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$K\beta$-to-$K\alpha$ x-ray intensity ratio studies of the valence electronic structure of Fe and Ni in Fe_xNi_{1-x} alloys

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$K\beta$-to-$K\alpha$ x-ray intensity ratios of Fe and Ni in pure metals and in Fe_xNi_{1-x} alloys ($x=0.20$, 0.50, 0.58) exhibiting similar crystalline structure have been measured following excitation by 59.54 keV γ rays from a 200 mCi ^{241}Am point source to understand why the properties of the Fe_xNi_{1-x} ($x=0.2$) alloy are distinct from other alloy compositions. The valence electronic structure of Fe and Ni in the samples has been evaluated by comparing the measured $K\beta$-to-$K\alpha$ intensity ratios with the results of multiconfiguration Dirac-Fock calculations. Significant changes in the $3d$ electron population (with respect to the pure metal) are observed for Fe and Ni for certain alloy compositions. These changes can be explained by assuming rearrangement of electrons between $3d$ and $(4s,4p)$ band states of the individual metal atoms. It has been found that the valence electronic structure of the $Fe_{0.2}Ni_{0.8}$ alloy is totally different from the other two alloys, which perhaps is connected to the special magnetic properties of this alloy.

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Fe_xNi_{1-x} alloys play an important role in fundamental and applied research due to the rapid advance of magnetoelectronics.[1] Although the Fe_xNi_{1-x} alloy crystallizes in the same γ (fcc) phase for all the compositions ($x=0.2$, 0.5, and 0.58) reported here, Permalloy, a member of the family of Fe_xNi_{1-x} alloys (with $x=0.2$), has some distinct physical properties of vanishingly small magnetostriction, low coercivity, and high permeability, which makes it the material of choice for magnetic recording media, sensors, and nonvolatile magnetic random access memory. The electronic density of states for $4s$ and $3d$ electrons at the Fermi surface plays a significant role for a quantitative understanding of the phenomenon of transport spin polarization.[2] It is therefore very important to have a detailed knowledge of the valence electronic structure of Fe and Ni in the Fe_xNi_{1-x} alloys.

The $K\beta$-to-$K\alpha$ x-ray intensity ratio has been reported[3–21] to be a sensitive physical parameter to investigate the changes in the valence electronic structure of $3d$ transition metals.[3] It has been found for various alloys[18–21] that the change of the alloy composition may cause a change in the $3d$ electron population of both transition metals in the alloy, what must result in a change of the $K\beta$-to-$K\alpha$ intensity ratio of these metals (because the change of the $3d$ electron population modifies the $3p$ orbitals more than the $2p$ orbitals[21]).

In this paper we present the results of our study on the valence electronic structure of Fe and Ni in Fe_xNi_{1-x} alloys for various compositions ($x=0.2$, 0.5, and 0.58), exhibiting similar crystalline structure to understand why the physical properties of $Fe_{0.2}Ni_{0.8}$ alloy are drastically different from the other alloy compositions. We have used our experimental information on the valence electronic structure of both metals in the alloys to estimate the average number of $3d$ electrons and average number of $(4s,4p)$ electrons of Fe and Ni.

The measurements were carried out using high-purity alloys (in powder form) procured from Alpha, a Johonson Mathey Company, U.K. The powder material is pelletized into the size of 10 mm diam × 3 mm thick for final use in the experiments. The experiments were performed using 59.54 keV γ rays from a 200 mCi ^{241}Am point source that ionize the target atoms. The emitted x-rays were detected by a 30 $mm^2\times3$ thick Canberra Si(Li) detector having a 12.7 μm thick beryllium window. The resolution of the Si(Li) detector was ∼165 eV [full width at half maximum (FWHM)] for a 5.9 keV x-ray peak. Pulses from the Si(Li) detector preamplifier were fed to an ORTEC-572 spectroscopy amplifier and then recorded in a Canberra PC based Model S-100 multichannel analyzer. The gain of the system was maintained at ∼16 eV/channel.

All the x-ray spectra were carefully analyzed with the help of a multi-Gaussian least-square fitting program[22] using a nonlinear background subtraction. No low-energy tail was included in the fitting as its contribution to the ratio was shown to be quite small[23]. A typical K x-ray spectrum of Fe_xNi_{1-x} alloy corresponding to the alloy composition $x=0.5$ is shown in Fig. 1. The $K\beta$-to-$K\alpha$ intensity ratios were determined from the fitted peak areas after applying necessary corrections to the measured data. Details regarding the experimental arrangement as well as data analysis have been reported elsewhere.[18,23–26]

The experimental results for the $K\beta$-to-$K\alpha$ x-ray intensity ratios of Fe and Ni in pure metals and in the Fe_xNi_{1-x} alloys

