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N. M. R. STUDIES OF Ni CONCENTRATED ALLOYS NEAR THE MAGNETIC CRITICAL CONCENTRATION (*)

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Résumé. — Dans cet article, nous présentons de nouvelles mesures de R. M. N. dans les alliages concentrés Ni_cCu ($C_{cr} \sim 46\%$) et Ni_cV ($C_{cr} \sim 87,5\%$) qui montrent l'importance des effets d'environnement dans les alliages concentrés proches de la transition de l'état paramagnétique à l'état ferromagnétique. Nous montrons que la différence quantitative entre les valeurs de la concentration critique (C_{cr}) dans ces deux types d'alliages entraîne des différences notables entre les propriétés du cuivre et du vanadium : les atomes de vanadium (statistiquement isolés ou en paires, dans leur majorité) sont beaucoup plus sensibles aux interactions avec les atomes magnétiques que les atomes de cuivre qui statistiquement ont, en majorité, 5, 6 ou 7 atomes de cuivre premiers voisins (dans la zone critique de transition). En particulier, le Knight shift et la largeur de raie du V^{51} varient avec la température comme $(T - \theta)^{-1}$ où θ est très proche de la température de Curie de l'alliage, tandis que la température caractéristique des variations en $(T - \theta)^{-1}$ des propriétés du cuivre est négative et sans relation avec la température d'ordre de l'alliage. Nous analysons ces effets d'environnement local dans les alliages Ni_cV en séparant les contributions, au spectre R. M. N. de V^{51} , des atomes isolés, des paires isolées et des atomes inclus dans de plus gros amas de vanadium : nous montrons alors que la susceptibilité locale d'un atome de vanadium décroît fortement lorsque le nombre d'atomes de vanadium augmente dans son voisinage.

Abstract. — In this paper we present new N. M. R. measurements in Ni_cCu ($C_{cr} \sim 46\%$) and Ni_cV ($C_{cr} \sim 87.5\%$) which show the importance of the environment effects in concentrated alloys near the paramagnetic-ferromagnetic transition. We show that in these two types of alloys the V and Cu properties are quite different from the different values of the critical concentration (C_{cr}): namely, the V atoms (most probably isolated or paired in the C_{cr} range) are much more sensitive to the interactions with magnetic atoms than Cu atoms which have statistically about 5, 6 or 7 Cu nearest neighbours in the C_{cr} range. Particularly, the temperature dependences of the V^{51} Knight shift and line width are Curie Weiss like with a characteristic temperature close to the Curie temperature of the alloys; on the contrary the characteristic temperature of the Curie Weiss temperature variations of the Cu properties is negative and is not related to the ordering temperature. We analyse such local environment effects in the Ni_cV alloys by separating the contributions to the V^{51} N. M. R. line of the isolated V atom, of the isolated V pairs and of the V atoms embedded in larger V groups: the local susceptibility of a V atom is shown to decrease strongly when the number of V nearest neighbours increases.

1. Introduction. — Many experiments (magnetization, neutron scattering measurements) show that ferromagnetism occurs in an inhomogeneous way in concentrated M_cX_{1-c} ($M = Fe, Co, Ni$) alloys. From the magnetization measurements it is possible to obtain detailed informations about the magnetic atoms [1]; in the paramagnetic state, the contributions to the bulk magnetization of the nearly magnetic and magnetic atoms are deduced from such analysis and the concentrations of such atoms are shown to depend strongly on the M concentration near the

critical concentration (C_{cr}). Below the ordering temperature, hyperfine specific heat measurements [2] can determine the number of magnetic atoms and their magnetic moment.

On the contrary, in the paramagnetic state, N. M. R. studies will be easily analysed only for non magnetic or weakly magnetic atoms whose resonance line are not too much broadened; they give data (1) on the local susceptibility of the observed atoms and (2) on some features of the magnetic or nearly magnetic atoms via the interactions between the observed atoms and such magnetic ones in their own environment.

The resonance line results from the superposition of the individual lines of the observed nuclei. The

(*) This work is part of a thesis to be presented in Strasbourg by P. Panissod.

