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MÖSSBAUER EFFECT MEASUREMENTS ON THE INTERMETALLIC COMPOUNDS Ni_3Al AND Ni_3Ga

Strongly Stoner enhanced materials like Ni_3Al and Ni_3Ga are of great interest for the
understanding of magnetism. These materials show a very high susceptibility and the so
called "giant moment" when iron is added in very low concentrations is about 25 and 40 μ_B
per iron atom in Ni_3Al and Ni_3Ga respectively (Schinkel et al., 1968, Schalwijk et al.,
1971). Generally a microscopic technique as the Mössbauer effect is very helpful in gaining
insight in magnetic materials. In Ni_3Al and Ni_3Ga two factors however may obscure the infor-
mation. Firstly the peculiar magnetic properties are due to the superstructure of these
alloys, which is derived from the fcc nickelstructure: nickel atoms are occupying the faces,
aluminium or gallium atoms the corners of a cube (Cu_3Au structure). Secondly the emitting
^{57}Co and the absorbing ^{57}Fe guest atoms may have a site preference for either the Ni or
the Al/Ga position. For at random distributed guest atoms the ratio of the occupation num-
bers of the Ni and the Al/Ga position of course will be 3. Especially in the Mössbauer
effect technique when absorbers and sources are given mechanical and heat treatments, these
factors must be understood. In a forthcoming paper we will discuss these effects on the
superstructure and the site occupation, and the possibility to test the material; with
X-ray, susceptibility and Mössbauer techniques. Here we mention only that the Mössbauer ef-
fect in the first place gives information about the short range order (see figure 1a and
1b) for room temperature spectra of disordered and ordered material. X-ray diffraction gives
the long range order parameter (Corey and Potter, 1967), but is not sensitive to small
ferromagnetic precipitates, which can obscure the magnetic behaviour of the alloys (De
Boer, 1969). A fast and reliable test for magnetic purity is susceptibility measurement.
For example filings of a $Ni_{74.75}Al_{25}Fe_{0.25}$ sample reduces χ by more than 50%. A heat treat-
ment of one week at 800° C recovers the bulk susceptibility completely. Full ordering as
concluded from susceptibility measurements has been confirmed by x-ray diffraction.

The site preference of cobalt or iron atoms can be obtained from Mössbauer spectra. We em-
phasize the importance of a comparison of source and absorber experiment for unravelling
the spectra. The emission spectrum of $Ni_{74.75}Al_{25}Fe_{0.25}$ as shown in figure 1c is interpreted
as consisting of a doublet due to ^{57}Co nuclei at Ni-sites and a singlet due to ^{57}Co nuclei
at Al-sites. The ratio of the occupation numbers $n_{Ni}:n_{Al}$ of Co atoms at Ni- and Al-sites is
4.4. This identification becomes clear after comparison with the absorption spectrum (figu-
re 1b). Here the single line is much more intense than the doublet because most of the iron
atoms go into the aluminium sites. From this spectrum we derive $n_{Ni}:n_{Al}=0.23$. In Ni_3Ga we
find the same trend. For a $Ni_{74}Ga_{25}Fe_1$ source for instance we find that all cobalt atoms
are going into the nickel sites, and for the same material as absorber we find for the iron
atoms $n_{Ni}:n_{Ga}=1.3$. These ratios are dependent on the thermal history of the sample.

The preference of cobalt for Ni- and iron for Al-sites is in agreement with the phase
boundaries (at 1150° C) in the ternary systems Ni-Al-Co and Ni-Al-Fe around the Ni_3Al com-
position (Guard and Westbrook, 1959). The direction of the solubility lobes (figure 2) for
cobalt and iron indicate that, at 1150° C, cobalt prefers the nickel position, whereas iron
has an equal preference for both positions. Combining these facts with our Mössbauer results,
which are obtained at low temperatures ($\leq 800^\circ$ C), we conclude that the preference of both
cobalt and iron at lower temperatures is shifted towards a stronger Al-site preference. In
order to get some insight in these matters one can use a "rigid ball" picture, and compare
atomic radii. Ni_3Al and Ni_3Ga have a cubic closest packing with the Cu_3Au structure, in which
the Al or Ga atoms are not nearest neighbours. Since these atoms are slightly larger than
the Ni atoms, this contributes to the stability of the ordered phase. For the understanding
of the site preference of guests we have listed in table I the lattice constants of the
various metals and alloys in the fcc structure. Comparing Co with Fe we expect that the

smaller Co atom prefers the Ni-site, and the bigger Fe atom has more preference for the Al/Ga position. Because Ga is bigger than Al, as shown by the lattice constants of Ni_3Ga and Ni_3Al, the Fe preference in Ni_3Ga will be less substantial, this in accord with our Mössbauer results.