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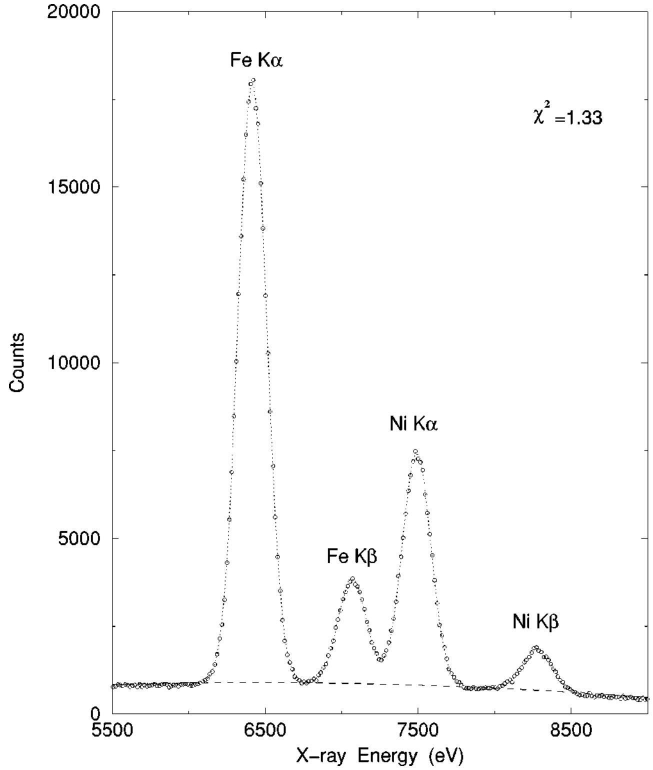

FIG. 1. A typical K x-ray spectrum of a $\mathrm{Fe}_x\mathrm{Ni}_{1-x}$ alloy corresponding to the alloy composition $x=0.5$. In the figure ○ corresponds to the experimental data, the dotted line corresponds to the fitted data, and the dashed line corresponds to the fitted background.

($x=0.2$, 0.5, and 0.58) before and after corrections are presented in Table I. The errors quoted in the table are statistical only. It can be found from Table I that for all the alloy compositions the $K\beta$-to-$K\alpha$ ratios for Ni are significantly different from those of pure Ni, whereas the $K\beta$-to-$K\alpha$ ratios of Fe differ slightly from those of pure Fe. For the alloy composition $x=0.2$ the $K\beta$-to-$K\alpha$ ratio of Ni is much lower than that of pure Ni, whereas for Fe the $K\beta$-to-$K\alpha$ ratio is found to be higher than that of pure Fe. For the other two alloy compositions the $K\beta$-to-$K\alpha$ ratios of Ni are higher than those of pure Ni and for Fe they are closer to those of pure Fe.

The $3d$ electron populations of Fe and Ni for various samples are presented in Table II. They have been evaluated by comparing the experimental values of the $K\beta$-to-$K\alpha$ intensity ratio with the results of multiconfigurational Dirac-Fock (MCDF) calculations[27–29] performed for various valence electronic configurations[3] of Fe and Ni. The obtained $3d$ electron populations for pure Fe and Ni metals (Table II) are in close agreement with the results of band structure calculations of Papaconstantopoulos[30] (6.93 for Fe and 8.97 for Ni) and Hodges *et al.*[31] (8.82 for Ni).

TABLE II. Evaluated $3d$-electron population values and total number of $(4s,4p)$ electrons for Fe and Ni in various samples.

Kind of sample	Evaluated $3d$-electron population for Fe	Total number of $(4s,4p)$ electrons for Fe	Evaluated $3d$-electron population for Ni	Total number of $(4s,4p)$ electrons for Ni
pure Fe	7.39 ± 0.29	0.61 ± 0.29	—	—
pure Ni	—	—	8.54 ± 0.39	1.46 ± 0.39
$\mathrm{Fe}_{0.2}\mathrm{Ni}_{0.8}$	6.69 ± 0.26	1.31 ± 0.26	9.93 ± 0.52	0.07 ± 0.52
$\mathrm{Fe}_{0.5}\mathrm{Ni}_{0.5}$	6.86 ± 0.24	1.14 ± 0.24	7.81 ± 0.21	2.19 ± 0.21
$\mathrm{Fe}_{0.58}\mathrm{Ni}_{0.42}$	7.31 ± 0.24	0.69 ± 0.24	7.44 ± 0.19	2.56 ± 0.19

Comparison of the changes in the $3d$-electron population of Fe in the $\mathrm{Fe}_x\mathrm{Ni}_{1-x}$ alloys (with respect to pure Fe) with the corresponding changes for Ni indicates that these changes cannot be explained by assuming the transfer of $3d$ electrons from atoms of one element (Fe or Ni) to atoms of the other element. However, the changes for all the alloys can easily be explained by the rearrangement of electrons between $3d$ and $(4s,4p)$ band states of individual metal atoms.

The approximate numbers of $(4s,4p)$ electrons (per one atom) for pure Fe and Ni have been obtained by subtracting from the total number of valence electrons of the neutral atom (eight for Fe and ten for Ni) the number of $3d$ electrons in the pure metal from Table II (7.39 ± 0.29 for Fe and 8.54 ± 0.39 for Ni). In the case of the $\mathrm{Fe}_x\mathrm{Ni}_{1-x}$ alloys it is also possible to estimate (in the way described above) the approximate numbers of $(4s,4p)$ electrons per one atom separetly for Fe and Ni in a given alloy (see third and fifth columns of Table II, respectively).

