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The influence of interstitial N, C and H atoms on the hyperfine fields at the yttrium and cobalt sites in Y_2Co_{17}

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Abstract

The spin echo nuclear magnetic resonance spectra of $Y_2Co_{17}A_x$ ($A \equiv N$, C, H) are presented. On the basis of the satellite pattern of the ^{89}Y spectra, we have deduced that N and C atoms occupy the 9e sites (rhombohedral compounds) or 6h sites (hexagonal compounds) around the yttrium site. A decrease in the hyperfine fields at the yttrium and cobalt sites caused by neighbouring interstitial atoms is observed, with a magnitude dependent on the site and the type of interstitial atom. The effect is discussed in terms of the influence of N, C and H atoms on the local electronic structure at the yttrium and cobalt sites and compared with the effect observed in the RE_2Fe_{17}-based compounds (RE, rare earth).

1. Introduction

The investigated compound Y_2Co_{17} belongs to the family of permanent magnetic materials of Sm_2Co_{17} type. Recently it was found that the iron-based compound can accommodate a significant amount of carbon and nitrogen. The effect is accompanied by a great improvement in the permanent magnetic properties. A Curie temperature of 750 K [1] and an anisotropy field as large as 14 T [2] have been reported recently for $Sm_2Fe_{17}N_x$. The changes in local magnetic properties upon substitution can conveniently be studied by means of spin echo nuclear magnetic resonance (NMR).

The compound Y_2Co_{17} crystallizes in a rhombohedral (Th_2Zn_{17}) or hexagonal (Th_2Ni_{17}) type of structure. The structures differ in the stacking

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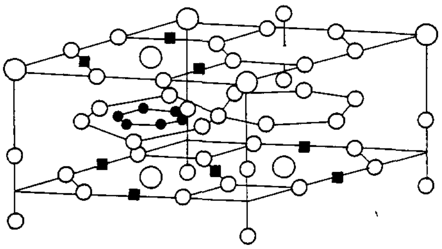

Fig. 1. Schematic representation of a building block associated with the crystallographic structure of the rhombohedral and hexagonal R_2Fe_{17} compounds. The large empty circles represent rare earth atoms, the small empty circles represent Fe atoms, the squares refer to octahedral 9*e* (6*c*) sites and the full circles refer to tetrahedral 18*g* (12*i*) sites.

sequence of the building blocks shown in Fig. 1. This leads to the occurrence of one yttrium site (6c) in the rhombohedral unit cell and two yttrium sites (2b, 2d) in the hexagonal unit cell. The four inequivalent cobalt sites 6c (4f), 9d (6g), 18f (12j) and 18h (12k) do not differ substantially between the two structures.

Recent neutron diffraction experiments [3, 4] on the iron-based isostructural compounds have shown that nitrogen and carbon occupy almost exclusively the three octahedral positions 9e (6h) around the rare earth (RE) sites. Hydrogen can also occupy the 18g (12i) sites [5] but has a preference for the 9e (6h) sites.

In recent papers [6, 7] we have reported on the large influence of interstitial N and C atoms on the transferred hyperfine fields (HFFs) and electric field gradients (EFGs) at the RE and transition metal (TM) sites in the iron-based compounds. We have also studied the $Y_2Co_{17}C_x$ system [8] and found that the limit of carbon solubility in the compound is at the level $x = 0.07$. In this work we present a spin echo NMR study of the isostructural cobalt-based series. The aim of this paper is to determine the influence of N, C and H atoms on the HFFs at the yttrium and cobalt sites and to compare it with that observed in the iron-based compounds.

2. Experimental details

A sample with the composition $Y_2Co_{17}N_{1.4}$ (sample (a)) and the hydrided equivalent were prepared from powdered Y_2Co_{17} material by absorption from an N_2 (H_2) gas atmosphere in a constant-volume reactor. The temperature was kept at 500 °C for the nitride and at 140 °C for the hydride. The nominal nitrogen (hydrogen) content was calculated from the pressure difference before and after reaction.

Sample (b) of $Y_2Co_{17}N_x$ was prepared by heating the powder of an annealed sample of Y_2Co_{17} in an atmosphere of N_2 gas at 500 °C for about 5 h.

The $Y_2Co_{17}C_{0.8}$ sample was the one presented in ref. 6.