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position of each of these lines is related to the local magnetization of the observed atoms, so that the observed spectrum (as far as inhomogeneities are the only source of broadening) is related to the statistical repartition of the magnetization on the observed atoms. The resonance line is characterized by (1) its position (Knight shift) and its width, (2) its shape and (3) its integrated intensity. Let us now examine briefly each of these features.

(1) The Knight shift is related to the average magnetization of the observed atoms in their average environment whereas the width of the line is due to the fluctuations of this environment. The temperature and field dependences will give information about the magnetic and nearly magnetic impurities which are coupled to the observed atoms. Qualitatively different behaviours are expected according as the local environment of the observed atoms is magnetic, nearly magnetic or non magnetic.

However, the concentration dependences of the Knight shift and line width may be more difficult to interpret from the simultaneous variations of (1) the characteristics of the magnetic atoms and (2) of the most probable local environments of the observed atoms.

(2) If structures are present in the observed line (satellites) the variations of the Knight shifts and the widths of the different lines can be measured separately; it is then possible to attribute each of these lines to nuclei in given environments (from the comparison between the relative intensities and probability calculations). The susceptibilities of atoms in given environments are then deduced.

(3) Finally, the integrated intensity of the whole line is proportional to the number of observed nuclei so that we can measure the number of atoms that are wiped out of the line.

However the observed features will depend drastically (1) on the value of the critical concentration which determine the most probable local environment and (2) on the nature of the observed atoms: atoms with strong electron-electron intraatomic interactions will exhibit very broad resonance lines as observed for rhodium in NiRh alloys [3] so that no detailed study can be performed about local properties.

This is why, it is easier to observe atoms of the first part of the transition serie (V) or non « d » atoms (Cu, Al...).

In this paper we discuss the informations we can obtain from N. M. R. measurements on the magnetic properties and on environment effects in concentrated NiV and NiCu alloys near the transition from the paramagnetic to the ferromagnetic state.

In these two kinds of alloys the critical concentrations (87.5 % for Ni_cV, 46 % for Ni_cCu) are quite different. The local environment of V and Cu atoms are then quite different and we show that V atoms (most probably isolated or paired) are much more

sensitive to the interactions with the magnetic atoms than Cu atoms which have statistically about 5, 6 or 7 Cu nearest neighbours. Particularly, the temperature dependence of the V atoms properties are Curie Weiss like with a characteristic temperature close to the Curie temperature of the alloy, whereas the temperature dependence of the Cu atoms properties is also Curie Weiss like but with a negative characteristic temperature. Let us now present this experimental study in more detail.

2. N. M. R. study of Ni_cV and Ni_cCu alloys in the critical concentration range. — In this section we present and discuss N. M. R. measurements in (2.1) Ni_cV alloys ($C_{cr} \sim 87.5\%$) and (2.2) Ni_cCu alloys ($C_{cr} \simeq 46\%$). These measurements were performed by pulsed N. M. R. technique at 4.2 K and in the 77 K ÷ 300 K temperature range.

Experimental results on alloys which are paramagnetic (« P ») at 4 K (Ni_cV = $c \leq 87\%$; Ni_cCu = $c \leq 47\%$) are not strongly varying with temperature and concentration as compared with those whose Curie temperature is above 20 K (« F » alloys).

In the Ni_cV « F » alloys ($c \geq 89\%$) we observe strong variations of the line shape and detailed structures (satellites). The relative intensities of these satellites and their variations with concentration are in agreement with a local environment model and are thus attributed to isolated vanadium atoms, isolated pairs of vanadium atoms and larger groups. The temperature variation of the Knight shift and width of the partial lines are proportional to $(T - T_c)^{-1}$ with a characteristic temperature T_c close to the Curie temperature of the corresponding alloy. When approaching the Curie temperature of the alloys more and more lines are shifted from the central line ($K \simeq 0$) and the N. M. R. line is no more detected below T_c .

On the contrary, in the Ni_cCu « F » alloys ($c \geq 48\%$) the Cu resonance line for $K \simeq 0$ does not disappear when approaching the Curie temperature of the alloys and only a part of the Cu nuclei are wiped out at low temperature, this part increasing when the nickel concentration increases.

