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Abstract. Co alloys with Cr, Fe, Ru and Cu in the low concentration range have been studied by ^{59}Co NMR. Regularly spaced satellite lines are observed that develop with increasing impurity concentration. The satellite intensities as a function of the impurity concentration have been compared with the binomial distribution law of particular Co environments. Deviations from the exact binomial law in some cases are briefly discussed against the properties of their respective phase diagrams. From this comparison it is concluded that satellite frequencies are primarily determined by the number of impurity atoms in the first neighbour shell: each additional impurity atom in the shell introduces a constant (element-dependent) modification to the hyperfine field value on a Co site. This assignment of satellite frequency shifts to given configurations in the first coordination shell provides references for structural investigations in related binary metallic systems such as metallic multilayers. Preliminary results for CoPt alloys are also presented which do not follow the systematics of the previous alloys but rather suggest an extended oscillating perturbation around Pt impurities.

1. Introduction

Recent developments in materials technology stress the importance of structural analysis on the nanoscopic scale. Nuclear magnetic resonance (NMR) can provide useful information in this matter since the hyperfine field (hereafter named HF) experienced by a nucleus depends very sensitively on the number and nature of atoms in its neighbourhood. If analysed carefully, the NMR spectrum reflects the probabilities of occurrence, in a given sample, of various chemical and topological configurations around the probed nuclei. From this point of view NMR and other nuclear techniques provide unique information which can be compared in terms of distance probed (1 to 2 atomic distances with the EXAFS technique. However, while EXAFS yields information about distances and average number of neighbours, NMR gives only qualitative information about distances but more detailed information about neighbour distributions. To this information should be added the possibility of discriminating between various phases, in particular different crystal structures of the same system, and evaluating their respective concentrations.

There have been recent advances in the theoretical *ab initio* calculations of HFs in ferromagnetic systems but they are practically limited to cases of extreme dilution (the HF on an isolated impurity and in some cases on the nearest neighbours of

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this impurity) ([1] and references therein). Cases of more concentrated binary alloys have also been investigated but mostly from the viewpoint of an average HF on both elements [2]. At the present stage such calculations yield HF values that are reasonably close to experimental results but predictions of the detailed relationship between the HF and the character of the local environment are still barely achievable, particularly in alloys and other systems that are inhomogeneous on an atomic scale. Moreover there have been much less theoretical investigations of Co-based systems than of Fe- and Ni-based ones, while NMR is more suitable for studies of Co-containing systems. Therefore in order to obtain quantitative information on the modification of the HF due to the presence of one, two or several impurity atoms in the neighbourhood of the matrix element, one has to rely on experimental studies of reference samples. For example, in order to study a particular system containing two species, one can consider for reference disordered bulk binary alloys, ordered compounds if they exist, or both. With such a purpose in mind we shall examine in this paper some Co-based alloys that can help to shed some light on the nanostructure of buried interfaces in corresponding metallic multilayers.

The crystal structure of Co consists of regularly arranged planes of densely packed Co atoms. Depending on the stacking order of the subsequent Co layers one of the two crystal structures will be formed: a hexagonal-close-packed (HCP) structure in the case of ABABAB stacking or a face-centred-cubic (FCC) structure for ABCABC stacking. In both structures the Co atom has 12 nearest neighbours (hereafter called NNs). The deviation from an ideal HCP stacking sequence leads to the two possible FCC stacking faults [3]: ABAbCBC (growth fault) and ABAbcACA (deformation fault). Similarly, in the FCC phase two kinds of HCP stacking faults are possible: ABCaCBA (twinning) and ABCacABC. At low temperatures, HCP is the most stable phase with a martensitic transition at 417 °C. Alloying with another metal can also stabilize one of the two phases. However, unless a special heat treatment has been applied, the mixture of the two phases as well as stacking faults are often encountered in a real material.