TABLE 1

Values of lattice constants (a, c) and relative increase in unit cell volume ($\Delta V/V$) for Y_2Co_{17}, $Y_2Co_{17}C_{0.8}$, $Y_2Co_{17}H_{3.3}$, $Y_2Co_{17}N_x$ sample (a) and $Y_2Co_{17}N_x$ sample (b)

Compound	a (Å)	c (Å)	$\Delta V/V$ (%)
Y_2Co_{17}	8.358	12.193	–
$Y_2Co_{17}C_{0.8}$	8.369	12.188	0.2
$Y_2Co_{17}H_{3.3}$	8.378	12.253	1.0
$Y_2Co_{17}N_x$ (a)	8.476	12.389	4.5
$Y_2Co_{17}N_x$ (b)	8.520	12.429	5.9

X-ray diffraction has shown that the samples contain the rhombohedral Th_2Zn_{17}-type phase as the majority phase together with traces of a cobalt-excess phase. The lattice constants are collected in Table 1.

The ^{89}Y NMR measurements have been done using a pulsed spin echo NMR spectrometer [9]. The ^{59}Co NMR spectra have been obtained using an automated computer-controlled NMR spectrometer [10]. Because in magnetically ordered materials the dominant contribution to the magnetic field at nuclei is of hyperfine origin and the local fields are much smaller, the term "hyperfine field" often stands for both local and hyperfine contributions. We will use it in this way unless we analyse both contributions separately.

The pulse sequence 0.5/50/0.7 μs for yttrium resonances and 0.2/100/0.2 μs for cobalt resonances were used.

In order to determine the origin of the NMR signals, measurements at various r.f. pulse power have been made. The transverse relaxation times were determined for the peak frequencies of the ^{89}Y spectra. For the same purpose some of the ^{59}Co spectra have been taken at two different pulse distances, 15 and 100 μs.

The spectra obtained are presented in Figs. 2 and 3. The positions of the resonance lines and the corresponding values of the effective magnetic fields at the nuclei are collected in Tables 2 and 3.

3. Discussion

3.1. ^{89}Y resonances

3.1.1. Y_2Co_{17}

The ^{89}Y NMR spectrum of Y_2Co_{17} consists of an intense line centred at 18.3 MHz and two weaker lines appearing at 18.9 and 21 MHz. The spectrum agrees well with that already published [11]. The large intensity of the 18.3 MHz line indicates that the rhombohedral phase is the majority phase. The two weaker lines have been assigned to the 2b and 2d sites of the hexagonal-type structure.

3.1.2. $Y_2Co_{17}C_{0.8}$

A strong line centred at 18.4 MHz and a weak line at 15.7 MHz have been detected [8]. In analogy to the iron-based carbide, we have assigned

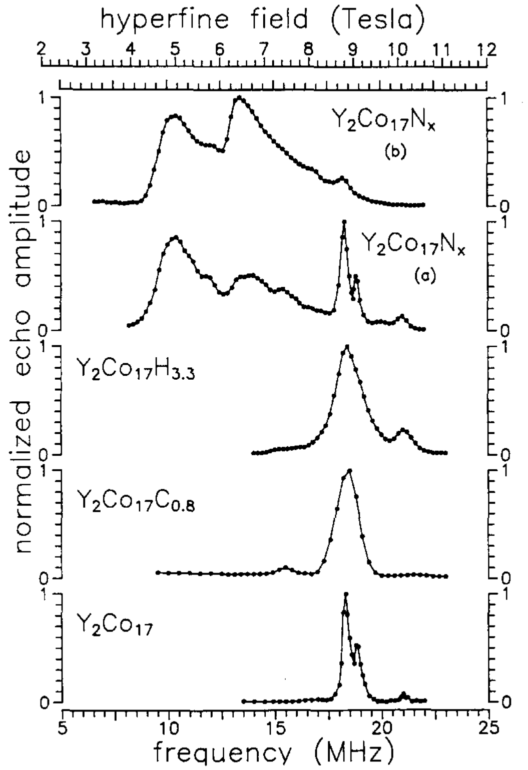

Fig. 2. ^{89}Y spin echo NMR spectra of Y_2Co_{17}, $Y_2Co_{17}C_{0.8}$, $Y_2Co_{17}H_{3.3}$, $Y_2Co_{17}N_x$ sample (a) and $Y_2Co_{17}N_x$ sample (b) at 4.2 K.