Furthermore, though no detailed analysis has still been made on the line shape in relation with a local environment model we can observe a Curie Weiss variation of the Cu line width with a negative characteristic temperature whose value increases when c increases; this suggests that the observed Cu atoms are polarized by nearly magnetic atoms and, except those which are wiped out at low temperature, not very sensitive to the atoms whose susceptibility is varying as $\frac{1}{T - T_c}$.

The different features of the vanadium and the copper N. M. R. lines are related to the quite different orders of magnitude of C_{cr} but qualitatively they

are understood in the same way from local environment effects.

Let us now present and discuss these results in more detail.

2.1 Ni_cV ALLOYS. — We studied the N. M. R. properties of V⁵¹ in Ni_cV alloys in the concentration range 85 % ≤ c ≤ 91 %.

2.1.1 «P» alloys. — The Knight shift, line width and relaxation rate measurements have been performed on three «P» alloys (c = 85 %, 86 %, 87 %). These results are summarized in table I. The Knight shift slightly decreases and the line width increases (1) when approaching the critical concentration and (2) when the temperature decreases. This is expected from the corresponding increase (1) of the average number of nearly magnetic Ni atoms and (2) of their magnetization. But the analysis of the Knight shift and relaxation rate data exhibits a decrease of both the vanadium «d» and orbital susceptibilities (50 to 40 × 10⁻⁶ emu/mole for χ_d and 120 to 100 × 10⁻⁶ emu/mole for χ_{vv}) when c increases from 85 % to 87 %. This may be rather surprising but it is consistent with other studies on CoV alloys [4] in the 0 % ≤ c ≤ 75 % cobalt concentration range which reveal a constant decrease of the vanadium susceptibility when the cobalt concentration increases. We will also see from the study of the «F» NiV alloys that only the susceptibility of the isolated vanadium atoms is strongly modified by the interactions with magnetic Ni atoms and there are less than 20 % of such isolated atoms in the «P» NiV alloys.

TABLE I

V⁵¹ NMR data in some paramagnetic V_{1-c}Ni_c alloys near the critical concentration

	c (Ni)	85 %	86 %	87 %
300 K	K (%)	0.41	0.40	0.40
	ΔH (G)	26	28	33
	(T ₁ T) ⁻¹ s ⁻¹ K ⁻¹	0.77	0.57	0.58
	K	0.39	0.33	0.34
77 K	ΔH	31	45	91
	(T ₁ T) ⁻¹	0.80	0.60	0.51
4.2 K	K	0.39	0.35	0.16
	ΔH	37	50	177
	(T ₁ T) ⁻¹	0.78	0.75	

However, exchange enhancement factors, which have not been taken into account in the previous analysis, may be quite different for the Knight shift and the relaxation rate [5] and it is then difficult to give a really positive conclusion about the local susceptibility of the vanadium atoms.

2.1.2 «F» alloys. — The resonance lines of V⁵¹ in the NiV «P» alloys were found to be symmetrical except for the Ni_{0.87}V alloys at 4.2 K. This last alloy is intermediate between the «P» and the «F» NiV

alloys. In the NiV «F» alloys the V⁵¹ NMR spectra is clearly not symmetrical as shown on figure 1. The resonance line practically disappears below T_c and the total line width varies as $\frac{1}{T - T_c}$ (T_c is the Curie temperature of the alloy). This Curie Weiss law is a general feature of all the vanadium properties in these alloys above the Curie temperature. As shown on figure 1 all the V⁵¹ resonance lines present a sharp edge for K ≈ 0 and a long tail for large negative

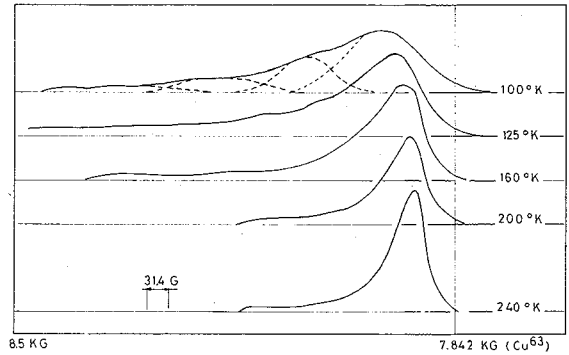


FIG. 1. — Experimental V⁵¹ NMR spectra in Ni₈₉%V₁₁% alloy.

