Mössbauer study of the hydrides of Nb$_3$Me with A15 structure

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Abstract

Hydrides of intermetallic Nb$_3$Me (Me $\equiv$ Au, Ir, Sn) with A15 structure were prepared at hydrogen pressures up to 7 GPa and studied by Mössbauer spectroscopy with the resonances on ^{197}Au (77.3 keV), ^{193}Ir (73.0 keV) and ^{119}Sn (23.9 keV). In all these systems, hydrogenation was found to lead to a reduction in the electron density at the Mössbauer nuclei, but the decrease for ^{119}Sn was much smaller than for ^{197}Au and ^{193}Ir. This difference suggests that in Nb$_3$Au and Nb$_3$Ir the hydrogen occupies interstitial sites which are closer to the metal atoms than those occupied in Nb$_3$Sn.

1. Introduction

A number of intermetallic compounds with A15 structure are known to form hydrides by cathodic charging, when they are boiled in acids or when they are exposed to gaseous hydrogen [1–11]; the latter method often requires hydrogen pressures of the order of gigapascals [10, 11]. The hydrogenation is accompanied by a susbtantial lattice expansion, but the hydrides usually retain the A15 structure. A major point of interest in the investigation of these hydrides is the way in which the superconducting properties are affected by the uptake of hydrogen. It turns out that the changes in the electronic structure resulting from hydrogenation nearly always lead to a reduction in the superconducting transition temperature [2–5, 7, 8, 10, 11], an exception being Nb$_3$IrH$_x$ [11] (see Table 1).

In a number of cases, these hydrides can be studied by Mössbauer spectroscopy, for example when the Me component is antimony, gold, platinum, iridium or osmium. Such experiments can provide further insight into the electronic structure of the hydrides and yield information about the type of interstitial sites occupied by the hydrogen atoms. This paper presents the first Mössbauer results on Nb$_3$AuH$_x$, Nb$_3$IrH$_x$ and Nb$_3$SnH$_x$ obtained with the resonances of ^{197}Au (77.3 keV), ^{193}Ir (73.0 keV) and ^{119}Sn (23.9 keV).

TABLE 1

Summary of results on hydrides of Nb_3Me intermetallic compounds with A15 structure

Compound and Mössbauer resonance	x	T (°C)	p_{H_2} (GPa)	a_0 (Å)	T_c (K)	S (mm s^{-1})	W (mm s^{-1})
Nb_3AuH_x	0	–	–	5.198	10.1	$+5.13 \pm 0.01$	2.10 ± 0.01
^{197}Au (77 keV)	2.8	325	0.85	5.411	3.5	$+3.09 \pm 0.01$	2.38 ± 0.02
	4.2	325	5.1	5.467	0.9	$+2.49 \pm 0.01$	2.72 ± 0.03
Nb_3IrH_x	0	–	–	5.135	1.9	$+0.98 \pm 0.01$	0.81 ± 0.02
^{193}Ir (73 keV)	4.3	325	7.0	5.415	3.0	$+0.07 \pm 0.03$	2.16 ± 0.05
Nb_3SnH_x	0	–	–	5.287	18.0	$+1.59 \pm 0.01$	1.05 ± 0.01
^{119}Sn (24 keV)	2.1	300	5.4	5.410	<1.5	$+1.57 \pm 0.01$	1.06 ± 0.02
	2.2	300	7.1	5.418	<1.5	$+1.50 \pm 0.01$	1.14 ± 0.02

T and p_{H_2} are the temperature and hydrogen pressure at which the hydrides were prepared, a_0 is the lattice constant, T_c the superconducting transition temperature, W the full width at half maximum of the Mössbauer pattern, and S the mean isomer shift relative to the respective source, i.e. ^{197}Pt in platinum metal for ^{197}Au, ^{193}Os in osmium metal for ^{193}Ir, and ^{119m}Sn in $BaSnO_3$ for ^{119}Sn.

2. Experimental details

Nb_3Ir and Nb_3Au were prepared from the elements by levitation melting in an induction furnace under an argon atmosphere and subsequent annealing at 1100 °C for 24 h [11]. Nb_3Sn was prepared by sintering the powdered elements in a sealed quartz tube at 1040 °C for 40 h.

The hydrides were prepared by exposing the intermetallic compounds to hydrogen pressures of up to 7 GPa at temperatures near 300 °C in high pressure cells using MnH_x as a hydrogen donor [12]. To avoid decomposition, the specimens were cooled to about 90 K while they were still under high pressure. They were then removed from the pressure cell, stored in liquid nitrogen, and later transferred into the Mössbauer cryostat without warming. The Mössbauer experiments were all performed with both the absorber and the source at 4.2 K.