The room temperature emission and absorption spectra of Ni_3Al and Ni_3Ga are computer analysed assuming a singlet and a doublet. The results are given in table II. The doublet is due to iron or cobalt atoms at the nickel site. Such an atom is in a tetragonal surrounding, giving rise to an axially symmetric electric field gradient. In general the lattice and the parent atom may contribute to the field gradient. If the surronding atoms in the lattice are responsible, charge between the Ni and the Al/Ga atoms has to be transferred, as assumed for fcc rare earth-aluminium intermetallic compounds (De Wijn et al., 1970). Assuming point charges at the lattice sites we find the usual formula for the electric field gradient a charge transfer of approximately 1 electron charge. This leads to highly ionic compounds, which seems contradictory to the metallic character of the alloys. It is more likely to assume that the 3d-change distribution of the iron atom is somewhat distored through the difference in size between the 8 nickel and the 4 other atoms in the first neighbouring shell. This also explains that the quadrupole splitting at ^{57}Fe nuclei in Ni_3Ga is larger than in Ni_3Al, viz 0.52 and 0.37 mm/sec respectively. An extra indication that the distorted 3d shell causes the field gradient is the temperature dependence of the quadrupole splitting, which at $600^\circ C$ has been reduced to 50% of its room temperature value.

As can be seen from table II the isomer shift at the Al/Ga position is very close to -0.02 mm/sec, which is found in metallic nickel. This may show that the electronic structure of the nickel atoms is not much affected through the aluminium or gallium atoms. On the other hand some changes can be expected through the expansion of the lattice. The isomer shifts belonging to the two positions in the Ni_3Ga lattice are both negative relative to the corresponding shifts in the Ni_3Al lattice. Thus the s-electron density at the ^{57}Fe nuclei in Ni_3Ga is lower than in Ni_3Al. Since an iron atom at an Al/Ga position in both cases has 12 nickel neighbours, we assume, neglecting the volume effect, that this lower s-electron density reflects a higher number of d-electrons in the Ni_3Ga 3d-band. Because this band is nearly filled, the 3d density of states at the Fermi level in Ni_3Ga is lower than in Ni_3Al. This is in agreement with the occurrence of ferromagnetism in stoichiometric $Ni_{75}Al_{25}$ with $T_c = 41^\circ K$ and only paramagnetism down to $0^\circ K$ in $Ni_{75}Ga_{25}$ (De Boer, 1969). The relatively low s-electron density at a nickel site in Ni_3Ga may show a more effective screening by the distorted 3d-shell of the iron atom.

The hyperfine magnetic fields at $4.2^\circ K$ are also given in table II. Considering the preference of ^{57}Co- and ^{57}Fe-atoms in the lattice, the fields at the nickel and aluminium sites are found to be 227 (± 1) and 238 (± 1) kOe respectively. The numbers between parentheses are the errors, given by the computer fit. The emission spectrum exhibits considerable line broadening, probably caused by inhomogeneous diffusion of ^{57}Co in the surface layer of the material. This inhomogeneity results in much higher hyperfine fields (Dudas et al., 1971, 1972), so that we consider the number of 227 kOe as an upper limit. The usually mentioned causes for differences in hyperfine fields are changes in the parent magnetic moment or effects from neighbouring magnetic moments through conduction electron polarization. Here however the more distorted 3d-shell of an iron atom in a nickel site, compared to that in an aluminium site, also has to be considered. Since the hyperfine magnetic field is a result from the contact interaction between the nuclear magnetic moment and the s-electron spin distribution with the same magnetic moment may cause a different hyperfine magnetic field.

References

F.R. de Boer, thesis, University of Amsterdam (1969)

C.L. Corey and D.I. Potter, J. Applied Phys. 38, 3894 (1967)

J. Dudáš, J. Kučera and T. Zemčík, Proc. Conf. on Möss. Spectr., Dresden, Phys. Ges. der
LDR, p. 289 (1971)

J. Dudáš, J. Kučera and T. Zemčík, Czech. J. Phys. B, 22, 332 (1972)

R.W. Guard, J.H. Westbrook, Trans. Met. Soc. AIME, 215, 807 (1959)

M.S. Schalwijk, P.E. Brommer, G.J. Cock and C.J. Schinkel, J. de Physique, Cl, 997 (1971)

C.J. Schinkel, F.R. de Boer and J. Biesterbos, Phys. Lett., 26A, 501 (1968)

H.W. de Wijn, A.M. van Diepen and K.H.J. Buschow, Phys. Rev. Bl, 4203 (1970).