Knight shifts. Shoulders and secondary bumps near the Curie temperature indicate the existence of several lines that we separate: we assume that the observed spectra result from the superposition of several symmetrical lines corresponding to vanadium atoms with different local environments and we consider the sharp edge as half of the first line; this line is then symmetrized and subtracted out of the spectra; the resulting spectra have the same shape (sharp edge, long tail) as the original one so that the same technique is used to determine the second line and so on, as far as there is still an obvious asymmetry (Fig. 1). Such a separation can be obtained in a limited temperature range since (1) for T ≫ T_c the difference between the Knight shifts of the partial lines is not large enough as compared with the line width and (2) for T ~ T_c the line width increases drastically and the amplitude of the most shifted lines is then too weak as compared with the signal to noise ratio and moreover extra lines are shifted out of the first, less shifted, line. However the deduced variations with temperature and concentration of the position K_i and the width ΔH_i of the partial lines show the consistency of the separation (i = 1, 2, ... labels the partial lines according to increasing values of |K_i|).

K_i and ΔH_i are varying with temperature according to:

$$K_i = K_{i\infty} - \frac{\alpha_i}{T - T_c(c)}$$

and

$$\Delta H_i = \Delta H_{i\infty} + \frac{\beta_i}{T - T_c(c)}$$

(cf. Fig. 2 and Fig. 3, table II).

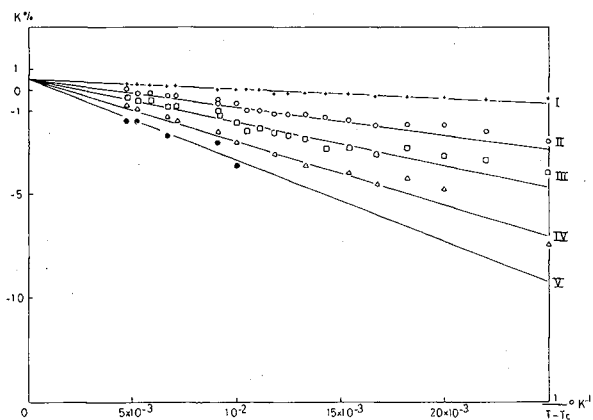


FIG. 2. — V^{51} NMR Knight shift variation with temperature in $Ni_{89}\%V_{11}\%$ alloy ($T_c = 50$ K).

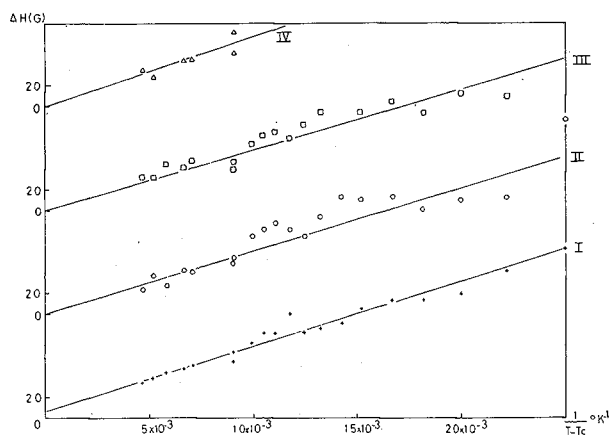


FIG. 3. — V^{51} NMR line width variation with temperature in $Ni_{89}\%V_{11}\%$ alloy ($T_c = 50$ K).

The high temperature terms ($K_{i\infty}$, $\Delta H_{i\infty}$) are characteristics of the vanadium atoms in their environment but decoupled from the magnetic impurities; for all the partial lines in the « F » alloys, $K_{i\infty}$ is nearly equal to the pure vanadium Knight shift whereas $\Delta H_{i\infty}$ is of the order of magnitude of the corresponding dipolar line width.