The lattice parameters were measured at 100 K by X-ray diffraction using Cu Kα radiation. The X-ray powder patterns confirmed that the hydrides had retained the A15 structure and yielded lattice expansions for Nb_3AuH_x and Nb_3IrH_x that agreed well with previous results [11]; the hydrogen content was determined with an accuracy of about 2% by hot extraction into a calibrated volume after the Mössbauer experiments. Because of difficulties in outgassing the Nb_3SnH_x specimens completely, the hydrogen content of Nb_3SnH_x was determined from the lattice parameter as measured by X-ray diffraction and an average value for the increase in lattice parameter with hydrogen content based on previous work [3, 5, 7]. Considering the large scatter of the previous results, the hydrogen contents for Nb_3SnH_x are only considered to be accurate to within about 20%. Details of the loading

conditions, as well as the results of X-ray diffraction and of measurements of the superconducting transition temperature are compiled in Table 1.

The sources for ^{197}Au and ^{193}Ir experiments were made by irradiating isotopically enriched metallic ^{196}Pt and ^{192}Os with thermal neutrons in the Munich Research Reactor. Owing to its f.c.c. structure, platinum metal yields a single emission line, while sources made of h.c.p. osmium metal emit an unresolved quadrupole doublet with a splitting of 0.48 mm s^{-1} [13]. This splitting was taken into account in the least squares fits of the Mössbauer spectra with appropriate superpositions of lorentzian lines. For the measurements with ^{119}Sn, a single line source of ^{119m}Sn in BaSnO$_3$ was used.

3. Results

3.1. Hydrides of Nb$_3$Au

The Mössbauer spectra of Nb$_3$Au and its hydrides are shown in Fig. 1. The Mössbauer line of Nb$_3$Au is a single line with an isomer shift of +5.13 mm s^{-1}, compared with −1.23 mm s^{-1} for metallic gold and +4.65 mm s^{-1} for dilute gold impurities in b.c.c. niobium [14–16]. Both before hydrogenation and after outgassing, the spectrum of Nb$_3$Au exhibits a shoulder near +3.5 mm s^{-1} which is attributed to the presence of impurities,
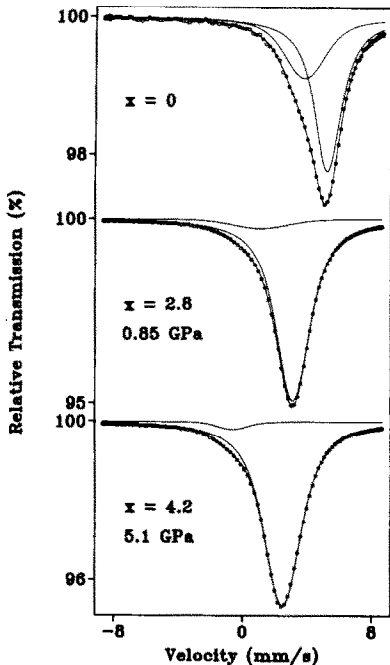

Fig. 1. ^{197}Au Mössbauer spectra of Nb$_3$AuH$_x$ compounds measured at 4.2 K with a source of ^{197}Pt in metallic ^{196}Pt.

presumably a b.c.c. Nb–Au alloy or one of the intermetallic phases, Au_2Nb_3 or $AuNb_2$, that have been reported to exist in the Nb–Au system [17].

The Mössbauer spectra of the hydrides of Nb_3Au exhibit slightly broadened peaks with isomer shifts that decrease with increasing hydrogen content (Table 1). The spectra are slightly asymmetric owing to the presence of a minor component at the low velocity side, but even the main peak cannot be fitted with a simple lorentzian line. We therefore adjusted a lineshape corresponding to a gaussian distribution in positions of lorentzian lines (Fig. 1). The widths given in Table 1 are the overall widths at half maximum of the peaks. The Mössbauer pattern of the impurity phase giving rise to the shoulder in the spectra of the unloaded specimen seems to be hidden under the main peak in the hydrides. Its presence may slightly affect the values of the mean isomer shifts for the hydrides, but will have little effect on the conclusions drawn from the data.