the small line to the Y atoms with one neighbouring C atom. The real concentration x of carbon in the compound evaluated on the basis of the relative intensity of this line amounts to 0.07. A very weak change in the lattice constants and the Curie temperature observed by us [8] is consistent with such a low carbon concentration in the compound. The value $x=0.07$ can represent the carbon solubility in the compound which can be reached by alloying. The corresponding decrease in the yttrium HFF caused by the nearest-neighbour C atom is found to be as large as 1.5 T (14.5%). The corresponding value obtained for the iron-based compound is 2.7 T (13%). The linewidths are about four times larger than those for Y_2Co_{17} so that the lines observed for Y_2Co_{17} at 18.3 and 18.9 MHz are no longer resolved in the carbide. The centre of gravity of the main line within a 0.16 MHz margin coincides with the common centre of gravity of the 18.3 and 18.9 MHz lines in Y_2Co_{17}. Their positions are equal to 18.36 and 18.52 MHz for the carbide and the pure compound respectively.

3.1.3. $Y_2Co_{17}N_x$

Two samples (denoted (a) and (b)) with different nitrogen concentrations were used. For sample (a) the nominal concentration x was 1.4. For sample

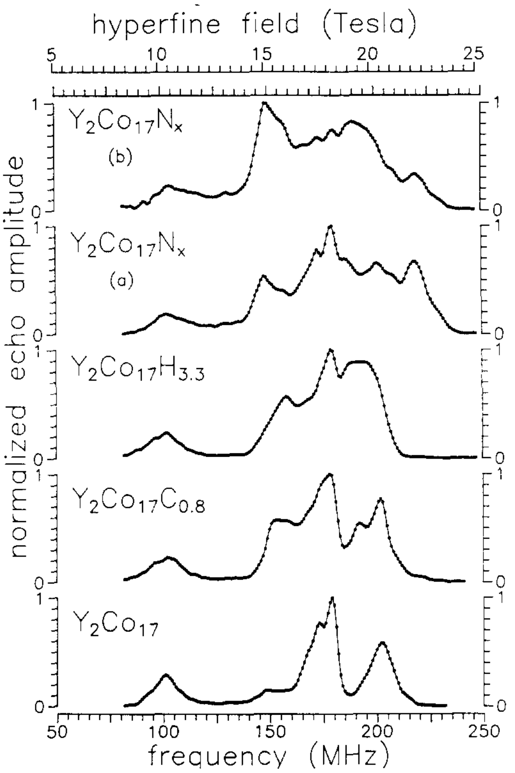

Fig. 3. ^{59}Co spin echo NMR spectra of Y_2Co_{17}, $Y_2Co_{17}C_{0.8}$, $Y_2Co_{17}H_{3.3}$, $Y_2Co_{17}N_x$ sample (a) and $Y_2Co_{17}N_x$ sample (b) at 4.2 K.

TABLE 2

^{89}Y resonance line positions (ν) and corresponding values of hyperfine fields (B_e)

Compound		1	2	3	4	5	6	7
Y_2Co_{17}	ν (MHz)	18.3	18.9	21.0				
	B_e (T)	8.77	9.06	10.07				
$Y_2Co_{17}C_{0.8}$	ν (MHz)	15.7	18.4	21.0				
	B_e (T)	7.53	8.82	10.07				
$Y_2Co_{17}H_{3.3}$	ν (MHz)	18.4	21.0					
	B_e (T)	8.82	10.07					
$Y_2Co_{17}N_x$ (a)	ν (MHz)	10.5	11.9	13.7	15.4	18.3	18.9	21.0
	B_e (T)	5.03	5.70	6.57	7.38	8.77	9.06	10.07
$Y_2Co_{17}N_x$ (b)	ν (MHz)	10.5	11.9	13.4	16.7	18.2		
	B_e (T)	5.03	5.70	6.42	8.01	8.72		

(b) the nominal concentration was not determined. However, X-ray diffraction evidenced a significant increase in the lattice constants corresponding to a 5% increase in the unit cell volume, which shows there was an uptake of

TABLE 3

^{59}Co resonance line positions (ν) and corresponding values of hyperfine fields (B_e)