The temperature dependent terms vary according to a Curie Weiss law with a characteristic temperature equal to the Curie temperature of the alloys: it is

TABLE II

Temperature variation of V^{51} resonance lines characteristics (see text) in some ferromagnetic $V_{(1-c)}Ni_c$ alloys above their Curie temperature.

c (Ni)	89 %	90 %	91 %
T_c (K)	50	120	220
$K_{i\infty}$ (°)	0.6	0.6	0.6
α_1 (% K)	50	60	65
α_2	125	160	180
α_3	200	250	240
α_4	300	380	
$\Delta H_{i\infty}$ (G)	≤ 6	≤ 6	≤ 6
β_i (G K)	6 000	8 700	8 500

thus arising from the polarization of V atoms by the magnetic atoms responsible for the ferromagnetism. The Curie constant α_i varies from one partial line to another and is roughly the same in the studied concentration range for a given line; this temperature dependent term is then thought to be characteristic of a local environment, the i th line corresponding to vanadium atoms in some basic configuration. Thus K_i results from the average environment of this basic configuration whereas ΔH_i is due to the effect on the local susceptibility of the fluctuations of this environment.

The relative intensities of the partial lines can be compared with probability calculations and they are shown to agree with the relative number of isolated vanadium atoms (i. e. with 12 Ni nearest neighbours), isolated pairs of V atoms (18 Ni n. n.) and V atoms in larger statistical clusters (table III).

This study shows then clearly that the V atoms susceptibility is closely related to the magnetization of atoms which are coupled for $T < T_c$ and depends on the local environment; more precisely the susceptibility of an isolated V atom will be larger than that of a V atom embedded in a pair configuration and so on. The vanadium atom embedded in groups of more than two V atoms are rather insensitive to the magnetization of other atoms and their susceptibility even decreases when the nickel concentration increases as suggested by the analysis of the NMR

TABLE III

Comparison between the relative intensities of the various V^{51} resonance lines and the calculated relative numbers of vanadium atoms, isolated (3, 4, 5), clustered in pairs (2) and in larger groups (1)

Line i	89 %			90 %			91 %		
	1	2	345	1	2	345	1	2	345
Relative Intensity (%)	54 ± 5	21 ± 4	25 ± 3	50 ± 5	22 ± 4	28 ± 4	52 ± 3	22 ± 4	26 ± 4
Calculated Relative Number (%)	59.1	16.2	24.7	53.8	18.0	28.0	48.0	19.8	32.2

measurements for «P» NiV alloys in which about 80 % of the V atom are statistically clustered in such groups. This decrease of the V magnetic susceptibility with increasing number of V nearest neighbour is in agreement with susceptibility and specific heat measurements in dilute alloy [6] and with recent susceptibility calculations [7].

2.2 Ni_cCu ALLOYS. — We study the NMR properties of Cu⁶³ and Cu⁶⁵ in Ni_cCu alloys in the 42 % ≤ *c* ≤ 52 % concentration range (*C*_{cr} ~ 46 %). As for the Ni_cV alloys we will separate the study of «P» alloys (*c* ≤ 47 %) and «F» alloys (*c* > 47 %).

2.2.1 «P» alloys. — The Knight shift and line width data are summarized in table IV for the Ni_cCu «P» alloys. These alloys exhibit a slight decrease of the Knight shift when increasing the Ni concentration and decreasing the temperature. Both effects are unambiguously related to the increase of the bulk magnetization. Nevertheless this variation is rather weak as compared with that of the bulk magnetism ; a corresponding increase of the line broadening is expected and actually observed. But as in the NiV «P» alloys no really striking effect is found. However unlike in the NiV «P» alloys the resonance spectra are not symmetrical for all the considered alloys but no detailed study of the line shape has still been performed.

TABLE IV

⁶³Cu Knight shift, linewidth as function of temperature in CuNi alloys paramagnetic for 4 K