TABLE I   Some relevant lattice constants in Å

Ni	Ni$_3$Al	Ni$_3$Ga	γ-Co	γ-Fe	Ni$_3$Fe (ordered)	Ni$_3$Fe (disordered)
3.524	3.552	3.582	3.545	3.591	3.552	3.554

TABLE II   RT and 4.2°K spectra of Ni$_3$Al and Ni$_3$Ga

| | RT | | | | | 4.2°K | |
	IS Al/Ga pos.	IS Ni pos.	QS Ni pos.	Γ	$\dfrac{n_{Ni}}{n_{Al/Ga}}$	H_{hf} (kOe)	1,6
Ni$_{74.75}$Al$_{25}$Fe$_{0.25}$							
source	+0.02	−0.03	0.39	0.23	4.40	227	0.86
absorber	+0.03	−0.03	0.35	0.27	0.23	238	0.39
Ni$_{74}$Ga$_{25}$Fe$_1$							
source		−0.12	0.53	0.31	inf.		
	−0.03	−0.12	0.48	0.29	1.3		
Ni$_{75}$Ga$_{25}$							
source	−0.02	−0.14	0.56	0.30	5.2		

All velocities are in mm/sec, IS relative to iron and calculated for the material as a sour-
ce. Γ and $\Gamma_{1,6}$ are the full widths at half height for the 3 RT-lines, and the 2 outermost
lines respectively.
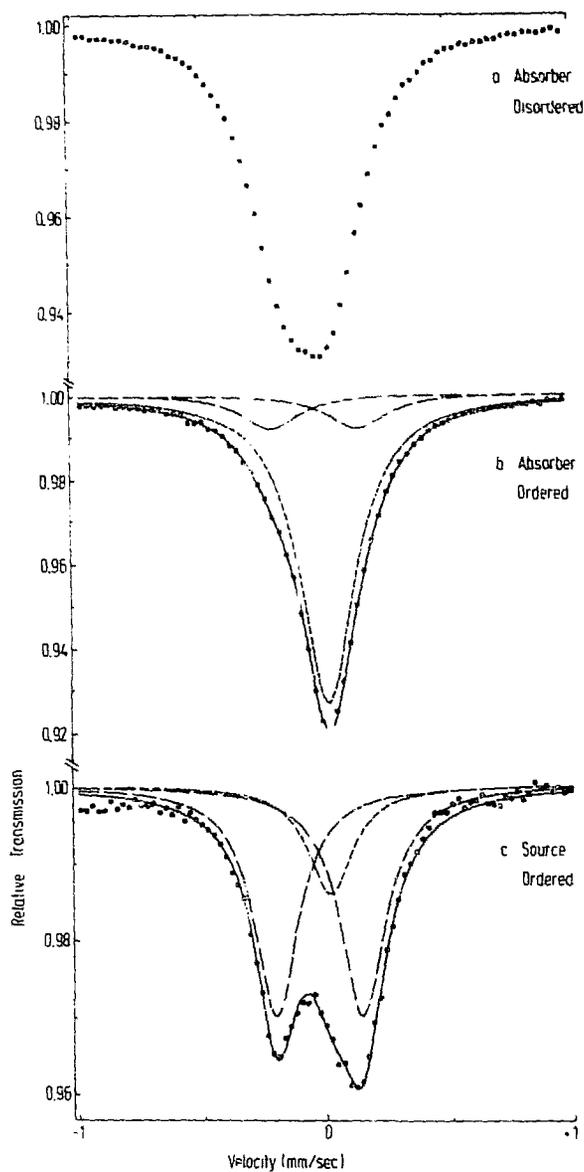
RT Spectra of Ni$_{74.75}$Al$_{25}$Fe$_{0.25}$

Fig.1. RT spectra of Ni$_3$Al. IS relative to iron, calculated for the material as a source
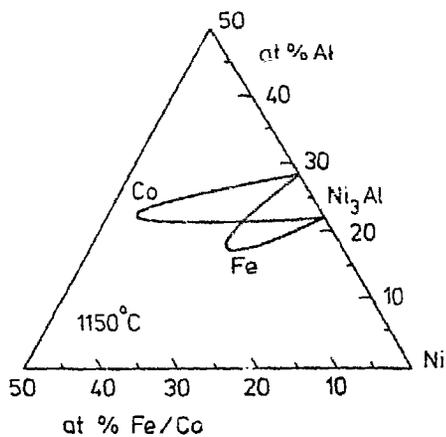

Fig.2. Solubility boundaries of Co and Fe in Ni$_3$Al. (Guard and Westbrook, 1959)