Both crystallographic Co phases are ferromagnetic, giving an NMR signal at slightly different frequencies. In FCC Co the NMR frequency extrapolated to 0 K is 217.2 MHz [4]. In HCP Co hyperfine fields reveal a considerable anisotropy which gives an NMR frequency along the c axis of 220 MHz, and in the c plane of 228 MHz [5]. In samples with some FCC/HCP phase admixture two more lines are observed corresponding to the stacking faults ([6, 7] for CW spectra and figure 1 for a spin-echo spectrum). In addition to the two stable crystallographic structures, HCP and FCC, Co can be artificially forced to assume a metastable BCC phase in certain conditions [8]. We and others have shown recently the presence of this phase in epitaxial Co/Fe multilayers [9, 10]. The NMR frequency of Co in the BCC phase is lower than in HCP and FCC (198 MHz at 1.6 K) [9].

When an alien element is introduced in the crystal lattice, local modifications of the electronic structure, of distances (relaxation), of the number and strength of surrounding moments, etc affect the HF on the surrounding matrix nuclei. Consequently one expects that the effects of local environment will manifest themselves in the form of new lines in the NMR spectrum. Such lines, systematically related to the main line (thus called satellite lines) have indeed been observed in a number of Co alloys. The first reports on Co NMR in a series of FCC Co alloys with Fe, Ni, Cu, Al, Mo and Cr were made by Koi *et al* [11]. Satellite structures on both sides of the Co line for CoFe and for CoNi and on the low-frequency side for other
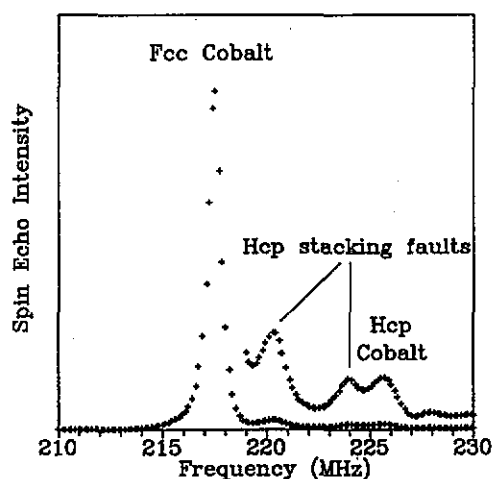
Figure 1. The spin-echo NMR spectrum of FCC Co containing a small amount of HCP stacking faults (the high-frequency side, magnified 10 times).

alloys have been observed and interpreted as due to the oscillatory polarization of s electrons around an impurity site.

Studies of FCC alloys with such elements as Ti, V, Cr, Cu, Al, Si, Ge, Nb at concentrations between 1% and 5% have been carried out at 77 K by Kobayashi *et al* [12]. One satellite line has been observed and interpreted as due to impurity atoms in the NN coordination shell. Alloys of HCP Co with 0.5% concentration of Ti, V, Cr, Mn, Fe, Ni and Cu have been studied by Kawakami [13] at 4.2 K. For Ti, V, Cr and Mn this author observes two well separated satellites which are interpreted as arising from a single impurity in the first shell; the modification of the HF would be different according to the position of the impurity in the same (00.1) plane as the central Co atom or in adjacent planes. For Fe, Cu and Ni, satellites close to the main line were observed for which no clear assignment was given.

A wide range of impurities has been studied by Durand [14], for concentrations between 0.5% and 3.5% at 300 K. Two types of satellite lines have been distinguished, based on their position with respect to the main line and the concentration dependence of the intensity. One is connected with isolated impurity atoms in the first coordination shell and the other with a strongly interacting pair of impurity atoms. In another study (CoCu alloys up to 8%) two satellites were observed and attributed to configurations with two impurity atoms in the first neighbour shell [15].

Also, a number of other alloys which are not in the scope of this paper, have been studied, such as CoV [16], CoNi [17], and iron-rich CoFe [18]. While all the authors agree that satellite lines are due to the matrix atoms which have impurities in their neighbourhood, their particular interpretations were controversial. The results are difficult to compare because the experiments were not performed under the same conditions. The studied concentrations were usually too low to observe more than one satellite. In addition, in very diluted alloys, the main line is narrow enough so that satellites can be resolved close to the main line (sometimes on both sides of that line) that are due to impurities in shells further than the nearest one. Indeed the purpose of these studies was different from ours as their main interest was in the modification of the matrix electronic structure due to diluted (non-interacting) impurities.

