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Hyperfine interactions and local environment effects in Fe_xNi_{100-x} (x = 55–67) Invar alloys: ^{57}Fe Mössbauer spectroscopy data at 5 K

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ABSTRACT

A systematic study of the magnetic hyperfine field distribution for ^{57}Fe in the Invar alloys Fe_xNi_{100-x} (x = 55, 60, 63, 65 and 67) have been performed by Mössbauer spectroscopy technique at 5 K. The composition dependences of the magnetic hyperfine fields (B_{hf}), isomer shifts and relative intensities of the magnetic subspectra were measured and analyzed. The reliable data on the correspondence between the B_{hf} magnitude and the type of locale atomic configuration were obtained. It is confirmed that the Fe–Ni Invar alloys in their ground state are predominantly collinear ferromagnets with well-defined atomic magnetic moments. Particular emphasis has been placed on the low-field (LF) component of the distribution (B_{hf} = 1.4 and 2.5 T) which is considered as corresponding to the Fe sites with the antiferromagnetic (AFM) alignment of the magnetic moment. The most striking feature of the LF component is the anomalous positive isomer shift that corresponds to a large reduction of the local electron density at the Fe sites. It may be proposed that the volume effect is one of the plausible reasons for the increase in the IS value for LF components. In this case, we should suggest that the formation of the AFM sites leads to some increase in the local atomic volume. The possible influence of the competition between energetically satisfied and unsatisfied exchange bonds on the stability of the AFM states of the Fe atoms is briefly discussed.

1. Introduction

One of the most remarkable phenomena observed in magnetic alloys is the Invar effect which consists of the vanishing of the thermal expansion coefficient of the fcc Fe–Ni alloys at Ni concentrations around 35 at.% and over a wide temperature range below the magnetic ordering temperatures. The macroscopic properties of the Invar alloys have been investigated in detail, however the microscopic mechanism of the Invar effect still has not got a commonly accepted explanation. There is no doubt that the Invar effect is strongly related to the magnetic ordering of the alloys but there is no general consensus on the origin of the effect. Although the origin of the Invar effect has been extensively theoretically investigated, it is still controversial. Among the theoretical models of the Invar effect, the theories based on the correlation between the volume and the magnitude of the Fe magnetic moment hold much favor [1–4]. It is believed that the Invar effect is related to a loss of local moment magnitude and an associated contraction occurring as the temperature is increased. In the theory, the electron configurations of the Fe atoms should change through the transition from the high-moment state to the low-moment one. However, at the same time it has been shown [5,6] that the basic macroscopic properties of the Invar alloys can be explained by theories in which Invar is predominantly a ferromagnetic alloy, having local magnetic moment magnitudes that are not affected by temperature. An alternative approach to the Invar problem is based on an assumption of non-collinear magnetic structure of the Invar alloys [7,8]. In terms of this theory, the magnetic structure of the alloy is characterized by the existence of nearly degenerate non-collinear states with differing magnetic moments and volumes. In the "frustration" model of the Invar alloys [9–11], particular attention has been paid to the antiferromagnetic exchange interaction Fe–Fe. If the Invar alloy is a predominantly collinear ferromagnet, the antiferromagnetic Fe–Fe exchange bonds are not energetically satisfied. As a result, a magneto-volume effect appears which is accompanied by an anomalous expansion of the lattice at low temperatures. The several theories of the Invar effect were recently critically reviewed [11]. None of the above-mentioned models have been unambiguously confirmed by experiment. In particular, the polarized neutron results obtained in the temperature range from 100 to 600 K [12] seem to be incompatible with the two-state models. The direct measurements by the neutron scattering technique showed [13,14] that the Invar Fe–Ni alloys are collinear ferromagnets over a wide range of temperatures.

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A common feature to all the aforementioned theories is that the possible local effects have been largely ignored. In other words, it is assumed that the magneto-volume striction (expansion or contraction) is uniform down to the microscopic scale. However, the Fe–Ni Invar is a concentrated random alloy in which the local environment effects may play a crucial role because the magnetic states of the Fe atoms as well as the structural parameters can be strongly influenced by the type of the local atomic configuration. For example, from the theoretical estimates [9] one would expect that the Fe sites surrounded by 10 or more Fe nearest neighbors have an antiferromagnetic alignment of its magnetic moment. Unfortunately, little is known about the local effects in the Fe–Ni Invar alloys. However, the recent experiments provide unambiguous evidence for the existence of such effects. Experimentally, it was found that the mean separation of Fe–Fe neighbor pairs is expanded relative to the average lattice [15]. The direct evidence for the existence of the locale environment effects has been obtained from the elastic diffuse scattering of neutrons [16]. For the $Fe_{65}Ni_{35}$ alloy, the results suggest the existence of microclusters with the average size of 2–5 nm. The features of the clusters are found strongly correlated with the behavior of the Invar alloys as a function of temperature and composition. It is important to emphasis that the formation of the clusters is directly related to the local deformations of the lattice. Recently, a theoretical study of static atomic displacements in the $Fe_{65}Ni_{35}$ alloy has been performed [17]. It was found that the Invar alloys are characterized by a huge dispersion of both the interatomic distances and the nearest neighbor exchange parameters. The individual static displacements can be quite large; for the Fe–Fe bonds, the difference in the interatomic distances can reach a value of up to 9%. Obviously, so large local displacements should have a strong influence on the behavior of the Invar alloy as a whole.