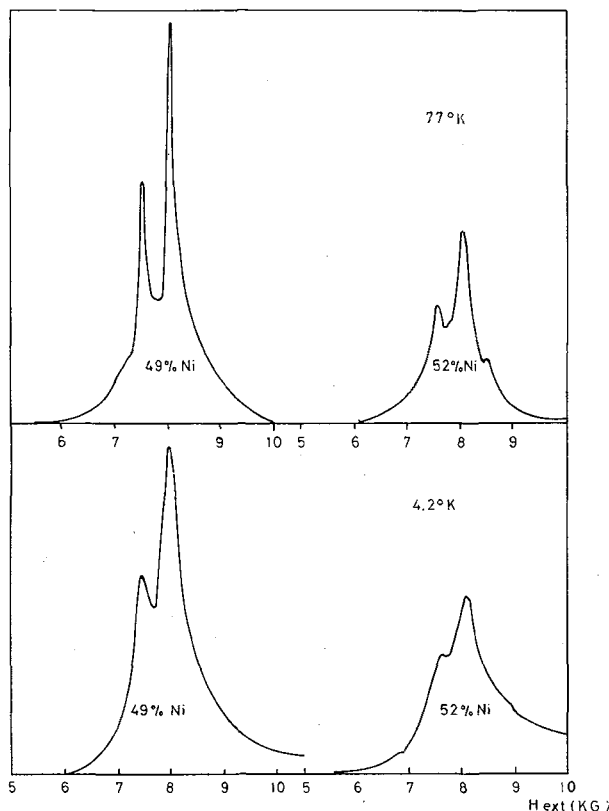
<i>C</i> (% Ni)	43	44	45	47
77 K	-0.19	-0.24	-0.21	-0.95
4.2 K	-0.25	-0.28	-0.45	-0.53
Δ <i>H</i> (G)	81	93	95	133
4.2 K	114	119	138	197

2.2.2 «F» alloys. — The resonance line of Cu⁶³ and Cu⁶⁵ in five Ni_cCu «F» alloys were studied (48 % ≤ *c* ≤ 52 %). Four examples of the observed spectra are given on figure 4. Let us briefly summarize the feature of these lines.

(1) The first striking point is that a Cu NMR line is still observed at 4.2 K when these «F» alloys are ferromagnetic and the Knight shift of the Cu nuclei observed at 4.2 K is not qualitatively changed.

(2) From the comparison of the line intensities at different temperatures in a given sample one can see (Fig. 5) that there are some Cu atoms that are wiped out of the line at low temperature and that the number of such Cu atoms increase for increasing Ni concentration : these wiped out atoms are thus presumably in the vicinity of atoms which are coupled below the Curie temperature.

(3) The variation of the Cu⁶³ line width is found to vary as $\frac{\beta}{T - \theta}$ (Fig. 6). The characteristic temperature θ of this Curie Weiss law was found to be negative and θ increases when the Ni concentration increases. The Cu atoms are then mostly polarized by nearly magnetic impurities whose characteristic temperature is quite different from the Curie temperature of the alloys as shown in table V.


 FIG. 4. — Experimental Cu NMR spectra in Ni_cCu_{1-c} alloys.

These features are quantitatively different from those observed in NiV alloys. This is certainly related to the different order of magnitude of the critical concentration. In NiV alloys the most probable V clusters are isolated V atoms, isolated pairs (in the *C*_{cr} range) so that V atoms are more sensitive to the magnetization of the surrounding Ni atoms which are coupled below *T*_c than the Cu atoms which are statistically clustered in larger groups (5, 6, 7). This explains why the Knight shift of the Cu nuclei in NiCu alloy is not much changed even below the Curie temperature. Thus these different features are well understood in a local environment model. However, in this analysis, the quadrupolar interactions have not been taken into account, but according to the work of Bloembergen and Weinberg [8] field dependence measurements indicate that the broadening in concentrated Ni_cCu alloy (*c* > 40 %) is of magnetic not quadrupolar