More generally, it should be remembered that those papers were pioneering

works in the field of NMR in magnetic materials and the experimental techniques were not very sophisticated. Recent progress in data acquisition and elaboration of results allow reproducible spectra to be obtained with reliable intensities over broad frequency ranges. Therefore it is now possible to follow reliably the evolution of satellite intensities as a function of concentration on a wider range, where a fair number of satellites can be observed (although detailed structures associated with the configuration of shells further than the NN shell are lost in the broadening of the lines). The need for a more extended concentration range is stressed by the ambiguities and disagreements that one can find among the previous studies where satellite assignment was simply speculated or merely based on the initial slope of one or two satellite intensities in the 1% impurity concentration range.

   Such a study has been undertaken in the present work for CoCr, CoCu, CoRu and CoFe alloys. The case of CoPt alloys will also be briefly presented. The fact that there have been no clear satellite assignments in the literature for the present alloys motivated us for this study. Besides, we like to process reference samples with the same instrument and analysis methods as the system which is the principal objective of investigation (corresponding multilayers in this case). The experimental NMR observations in these alloys will be discussed in the last section of the paper in terms of applicability as references for structural (chemical short-range-order) investigations of related binary systems.

2. Experimental details

The alloys of Co with Cr, Cu, Ru, Fe and Pt with at least three different impurity concentrations (2, 6, and 10%) were prepared by quenching from the melt then ground and heat treated appropriately to stabilize a solid solution and, as far as possible, a single phase as determined from the respective phase diagrams. In the case of CoFe and CoPt alloys the studied crystallographic phase was FCC. Cr and Ru favour the HCP phase. To avoid demixing in CoCu alloys no annealing treatment was performed on those samples and although Cu favours an FCC growth the present bulk samples present some phase admixture.

   ^{59}Co NMR experiments were performed in zero magnetic field at 4.2 K. The integrated spin-echo intensity was recorded every 1 MHz using a coherent pulsed NMR spectrometer with phase-sensitive detection and automated frequency scanning. The NMR spectra were taken at five different values of the excitation RF field, covering a range over more than one order of magnitude. Such a procedure allowed us to determine the optimum excitation field at each frequency and to correct for the variation of the local electronic susceptibility and thus of the NMR enhancement factor as a function of frequency. After this a further correction for the usual ω^2 frequency dependence of the NMR signal was applied. The NMR amplitudes obtained in such a way represent the true distribution of nuclei with a given HF.

3. Results

Figure 2 represents the corrected NMR spectra for a series of CoCr alloys at various concentrations (2–14%). For 2% Cr, in addition to the main line corresponding to Co with pure Co surrounding, a first satellite line becomes visible that is asymmetric. This

asymmetry is a reminiscence of the twin satellites observed by Kawakami [13] which broaden and merge with increasing Cr content, confirming this author's interpretation that they have the same origin, one neighbour impurity, but that they are split by the anisotropy of HCP Co. At increasing Cr concentration, up to three satellite lines are resolved followed by an unstructured tail at lower frequencies. At 14% the intensity of the first satellite is already stronger than that of the main line and the whole spectrum is shifted towards low frequencies.
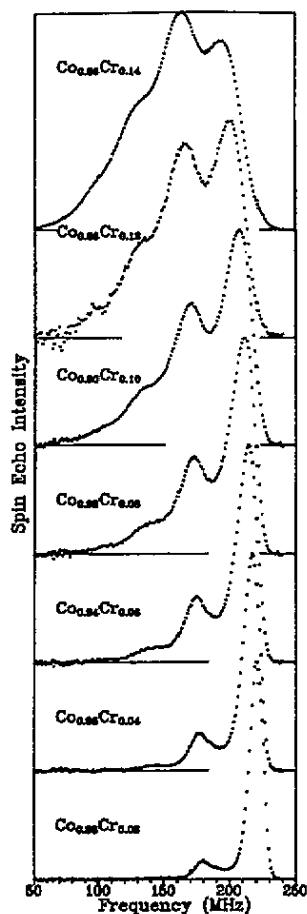