Compound		1	2	3	4	5	6	7
Y_2Co_{17}	ν (MHz)	101	148	173	179	202	219	
	B_e (T)	10.0	14.7	17.1	17.7	20.0	21.7	
$Y_2Co_{17}C_{0.8}$	ν (MHz)	102	152	158	178	192	202	
	B_e (T)	10.1	15.0	15.6	17.6	19.0	20.0	
$Y_2Co_{17}H_{3.3}$	ν (MHz)	101	158	179				
	B_e (T)	10.0	15.6	17.7				
$Y_2Co_{17}N_x$ (a)	ν (MHz)	102	148	173	180	191	201	219
	B_e (T)	10.1	14.7	17.1	17.8	18.9	19.9	21.7
$Y_2Co_{17}N_x$ (b)	ν (MHz)	103	149	174	180	190		
	B_e (T)	10.2	14.8	17.2	17.8	18.8		

a considerable amount of nitrogen by this sample. As will be shown below, one can try to determine the concentration of nitrogen on the basis of the NMR spectra.

Besides the lines detected for the host compound, two broad, intense lines at 10.5 and 13.7 MHz appear in the spectrum of sample (a). These two lines persist in sample (b), but the lines corresponding to the host compound, except for a weak one centred at 18.2 MHz, are much less intense. In analogy to the effect observed by us in $Y_2Co_{17}C_x$ and $Y_2Fe_{17}N_x$, these lines can be assigned to the Y atoms with N atoms in the nearest neighbourhood.

In order to correlate the lines with the number of N atom neighbours, let us compare the corresponding effects observed in $Y_2Fe_{17}C_x$, $Y_2Fe_{17}N_x$, $Y_2Co_{17}C_x$ and $Y_2Co_{17}N_x$. The decrease in the yttrium HFF caused by one C atom in the iron-based compound amounts to 13%, whereas in the cobalt-based carbide it is as large as 14.5%. The ratio of the relative effects is therefore about 1.12. Assuming the same ratio for the corresponding nitrides, one comes from the 14% HFF reduction observed for one N atom in the iron-based nitride [6] to about 15.7% HFF reduction for $Y_2Co_{17}N_x$. Using the results obtained for $Y_2Fe_{17}N_x$, where the reductions in HFF observed for the two- and three-nearest-neighbour N atom configurations equal 30% and 38% [6], one finds that the corresponding reductions in the cobalt-based compounds should be $1.12 \times 30\% = 34\%$ and $1.12 \times 38\% = 43\%$ respectively. The observed cobalt-based nitride satellite lines at 10.5 and 13.7 MHz correspond to 43% and 26% reductions in HFF when related to 18.5 MHz—the position of the centre of gravity of both the 18.3 and 18.9 MHz lines representing the sites with no N atoms as nearest neighbours. The agreement of the HFF reduction corresponding to the 10.5 MHz line with the value predicted in the above analysis for three N atoms as nearest neighbours is excellent. Thus the 10.5 MHz line can confidently be assigned to Y atoms having three N atoms in the nearest-neighbour shell. Consequently, the

13.7 MHz line can be assigned to two N atom nearest neighbours and the well-pronounced shoulder for sample (b) on the high frequency slope of this line at 16.7 MHz can be assigned to one nearest-neighbour N atom.

The well-pronounced shoulders on the high frequency side of the 10.5 MHz line in the spectrum of sample (a) at 11.9 and 15.4 MHz are interpreted as the satellite lines of the 21 MHz line corresponding to the hexagonal 2b site with three and two N atoms respectively as nearest neighbours.

The relatively high intensity of the lines corresponding to the host compound observed for sample (a) can be explained by the presence of an unreacted Y_2Co_{17} phase, traces of which are visible in the X-ray spectrum. The effect is commonly met in this type of compound and is caused by a slow diffusion of nitrogen. For this reason the inner parts of grains usually contain a smaller amount of nitrogen. Sample (b), however, shows much better homogeneity.

