls, while most of the Mössbauer signal involved nuclei within domains. In the Möss-

TABLE I. Derived parameters for Fe(^{193}Ir).

Sample	ν_0 (MHz)	$eqQ/2h$ (MHz)	Isomer shift (mm/sec)	Reference
$Os_{0.001}Fe_{0.999}$	119.5(4)	−2.13(37)	1.017(7)	This work
$Os_{0.001}Fe_{0.999}$	119.6(4)	−1.98(34)	1.027(8)	This work
Average	119.6(3)	−2.05(25)	1.022(5)	This work
$Ir_{0.003}Fe_{0.997}$	119.0	2.5[a]	· · ·	1
$Ir_{0.03}Fe_{0.97}$	121.4(1.7)[b]	−1.6(3)	· · ·	2

[a]Only absolute value measured.
[b]Derived from parameters given in Ref. 2.

bauer spectra, but not the NMR spectrum, the sign of e^2qQ is detectable. Finally, the concentration of Ir in the 3-at. % sample studied by Wagner and Potzel was so high as to compromise its value as a dilute Fe(Ir) system.

We note that the average ground-state hyperfine frequency $\Delta\nu_\mu = g(\frac{3}{2})\mu_N H_{hf}$ given by Aiga and Itoh agrees quite well with our value [119.0 vs 119.6(3) MHz]. Thus the hyperfine fields in domains and walls appear to be essentially the same. The higher value of 121.4(1.7) MHz calculated from the data quoted by Wagner and Potzel presumably arises through the inclusion of unresolved high-frequency satellites in the analysis of their spectrum. A simple statistical calculation shows that in a 3-at. % alloy, 55% of the Ir atoms will have at least one Ir atom among its first-three-neighbor shells.

Because of the large perturbative effect of neighboring solute atoms on NMR spectra in alloys of a few percent concentration, manifest as intense satellite lines,[4] together with the large field gradients that these neighbors probably create, one might expect the value of e^2qQ obtained from the $Ir_{0.03}Fe_{0.97}$ alloy[2] to bear little relation to the NMR value.[1] In fact, as Table I shows, the earlier Mössbauer value agrees with ours in sign and is surprisingly close in magnitude. The reason for this

FIG. 1. Mössbauer absorption spectrum of a Fe(^{193}Ir) source against a 90-mg/cm^2 Ir absorber at 4.2 °K, with a least-squares fit. The derived linewidth was $\frac{1}{2}\Gamma$ = 0.460(8) mm/sec. If the lines are numbered 1 − 8 from the left, the quadrupole interaction is manifest as a barely perceptible relative shift of lines 1, 4, 5, and 8 to the right.

behavior is of some interest because of its general applicability in comparing Mössbauer and NMR spectra. To understand this result let us consider first a case in which the quadrupole coupling arises entirely through spin-orbit interaction plus spin polarization. In a 3-at. % (or even 1-at. %) alloy, near-neighbor interactions would lead to various hyperfine magnetic fields statistically distributed among the solute atoms, and most likely the quadrupole interaction would be completely obscured in an NMR spectrum. The Mössbauer spectrum is sensitive to the *sign* of e^2qQ, however. By applying Eq. (1) to the excited and ground states, taking differences, allowing H_{hf} to vary slightly, and performing a weighted sum, it is easily shown that e^2qQ contributes coherently to the average, shifting the energy of each line by $\frac{1}{4}e^2qQ$, with the sign of the shift for each component determined by whether the corresponding ground-state $|\mu_I|$ value is $\frac{3}{2}$ or $\frac{1}{2}$. Thus in Fig. 1, for example, the two lines at − 5 and − 7 mm/sec are separated in energy by e^2qQ more than those at + 7 and + 9 mm/sec. Thus the *presence of magnetic satellites arising from solute-solute interactions would have little effect on the value of e^2qQ derived from a Mössbauer spectrum.*

If solute near neighbors induce substantial field gradients the situation is changed somewhat, but not as much as one might expect. The magnetic interaction is still dominant, and the quantization axis is essentially along $\vec{H}_{hf}$. Since the contributions to the field-gradient tensor arising from $\langle S_z \rangle$ plus $\vec{I} \cdot \vec{s}$ would, if taken alone, have a principal axis collinear with $\vec{H}_{hf}$, this ($\langle S_z \rangle$ plus $\vec{I} \cdot \vec{s}$) interaction is not affected by the magnetic hyperfine interaction: it gives diagonal contributions to the energy matrix and contributes linearly to shifts in the spectral lines as indicated above. In contrast, contributions to the quadrupole interaction from near neighbors will be practically random relative to $\vec{H}_{hf}$. The diagonal components of this interaction will have both positive and negative signs, and they alone would contribute incoherently to line shifts, in the ensemble average. Since the two quadrupole interactions have different principal axes, the net effect of the neighbor-induced quadrupole interaction is a
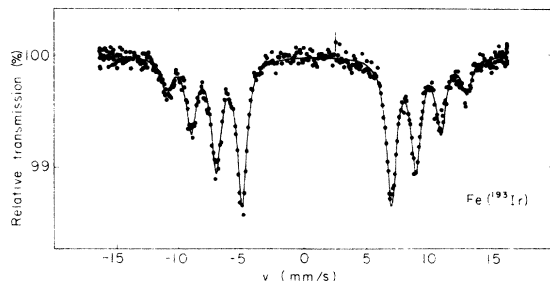
reduction of the observed quadrupole shifts, as is apparently observed in the $Ir_{0.03}Fe_{0.97}$ alloy (Table I).

There appears to be a discrepancy between the $e^2qQ/2h$ value of Aiga and Itoh (2.5 MHz)[1] and ours (2.05 ± 0.25 MHz), although the width and asymmetric structure of their quadrupole satellites casts some doubt on this conclusion. Higher-resolution NMR studies will be valuable in elucidating this question. Budnick and co-workers[5] have recently been able to obtain higher-resolution NMR spectra showing well-resolved quadrupole satellites.

In summary this work strongly supports the existence of quadrupole interactions in dilute Fe(Ir) systems and establishes the sign of e^2qQ as negative, in agreement with the more concentrated alloy results of Wagner and Potzel. Taken together, the three studies to date may be interpreted in terms of a quadrupole interaction at Ir nuclei in iron that arises through spin-orbit plus spin-polarization ($\vec{I} \cdot \vec{s}$ plus $\langle S_z \rangle$) effects, and that is present both in domains and in walls. Aiga and Itoh suggested this mechanism to explain their observations.[1,3] They showed that only a very small value of $\langle S_z \rangle$ is required, together with the large spin-orbit coupling constant in iridium, to explain quadrupole coupling of the observed magnitude. The apparent value of e^2qQ decreases slowly with concentration, as expected. The magnetic hyperfine field is the same within 0.3% between domains and walls, but appears to increase in the 3-at.% alloy.

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[3]J. Itoh (private communication to D. A. Shirley).

[4]J. I. Budnick, T. J. Burch, S. Skalski, and K. Raj, Phys. Rev. Lett. 24, 511 (1970).

[5]J. I. Budnick (private communication to D. A. Shirley).