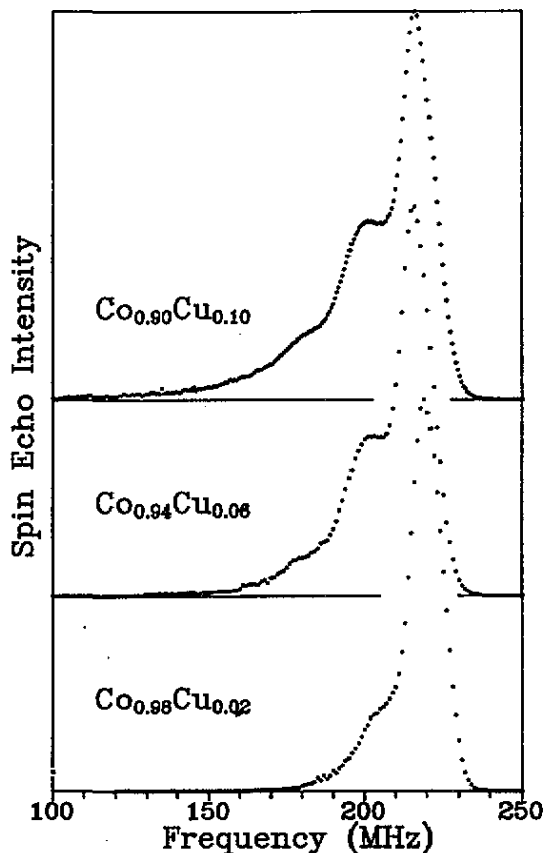**Figure 2.** ^{59}Co NMR spectra in CoCr HCP alloys ($T = 4.2$ K).

Figure 3. ^{59}Co NMR spectra in CoCu HCP alloys ($T = 4.2$ K).

^{59}Co NMR spectra in CoCu, CoRu and CoFe alloys are presented in figures 3, 4 and 5, respectively. All of them exhibit a structure with at least two resolved satellites.

The integral intensity of these satellites must be related to the probability of finding a particular configuration in the sample at a given impurity concentration. If the impurity is distributed randomly in the sample this probability should follow the binomial distribution law. A comparison of theoretically calculated probabilities with the experimental intensities of satellites as a function of Cr concentration is presented
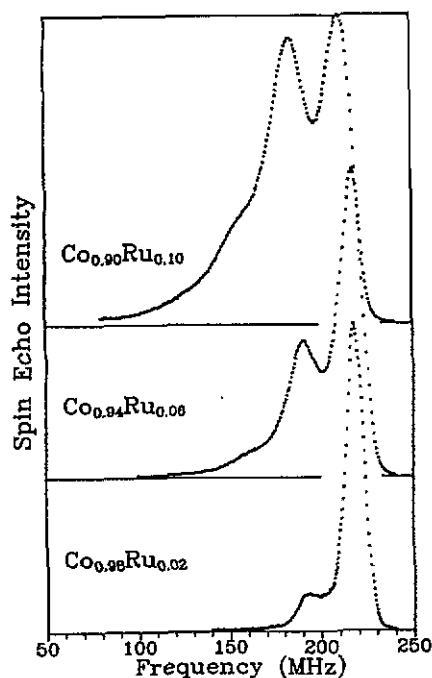
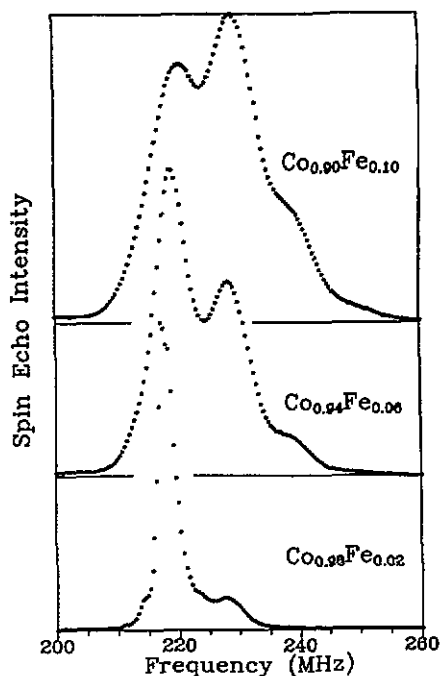**Figure 4.** ^{59}Co NMR spectra in CoRu FCC alloys ($T = 4.2$ K).