Using the relative intensities of the satellite lines as the measure of the population of the corresponding yttrium sites with various numbers of nearest-neighbour N atoms, one can evaluate the real concentration of nitrogen in the compound. The relative line heights derived from the spectrum of sample (b) remain in the ratio 0.11:0.14:0.41:0.34 for zero, one, two and three nearest-neighbour N atoms. The corresponding ratios for the areas are 0.7:0.14:0.42:0.37. The concentration of nitrogen, x, can be obtained by summation of the relative line intensities multiplied by the corresponding number of nearest-neighbour N atoms, which leads to the values 1.98 for the heights and 2.09 for the areas, with the average 2.04. Thus the value $x=2.0$ can be considered as reasonable for the real concentration of nitrogen in sample (b). The same procedure applied to the spectrum of sample (a) gives the ratio 0.24:0.10:0.25:0.41 for the areas and 0.38:0.8:0.20:0.33 for the heights. The average value obtained for x is 1.65, in fair agreement with the nominal value of 1.4.

Both samples reveal different distributions of the environment with zero, one, two and three N atoms as nearest neighbours, deviating from a random one.

3.1.4. $Y_2Co_{17}H_{3.3}$

The ^{89}Y resonance spectrum of this sample consists of an intense line centred at 18.4 MHz and a small one at 21 MHz. Within a margin of 0.1 MHz the lines remain at the same positions as in the host compound. The linewidth, however, 0.4 MHz in Y_2Co_{17}, increases in the hydride by about four times. The same effect is also observed for the carbide.

3.2. ^{59}Co resonances

3.2.1. Y_2Co_{17}

The spectrum consists of five lines of different intensities. The line positions and their relative intensities are in good agreement with the NMR spectrum of Y_2Co_{17} published previously [12].

In the NMR experiment at zero applied field the measured magnetic field at the cobalt nucleus can be expressed as the sum

$$B_e = B_{hf} + B_{loc} \tag{1}$$

where B_{hf} is the hyperfine field and B_{loc} is the local field. The only contribution to B_{loc} which can significantly vary along our series is the dipolar field B_{dip}. This is an anisotropic term represented by a vector sum of the magnetic fields produced at the nucleus by the magnetic moments of the neighbouring atoms. For an arbitrary direction of magnetic moments, B_{dip} can be different for Co atoms at crystallographically equivalent positions.

The calculations of the dipolar fields have been done for various directions taking the values of the magnetic moments as $\mu_{Co} = 1.6\ \mu_B$ and $\mu_Y = 0$. The values obtained for B_{dip} amount to ± 0.4 T. The variation in B_{dip} with a change in direction of magnetic moments within a plane perpendicular to the *c* axis amounts to 0.4 T, whereas the difference between *c* axis and *c* plane is as large as 0.5 T. The largest difference between atoms of the same site is found for the 18h site and corresponds to the direction in the plane perpendicular to the *c* axis. The difference equals 0.6 T. The differences within other sites are much smaller: 0.06 T for 18f, 0.23 T for 9d and zero for 6c. The distance between the peaks at 173 and 179 MHz corresponds to 0.6 T — the difference in the dipolar fields for the 18h site for the cobalt moment in the in-plane-type domain walls — so that these peaks can be assigned to the 18h site.

3.2.2. $Y_2Co_{17}C_{0.8}$

Besides the lines observed for Y_2Co_{17}, two additional small peaks appear at the low frequency sides of the most intense 201 and 173–179 MHz lines. Their distances from the main lines amount to 10 and 20 MHz for the 201 and 179 MHz lines respectively. The derived values of 1.1 and 2.0 T reduction in HFF correspond respectively to their 5% and 11% relative changes.

The corresponding values are much larger than the evaluated possible variations in B_{loc}, so that we assign the effect to the change in HFF (B_{hf}) associated with the interstitial site occupation by C atoms.

In order to analyse the effect in detail, let us recall that the 18h and 18f sites have one C(9e) site in the nearest-neighbour shell whereas the remaining two cobalt sites have no nearest-neighbour 9e sites. On this basis the observed satellite lines at about 155 and 191 MHz can be assigned to the 18h and 18f sites with one C atom as nearest neighbour. Consequently, the intense line at 202 MHz can be assigned to the 18f site rather than to the 9d site [12]. A less intense line at 101 MHz keeps its assignment to the 9d site and a weak line at 148 MHz can be assigned to the 6c site.

Another possible explanation of the effect is the change in orbital contribution to the hyperfine field. Its value can vary significantly with the direction of the magnetic moment, as was observed experimentally for the $(NdY)_2Co_{14}B$ series [13]. However, the presence of the unchanged line of the low symmetry 9d site at the same position as in Y_2Co_{17} testifies in favour of the former explanation.