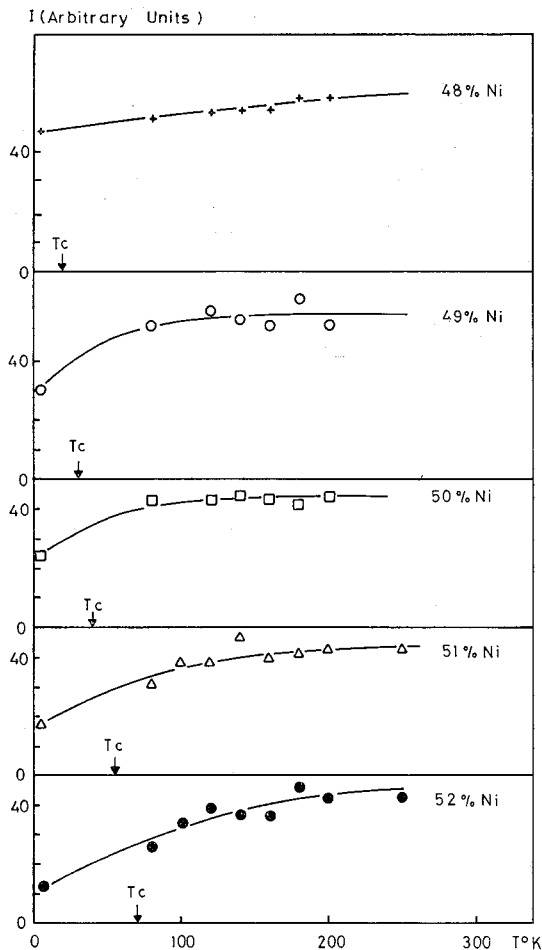


FIG. 5. — Integrated intensities of the Cu NMR line in concentrated Ni_cV alloys as function of temperature.

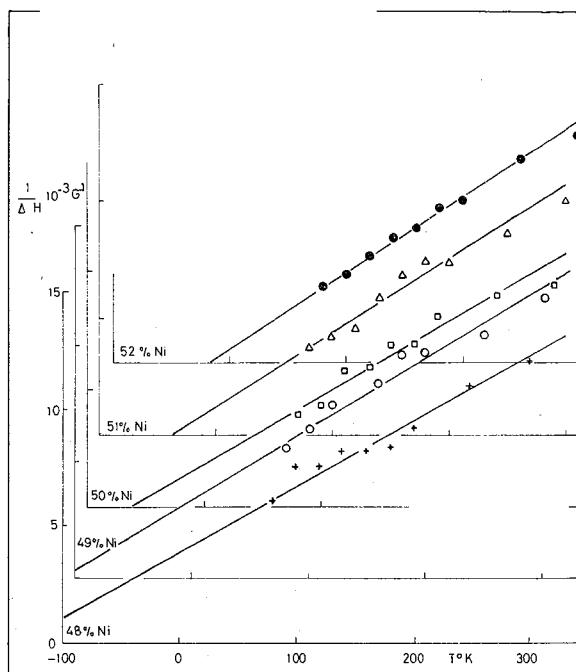


FIG. 6. — Temperature dependence of the Cu⁶³ NMR line width in Ni_cV alloys ($\frac{\beta}{\Delta H} = (T - \theta)$).

origin ; moreover the Curie Weiss temperature dependence of the line widths that we observe confirm this statement.

TABLE V

Characteristic constants of the temperature variation of the Cu linewidth in CuNi alloys ($\Delta H = \frac{\beta}{T - \theta}$) above their Curie temperature (T_c).

C (% Ni)	T_c	θ	β
48	20 K	- 140 K	36×10^3 G K
49	30 K	- 110 K	33×10^3 G K
50	40 K	- 65 K	34×10^3 G K
51	55 K	- 40 K	32×10^3 G K
52	70 K	- 15 K	31×10^3 G K

3. Conclusion. — Though the N. M. R. measurements are rather difficult to interpret in concentrated alloys, we have shown that for some atoms (such as V and Cu) with no strong electron-electron intra-atomic interactions the line broadening is sufficiently small to analyse the N. M. R. spectra in terms of local environment. Previous studies have been performed in NiV [9] and NiCu [8] concentrated alloys but the main features were not analysed in terms of local effects.

There is no doubt that an extended experimental temperature range will allow a more accurate study in an extended concentration range. These studies are currently in progress.

Nevertheless these preliminary experiments already show the very important role of the local environment on the magnetic properties of concentrated alloys. We have shown particularly that the local susceptibility of isolated V atoms in NiV alloys is much larger than that of V atoms clustered in isolated pairs in larger groups. We observed a $(T - \theta)^{-1}$ temperature dependence of the Knight shift and line width of the V and Cu N. M. R. lines above the Curie temperature of ferromagnetic NiV and NiCu alloys ; but for V atoms the characteristic temperature θ is close to the Curie temperature of the alloy whereas for Cu atoms it is negative ; this shows clearly that Cu atoms are much less sensitive than V atoms to the magnetization of the atoms responsible for the ferromagnetism : this can be related to the most probable local environment of a Cu atom in the (Ni_cCu)C_{cr} range (5, 6, 7 Cu atoms nearest neighbours) as compared to that of a V atom in the (Ni_cV)C_{cr} range (0, 1, 2 V n. n.).

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