Figure 5. ^{59}Co NMR spectra in CoFe FCC alloys ($T = 4.2$ K).

in figure 6(*a*). The general behaviour of satellite intensities is correctly predicted by the binomial distribution on 12 sites; this makes us assign with confidence the first, second and third satellites to Co with one, two and three Cr NNs. The deviation from an exact binomial law (higher content of Co atoms surrounded by 12 Co neighbours and missing intensity of all the satellites, especially in the low concentration range) indicates a tendency to segregate between Co and Cr and a reduced miscibility of the two atoms for low concentrations of Cr. Indeed, there is still quite a lot of confusion concerning the phase diagram for CoCr and several versions of it have been published in the literature. Theoretical calculations predict a miscibility gap in the 2–22% Cr concentration range [19]. This shows that the system is not yet well understood and a more detailed NMR study, which we have undertaken and which will be published elsewhere, may shed some light on its phase diagram.

The satellite assignment in the other alloys was founded on the same basis as for CoCr above. Indeed, the concentration dependence of the satellite intensity, as shown in figure 6(*b*)–(*d*), demonstrates that CoRu and CoFe alloys follow quite closely the binomial distribution law. Actually, CoRu alloys exhibit quite a simple phase diagram with a solid solution extending over the full concentration range, this explaining the present result. The situation is more complicated for CoFe alloys as there is a transition from the FCC to the BCC phase quite early in the phase diagram. Our result shows that the vicinity of this transition does not really affect the good solubility of Fe in Co. CoCu deviates much more from the binomial law towards segregation (the experimental probability for Co to be surrounded by 12 Co stays quite high) which is in complete agreement with the well known low miscibility of Cu in Co.
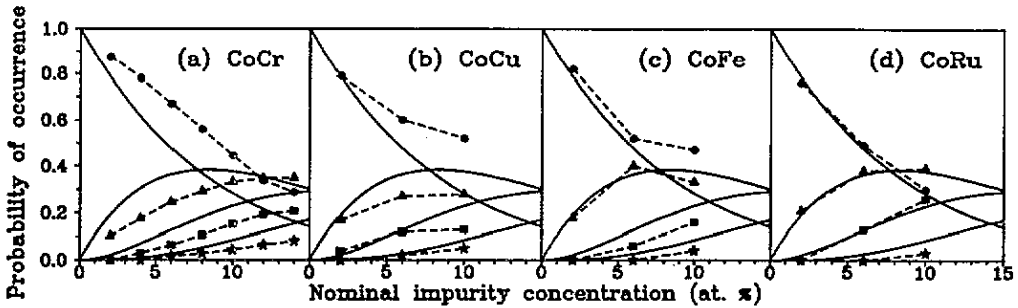
Figure 6. A comparison of the integral intensities of the main NMR line and its satellites with the binomial distribution law for twelve sites. (*a*) CoCr, (*b*) CoCu, (*c*) CoFe, (*d*) CoRu. ●, main line; ▲, first satellite; ■, second satellite; *, third satellite.

A characteristic feature of the spectra is a constant spacing between the satellites, the value of which is element dependent. Table 1 gives the values of frequency spacings Δf between the satellites for the different alloys (the centroid of the first asymmetric satellite was used for diluted CoCr alloys rather than a peak position). The resonance frequency is reduced by a value of 16 and 25 MHz for each additional Cu and Ru impurity, respectively, in the NN shell. This is understood, in a simple way, as resulting from the replacement of a moment carrier (Co) by a 'non-magnetic' atom (although it is not excluded that diluted Ru impurities in Co could carry a weak moment). The larger separation (32 MHz) in the case of CoCr alloys suggests that the |HF| on Co is lowered not simply because of the absence of a magnetic atom in the NN shell, but that Cr could carry a moment antiferromagnetically coupled to Co moments or that the Co moment is strongly depressed by the vicinity of a Cr atom. For the CoFe system Δf has a positive value and satellites are on the high-frequency side of the Co line; this is understood, in the same naive picture, as resulting from the larger moment, ferromagnetically coupled, of the Fe neighbours. However, it is known that the detailed influence of impurities on the HF of its neighbours (particularly the sign of the conduction electron contribution to HF) needs more elaborate explanations which are out of the scope of the present paper.