3.2. Hydrides of Nb_3Ir

The Mössbauer spectrum of Nb_3Ir (Fig. 2) is a single line with an isomer shift of $+0.98$ mm s^{-1}, which is close to the shift of $+0.70$ mm s^{-1} for dilute iridium impurities in b.c.c. niobium [14]. The spectrum of $Nb_3IrH_{4.3}$ is a broad, structured peak that extends practically from the peak position of the pure compound at $+1.0$ mm s^{-1} to about -0.8 mm s^{-1}. The broad structure appears to be mainly due to a distribution of isomer shifts, although contributions from electric quadrupole splittings cannot be ruled out. The wide range of isomer shifts indicates that the number of hydrogen neighbours around individual iridium atoms varies from zero to a maximum number that gives rise to an isomer shift of about -1.8 mm s^{-1} with respect to the

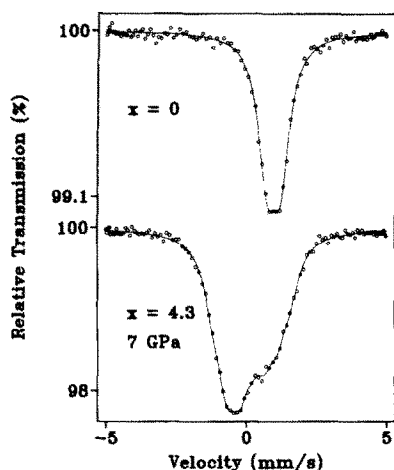Fig. 2. ^{193}Ir Mössbauer spectra of Nb_3IrH_x compounds measured at 4.2 K with a source of ^{193}Os in metallic ^{192}Os.
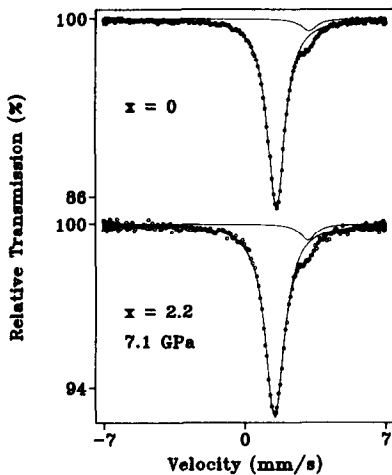
Fig. 3. ^{119}Sn Mössbauer spectra of Nb$_3$SnH$_x$ compounds measured at 4.2 K with a source of ^{119m}Sn in BaSnO$_3$.

hydrogen-free compound. Such a distribution could arise from a macroscopically inhomogeneous hydrogen distribution in the specimen, but this is unlikely since X-ray diffraction did not show indications of macroscopic inhomogeneities. Rather, the distribution of isomer shifts appears to be due to microscopic inhomogeneities in the hydrogen distribution, as will be discussed below.

3.3. Hydrides of Nb$_3$Sn

The Mössbauer spectrum of Nb$_3$Sn (Fig. 3) is a single line at $+1.59$ mm s^{-1} with respect to the source of BaSnO$_3$. A small shoulder on the high velocity side near $+2.6$ mm s^{-1} may be unreacted β-Sn, which in its pure form yields an isomer shift of $+3.00$ mm s^{-1} and has also been observed in the Nb$_3$Sn samples by X-ray diffraction. Tin impurities in b.c.c. niobium have an isomer shift of $+1.65$ mm s^{-1} [15, 16] and would therefore be indistinguishable from Nb$_3$Sn by Mössbauer spectroscopy, but no b.c.c. niobium was found by X-ray diffraction.

Hydrogenation up to $x = 1.68$ caused only a very slight change in the isomer shift by no more than -0.09 ± 0.02 mm s^{-1} and a marginal broadening of the Mössbauer line. In Mössbauer experiments on dilute tin impurities in NbH$_x$, hydrogen loading was also found to induce only very small changes in the isomer shift, e.g., of -0.04 mm s^{-1} between $x = 0$ and $x = 0.85$ [15, 16]. The smallness of this shift has been explained by a repulsive interaction between the tin atoms and the hydrogen interstitials. This prevents the latter from occupying sites next to the tin impurities. In the present case, one cannot argue in this way since the tin is a major constituent of the lattice. In the following, a different explanation will therefore be attempted, which is, however, also based on a strongly repulsive interaction between the tin and the hydrogen.

4. Discussion

In all three systems, hydrogenation results in a decrease in the isomer shift, which corresponds to a reduction in the electron density at the metal nuclei. In Nb_3Au and Nb_3Ir this reduction is quite substantial, but in Nb_3Sn it is extremely small. This becomes clear when the shifts resulting from hydrogenation are compared with those caused by changing the oxidation state of the metal in simple chemical compounds. For instance, the isomer shift between Au(III) in $KAuCl_4$ and Au(I) in $AuCl$ is $+2.20$ mm s^{-1}, the shift between Ir(IV) in K_2IrCl_6 and Ir(III) in K_3IrCl_6 is $+1.31$ mm s^{-1}, and the shift between Sn(II) in $SnCl_2$ and Sn(IV) in $SnCl_4$ is $+3.22$ mm s^{-1} [18].