A detailed knowledge of the properties of electron states of the Fe atoms on microscopic level is necessary for a further understanding of the nature of the Invar effect. So far, there are few data dealing with this problem. As a result, the physical grounds, which are needed to make a decision between alternative models of the Invar effect, are still lacking. Unfortunately, experimental tools to observe directly magnetic behavior of particular atoms in disordered alloys are very limited. At present seemingly that the Mössbauer spectroscopy is a uniquely suited technique for this purpose, since its site selectivity allows probing the electron and magnetic properties of the Fe atoms reside in the non-equivalent sites in the crystal. The technique offers a possibility to observe spin configurations of different types and to classify these states by using an analysis of the hyperfine parameters. In addition, for the Invar problem, an important parameter is the isomer shift which value is a source of information on both the electron configuration of the Fe atoms and the variations of the atomic volume [18,19].

The Mössbauer spectroscopy technique has been used in the Invar alloys studies repeatedly. The basic results were deduced from the analysis of the hyperfine field distributions (HFD) [20–22]. It was found that, at low temperatures, more then 90% of the full intensity forms the main maximum (MM) of HFD [22,23]. The components of MM correspond to the Fe atoms located in the ferromagnetic atomic configurations. For these configurations, the values of the hyperfine field (B_{hf}) at the central Fe site exceed 20–25 T. The width of MM is determined by statistical variations of the number of the Fe atoms in the nearest environment of the central Fe atom [20,23,24]. Apart from MM, the rather small low-field (LF) component is present for which the B_{hf} magnitude not exceeds 5–10 T. The presence of the LF component in the Mössbauer spectra of the Fe–Ni Invar alloys is recorded repeatedly (for examples, see Refs. [22,23,25]) but this component has never been studied in detail. Until now, most research has focused on the behavior of the Fe atoms in certain ferromagnetic configurations belonging to MM. Little attention is given, however, to other components of the spectra that may play an important role. Taking into consideration the above-mentioned possibility of the local effects, a close examination of all spectral components appears especially important. The careful study of the behavior of the parameters of the spectra as a function of composition is also very important.

In this paper we present the results of a systematic study of the magnetic ground state (at $T = 5$ K) of the Fe–Ni Invar alloys in the concentration range of 55–67 at.% Fe by means of the ^{57}Fe Mössbauer spectroscopy. The particular aim of this work is detailed measurements of the concentration dependences of the main parameters of the Mössbauer spectra (the magnetic hyperfine fields, the relative intensities of magnetic subspectra and the isomer shifts). As a result, the reliable data on the correspondence between the B_{hf} magnitude and the type of the atomic configuration were obtained. A special attention has been paid to the LF components of the hyperfine field distribution, which may be assumed to relate to local environment effects.

2. Experimental

Samples of Fe_xNi_{100-x} (with $x = 55$, 60, 63, 65 and 67) were prepared using the standard procedure which assures production of the disordered Invar alloys with the fcc crystal structure. Alloys ingots were prepared by arc melting in argon using metals with purity not worse than 99.98%. The samples were re-melted several times for homogenization. The ingots were annealed in a quartz tube under a protective argon atmosphere at 1200 K and quenched. Then the ingots were filed into fine powders for Mössbauer measurements. The powder samples were annealed at 1200 K and quenched. In order to check the purity of the alloys the samples were examined by X-ray powder diffraction. Analysis of the data has conformed unambiguously that the samples have expectation fcc structure without visible contamination by the other phase. The lattice parameters were in a good agreement with results given in the literature ([10,26] and references therein). The Mössbauer absorption spectra were measured at 5 K using a ^{57}Co source in a Rh matrix. In order to enhance the effect of resonance absorption and resolution in detecting the Mössbauer radiation, a resonance detector was used. Isomer shifts (IS) are given relative to α-Fe at room temperature.

Two different fitting procedures were applied to the Mössbauer spectra analysis. First, the hyperfine field distributions were calculated by the histogram method. The widths of the histogram intervals were chosen so that would be nearly equal to the instrumental line width. This allowed us to use the direct method for minimizing the χ^2 functional and to eliminate ambiguities associated with smoothing procedure. Second, the spectra were least-squares fitted by a superposition of discrete magnetic subspectra. The line intensity ratios in each sextet were constrained to 3:2:1:1:2:3. All the other parameters (including the relative intensities of the magnetic subspectra and the isomer shifts) were set free in the fitting procedure. The quadrupole shifts of the components of the magnetic subspectra are very small (not more than 0.03 mm/s). Such quadrupole interaction causes only very small asymmetry of the spectra but does not affect the parameters of the spectra appreciably. The number of subspectra required for correct approximation was not fixed but was determined during processing. The velocity resolution was typically 0.11 mm/s/channel. The investigation of the central part of the spectra, where the LF components of HFD are localized, has been performed under specialized conditions with the velocity scale factor of 0.018 mm/s/channel. Below, the alloys are abbreviated by an indication of the Fe concentration only (Fe55, Fe60, etc.).

3. Results

A typical example of the Mössbauer spectrum and corresponding HFD is given in Fig. 1. As a whole, our results for the HFD are rather similar to the previously reported data (see references cited in Section 1). We find that more then 90% of the full intensity form the MM of HFD. For atomic configurations consisting MM, the values of B_{hf} at the central Fe atom exceed 25 T. In addition, for all alloys under consideration, the LF component ($B_{hf} < 5$ T) with the intensity less than 10% is present. It is important to note that, all over from the LF component up to the MM, the hyperfine fields are absent completely. Thus, in the ground state of the Fe–Ni Invar alloys, only two types of the magnetic states of the Fe atoms are present: ferromagnetic states which form the MM's configurations and non-ferromagnetic ones (LF components of HFD). As the intensity of the LF component is rather small, this picture is consistent with the assumption that the Invar is predominantly a ferromagnetic alloy