Besides this NN effect and the impurity concentrations that we were interested in, the influence of second and further neighbour shells manifests itself by a line broadening of each satellite and a general shift of the whole spectrum associated with the decrease of the average magnetization with increasing impurity concentration. Main and satellite lines stay equally spaced but shift towards lower (Cr, Ru, Cu) or higher (Fe) frequencies (see figure 7). This effect of second and further neighbour shells is nearly negligible for Cu but quite strong in CoCr alloys where an increase of 15% of the Cr concentration results in a modification of the Co HF as large as the effect of one Cr NN.

One must also be aware that the modification of the HF by impurities in different neighbour shells may differ not only in strength but also in sign as observed for Co diluted in BCC Fe [20]. If the perturbation of the HF around the impurity sites is strong, extended and oscillating the empirical approach presented here is then quite tough since well resolved satellites are observed on both sides of the main line. We have encountered such effects for CoPt alloys (figure 8) for which we do not as yet have any clear assignment of the observed satellites.
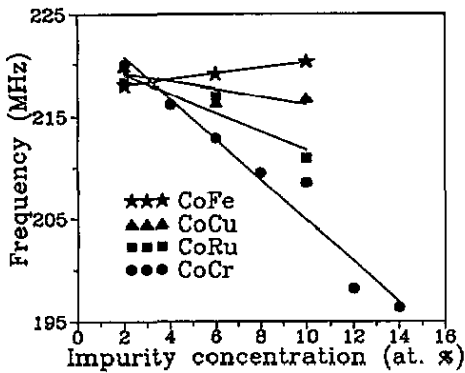
Figure 7. The frequency shift of the main line of the ^{59}Co NMR spectrum as a function of impurity content (the satellite lines move parallel to the main line).
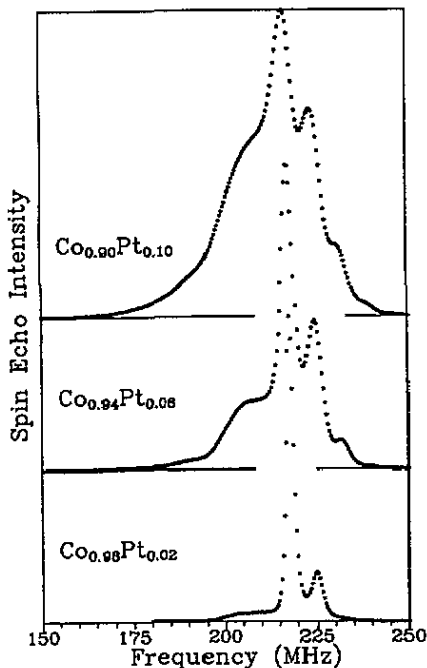

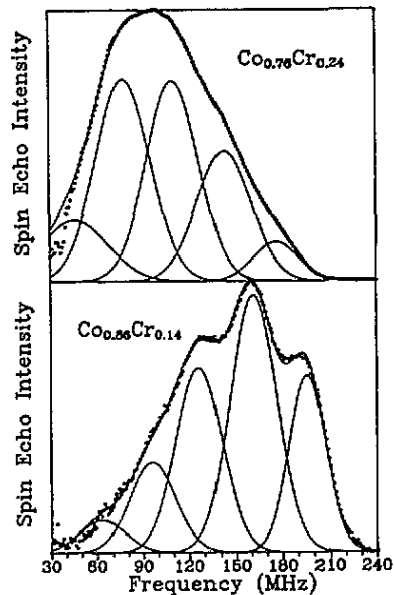**Figure 8.** ^{59}Co NMR spectra in CoPt FCC alloys ($T = 4.2$ K).

Figure 9. The Gaussian deconvolution of the NMR spectrum in concentrated $Co_{0.86}Cr_{0.14}$ and $Co_{0.76}Cr_{0.24}$ alloys.