The differences in the magnitude of the hydrogen-induced change in the electron densities in Nb_3Sn on the one hand and in Nb_3Au and Nb_3Ir on the other might be attributed to peculiarities of the electronic structure of main-group elements such as tin and transition elements such as iridium or gold, but it appears more probable that these differences arise because the hydrogen occupies different interstitial sites in the different Nb_3Me compounds, depending on whether the metal element is a main group element such as tin or antimony, or a transition metal such as iridium, platinum or gold.

The only hydride with A15 structure for which information on the sites occupied by the hydrogen has been obtained by neutron diffraction is Nb_3SnH_x [3]. In this case, the hydrogen was found to occupy randomly the sixfold d positions of the space group $O_h^3 - Pm3n$, i.e. the positions in the faces of the unit cell not occupied by niobium. Complete occupancy of these sites allows a maximum hydrogen content of $x = 3$. In fact, even at a hydrogen pressure of 7 GPa, only $x = 2.2$ could be reached in Nb_3SnH_x (Table 1). The maximum x values for hydrides of Nb_3Me with Me $\equiv$ Au, Pt, Ir and Os, however, lie well above 4 [11], which requires that other interstitial sites are occupied either alone or in addition to the d sites. Possible alternative sites are the 16-fold i positions on the space diagonals of the unit cell. There are two such sites between each pair of Me atoms in the $\langle 111 \rangle$ direction, but both of these sites certainly cannot be occupied at the same time, since this would lead to unrealistically close H–H pairs. With at most half of the i positions filled, a maximum hydrogen content of $x = 4$ is possible. Hydrogen contents above $x = 4$, as are actually observed, require the occupancy of additional sites, i.e. either the d positions or still other interstitial sites, possibly the 24 fold k positions. The latter are occupied in UH_3, which also has the A15 structure with uranium occupying both metal sites [19]. However, the lattice constant of UH_3, $a_0 = 6.64$ Å, is substantially larger than those of the Nb_3MeH_x hydrides, where the k interstices are therefore rather small and less likely candidates.

The largest interstices are the half filled i positions, with one metal and three niobium atoms at a distance of 1.98 Å if the four distances are assumed to be equal and the lattice constant is $a_0 = 5.4$ Å. Hydrogen in the d positions would be surrounded by a tetrahedron of nearest niobium atoms at a distance

of 1.91 Å. Its distance to the nearest Me atom is 3.02 Å, *i.e.* much larger than for hydrogen in the i positions. Hydrogen that far from the Me atoms will conceivably have only a minor influence on the electron density at the Me nuclei. This is the situation in Nb_3SnH_x, where the hydrogen is known to occupy the d positions [3]. The large isomer shifts observed when Me $\equiv$ Au or Ir suggest that in these cases the i positions are preferred, although for $x > 4$ the occupation of additional sites is required. Most probably these additional sites are the d positions, although the k positions should not be ruled out completely despite their small size. At present one cannot say whether the d positions are filled only when practically no unoccupied i positions are left (*i.e.* at $x > 4$), or whether both sites become partially occupied at lower hydrogen contents. Detailed studies of the dependence of the isomer shifts on the hydrogen content might, however, contribute to clarifying this question. Further hints come from the shape of the Mössbauer spectra. Thus, the broad pattern of $Nb_3IrH_{4.3}$ and the relatively narrow pattern observed for $Nb_3AuH_{4.2}$ (Figs. 1 and 2) can be understood if in the latter case the i positions become filled preferentially, which will result in a rather well defined configuration of nearest hydrogen neighbours around each gold atom, and hence in a rather narrow Mössbauer peak, whereas in Nb_3IrH_x the d positions are filled first or at least simultaneously with the i positions, which will result in a rather wide distribution of different i site occupancies around the iridium atoms. Since only hydrogen on the i sites is close enough to the iridium to have much influence on the isomer shift, this will result in the distribution of isomer shifts observed in $Nb_3IrH_{4.3}$.

The reason for the different occupancies of the various kinds of possible hydrogen sites can be seen in the electronic interactions between the hydrogen and the Me atoms. As has been observed previously [20], hydrogen in intermetallic compounds generally appears to avoid sites with main group elements as nearest neighbours. It is in line with this view that in Nb_3SnH_x the d sites surrounded by four niobium neighbours are occupied and that it has been impossible to make this hydride with hydrogen concentrations that would require the occupancy of interstitial sites with tin neighbours.

Acknowledgment

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