Trying to answer the question why the physical properties of $\mathrm{Fe}_{0.2}\mathrm{Ni}_{0.8}$ alloy are distinct as compared to the other two alloys, we calculated the *weighted average* numbers of $3d$ electrons per one atom for all the $\mathrm{Fe}_x\mathrm{Ni}_{1-x}$ alloys presently studied (the second column of Table III). We took in this average the numbers of $3d$ electrons evaluated separately for

TABLE I. Experimental $K\beta$-to-$K\alpha$ x-ray intensity ratios for Fe and Ni in $\mathrm{Fe}_x\mathrm{Ni}_{1-x}$ alloys.

	$K\beta$-to-$K\alpha$ ratio of Fe		$K\beta$-to-$K\alpha$ ratio of Ni	
Composition (x)	Before correction	After correction	Before correction	After correction
0	—	—	0.1808 ± 0.0016	0.1346 ± 0.0012
0.2	0.1737 ± 0.0010	0.1326 ± 0.0008	0.1723 ± 0.0010	0.1314 ± 0.0008
0.5	0.1743 ± 0.0009	0.1321 ± 0.0007	0.1808 ± 0.0010	0.1371 ± 0.0008
0.58	0.1726 ± 0.0008	0.1309 ± 0.0006	0.1822 ± 0.0010	0.1386 ± 0.0008
1.0	0.1764 ± 0.0009	0.1307 ± 0.0007	—	—

TABLE III. Comparison of estimated weighted average number of $3d$ and $(4s,4p)$ electrons for various Fe_xNi_{1-x} alloys with the superposition values of $3d$ and $(4s,4p)$ electrons obtained from the pure metal values.

Kind of sample	Weighted average number of $3d$ electrons	Superposition of $3d$ electrons obtained from pure metal values	Weighted average number of $(4s,4p)$ electrons	Superposition of $(4s,4p)$ electrons from pure metal values
$Fe_{0.2}Ni_{0.8}$	9.28 ± 0.42	8.31 ± 0.32	0.32 ± 0.42	1.29 ± 0.32
$Fe_{0.5}Ni_{0.5}$	7.34 ± 0.16	7.97 ± 0.24	1.66 ± 0.16	1.03 ± 0.24
$Fe_{0.58}Ni_{0.42}$	7.36 ± 0.16	7.87 ± 0.24	1.48 ± 0.16	0.97 ± 0.24

Fe and Ni in a given alloy (from Table II) with the weights equal to x and $1-x$, respectively. Similarly, we evaluated the weighted average number of the $(4s,4p)$ electrons per one atom for the examined alloys (the fourth column of Table III). It can be seen from the second (and the fourth) column of Table III that in the case of $Fe_{0.2}Ni_{0.8}$ alloy the weighted average number of $3d$ electrons is considerably larger [and the weighted average number of $(4s,4p)$ electrons is much smaller] than in the case of other two alloys. Accordingly, it is very important to find out the cause of this considerable difference of the valence electronic structure of $Fe_{0.2}Ni_{0.8}$ alloy with respect to the other two alloys. One reason that can be ascribed to the drastically different valence electronic structure of the $Fe_{0.2}Ni_{0.8}$ alloy from the other two alloys is that this is a highly asymmetric alloy with a higher concentration of nickel atoms.

It is also interesting to find to what extent the valence electronic structure of the Fe_xNi_{1-x} alloy (of certain composition x) differs from a superposition of the valence electronic structure of pure Fe and Ni metals. Therefore, in the third and the fifth columns of Table III we have additionally presented for every alloy composition x the superposition (with the weights x for Fe and $1-x$ for Ni) of the number of $3d$ and $(4s,4p)$ electrons taken from Table II for *pure* Fe and Ni metals. It can be seen from Table III that in the case of $x=0.5$ and 0.58 the weighted average numbers of $3d$ electrons in the Fe_xNi_{1-x} alloys (the second column of Table III) are smaller than the superpositions of the number of $3d$ electrons of pure Fe and Ni metals (the third column of Table III). However, in the case of the $Fe_{0.2}Ni_{0.8}$ alloy the weighted average number of $3d$ electrons is very large (9.28 ± 0.42) and differs considerably from the superposition of the number of $3d$ electrons of pure Fe and Ni metals (8.31 ± 0.32). In the case of $(4s,4p)$ electrons the situation is opposite, i.e., the weighted average number of $(4s,4p)$ electrons for the $Fe_{0.2}Ni_{0.8}$ alloy (0.32 ± 0.42) is dramatically smaller than the superposition value (1.29 ± 0.32), whereas for the other two alloys the weighted average is higher than the superposition value. The large weighted average number of $3d$ electrons (9.28 ± 0.42) and the negligible weighted average number of $(4s,4p)$ electrons (0.32 ± 0.42) in the case of the $Fe_{0.2}Ni_{0.8}$ alloy may possibly be the reason for the high permeability and other magnetic properties of this alloy.

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