4. Discussion

The above study, carried out on four Co-based alloys (CoPt excepted), with different crystal structures, magnetic and non-magnetic impurities, shows some systematics: each additional impurity atom in the first coordination zone changes the HF by a constant value, characteristic to a given alloy. If one wants to analyse a spectrum extending further in frequency than the reference ones the question is asked whether the observed linear dependence of the HF on the number of alien nearest neighbours extends to larger numbers of impurities than three or four, as observed in the present

study. Experimentally this question is hard to answer as one needs, in order to get a non-negligible amount of such configurations, to increase the concentration to a range where the inhomogeneous broadening of the lines is larger than the satellite separation. Consequently, satellite lines are no longer clearly resolved (particularly far and weak lines) and one must rely on spectrum deconvolution methods that may be biased. Figure 9 displays such a deconvolution of four satellites in CoCr, which shows that the assumption of regular spacing of the lines is consistent with the experimental observation. On the other hand, indirect arguments can be given against a fully linear dependence. Indeed, from previous studies of concentrated alloys it is known that the moment of a magnetic atom may be quenched above a critical number of non-magnetic alien neighbours. It is then possible that in Co-based alloys there is a significant change in the regime of variation of the Co HF close to such critical numbers (if any). However, the HF is then too weak for the corresponding lines to be observed which makes the discussion meaningless: for example, the CoCr samples of up to 25% Cr content that we have studied do not exhibit any NMR signal below the frequency range of the fourth satellite. From the viewpoint of structural investigations the main problem that arises in such cases is the lack of information resulting from part of the nuclei not being observed! On the other hand, in CoFe alloys, Co is always magnetic but it is known that the average alloy magnetization and the average |HF| on Fe [21, 22] go through a maximum around 30% Co content; however, the average HF on Co varies almost linearly in the full concentration range of CoFe alloys [23]; hence, although it would be surprising that the Co HF depends linearly on the number of Fe NNs from 0 to 12, the deviation from linearity is most probably small. It is then believed that for an analysis of spectra extending further in frequency than the reference ones, a few extra satellites may be assumed regularly spaced in a first approximation.

When attempting to interpret a spectrum in terms of densities of NN configurations in a sample, another problem arises that no absolute frequency can be assigned to a particular NN configuration in cases like CoCr (or CoRu) because of the strong shift of the spectrum with increasing impurity content. Our study of CoCr alloys, which can be considered as a worst-case situation, has shown that the distance between satellites stays rather constant over a broad concentration range (from 35 MHz for 2% Cr content to 30 MHz in $Co_{75}Cr_{25}$ which is close to the disappearance of ferromagnetism). Thus, in a spectrum analysis, the lines corresponding to various environments can be tentatively identified and deconvoluted assuming a separation close to values quoted in table 1 provided long-range effects (connected with average concentration or magnetization) are taken into account.

Table 1. Incremental frequency shift of ^{59}Co NMR due to the substitution of an impurity atom for Co in the nearest-neighbour shell ($T = 4.2$ K).

Alloy	CoCr	CoRu	CoCu	CoFe
Structure	HCP	HCP	FCC(HCP)	FCC
Satellite shift (MHz)	-32 ± 2	-25 ± 2	-16 ± 1	$+9 \pm 1$

Finally some caution must be taken when using reference results from random alloys (where impurities are isotropically distributed) in order to study systems that are topologically different (like multilayers). Indeed, besides the number and nature of the nearest neighbours, their position may also play some role in determining the

HF (see the case of the twin satellites in CoCr diluted alloys). Another situation that may occur is the formation of ordered compounds in which the HFs may differ significantly from those in disordered alloys of the same composition (for example in CoFe [23]). Then the spectra observed in the ordered compound should also be considered.

5. Conclusion

In conclusion the present results may be used (with various levels of confidence) as a reference for local magnetic and structural investigations of Co/X multilayers, based on the assignment of the observed satellites to the chemical composition of the Co nearest-neighbour shell. The observed quasi-linear dependence of the Co hyperfine field with the number of alien atoms (Cr, Ru, Cu and Fe) in its neighbourhood gives a possibility of interpreting the spectra further than the three or four first satellites observed in reference samples (keeping in mind that far extrapolations of the behaviour may have limited validity). Results obtained for CoCu alloys (and to a lesser extent CoRu alloys) provide rather safe references that have already been used in CoCu multilayers [24]. For Co/Cr (Co/Ru) systems the quantitative influence of distant neighbours must be considered. For Co/Fe multilayers, although the present results are quite simple, the possibility of occurrence of a non-compact BCC structure has to be considered for which the study of metastable BCC alloys in the low Fe concentration range is needed. A better understanding of CoPt alloys is needed before the results are used for magnetic and structural investigations of Co/Pt multilayers.

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