The resonance line of the 6c site is also assumed to be found at the same position as in Y_2Co_{17}, 148 MHz, overlapped with the 18h satellite.

3.2.3. $Y_2Co_{17}N_x$

In the spectra of both samples a more developed line structure than in the carbide is observed. The most intense lines are centred at 149 and 190 MHz. However, traces of the 173–179 MHz (18h) and 201 MHz (18f) lines are well visible, especially in the spectrum of the sample with lower nitrogen concentration, sample (a). The 9d line also remains almost unchanged, as is observed for the carbide.

The line at 219 MHz exhibits a different power dependence and a much shorter relaxation time than the other lines of the spectrum. Its position corresponds to the resonant line of metallic cobalt, so that this line can with confidence be assigned to the cobalt-excess phase precipitating during the process of nitrogenation.

In the same way as for the carbide we assign the lines at 149 and 189 MHz respectively to the 18h and 18f Co atoms with one N atom as nearest neighbour. The observed increase in the intensities of the satellite lines with nitrogen concentration between samples (a) and (b) as compared to the lines representing cobalt sites with no nitrogen neighbours can be an additional argument in favour of such an interpretation.

The remaining lines corresponding to the spectrum of the host compound are attributed to the cobalt sites with no N atoms as nearest neighbours. The decrease in HFF caused by N atom neighbouring to the 18f site equals 1.2 T, which corresponds to a relative reduction in HFF by 6%. The corresponding values for the 18h site amount to 2.7 T and 14% respectively.

3.2.4. $Y_2Co_{17}H_{3.3}$

Besides the lines at the positions corresponding to the spectrum of Y_2Co_{17}, an intense satellite line at 158 MHz and a line at 190 MHz overlapping the 201 MHz line have been detected. In a similar way to that used for the carbide and the nitride, the 158 and 190 MHz lines can be assigned to the 18h and 18f cobalt sites with H atoms in the nearest-neighbour shell. The corresponding reduction in HFF amounts to 1.2 T (6%) for the 18f site and 1.8 T (9%) for the 18h site. Since the maximum value of x corresponding to complete filling of the 9e octahedral holes with hydrogen is $x=3$, some hydrogen also occupies the tetrahedral 18g sites. The closest Co atoms to the 18g site are of the 18h type. However, because of the poor resolution of the spectra, the effect of the H atoms at the neighbouring 18g sites on the cobalt hyperfine field cannot be distinguished from that of H atoms at 9e sites. Because the intensity of the 158 MHz satellite line is much lower than expected for the nominal hydrogen concentration considered here and because the resonance spectrum reveals some dependence on the excitation conditions, stronger than for other compounds studied, the values of HFF obtained can be treated only as an approximation. Further studies of this problem are necessary.

4. Conclusions

The introduction of N and C atoms into the Y_2Co_{17} lattice leads to a significant decrease in the hyperfine field at the yttrium site. We have been able to distinguish the effects of one, two and three nearest-neighbour N atoms. In the case of carbon, whose solubility in the compound is limited to $x \approx 0.07$, the effect of one C atom neighbour has been detected. For hydrogen only a slight decrease in the hyperfine field, with no local effects, is observed. The values of the relative decrease in the yttrium hyperfine field for all substituents are close to those observed by us in the iron-based series.

The presence of interstitial N, C or H atoms in the nearest-neighbour shell of a Co atom also leads to a remarkable reduction in the cobalt hyperfine field. The strongest effect is observed for nitrogen. The reduction in the hyperfine field is about two times larger for the 18h than for the 18f site, which we attribute to a closer distance of the 9e octahedral site to the 18h than to the 18f cobalt position.

The hyperfine fields at the yttrium and cobalt sites with no interstitial atoms as nearest neighbours are insensitive to the expansion of the lattice caused by interstitial site occupation, in contrast to the iron hyperfine fields in the iron-based series.

The observed effects are the consequences of the changes in local electronic structure at the rare earth and 3d metal sites with interstitial site occupation. The local character and strong distance dependence of the observed influence suggest that its origin is the covalency of the chemical bonding formed by the interstitial atom with the nearest neighbours in the lattice.

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