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$Sm_2(CoTM)_{17}$ COMPOUNDS

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Abstract

The crystallographic positions of Fe and Mn atoms in a $Sm_2(CoFeMn)_{17}$ permanent magnet have been investigated using electron channelling/blocking techniques. Using the tilting and diffraction capabilities of an analytical transmission electron microscope, an electron beam was made to propagate along specific crystallographic directions in the magnet. By monitoring the characteristic x-ray spectrum as a function of incident electron beam orientation, it was possible to determine that 88.5% of the Mn and 85.1% of the Fe atoms occupy sites in the mixed planes in this compound.

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Introduction

The magnetocrystalline anisotropy of $(RE)_2Co_{17}$ intermetallic compounds can be appreciably modified by limited substitution of transition metals for Co in the structure.[1] In many cases, the magnitude of the anisotropy increased dramatically with relatively small amounts of ternary substituent. For $Ce_2Co_{17-x}Fe_x$, an increase of x from 0 to 1 increases the anisotropy field (H_A) from 11 to 18 kOe.[1] Similar effects occur for many other such ternary systems; perhaps the most dramatic effects are observed in the $Sm_2Co_{17-x}Zr_x$ system where an increase of x from 0 to 1 causes H_A to increase from 65 to 110 kOe.[2] From a practical standpoint, it is only because the anisotropy field can be significantly improved by substitutions that the 2:17 compounds can compete with the 1:5 compounds as permanent magnet materials.

The magnitude of the effects of substitution on the anisotropy has been variously attributed to preferential occupation of the substituent at specific sites in the structure[3] or to the effects of changed electron concentration on the overall band structure of the compound.[4] It is commonly recognized that the dumbbell sites (6c sites) in binary $(RE)_2Co_{17}$ compounds exhibit a strong anisotropy favoring magnetization perpendicular to the crystallographic c-axis. This planar anisotropy is detrimental to the desired axial anisotropy and if its magnitude could be reduced, the overall anisotropy would become more strongly axial. Thus, any element which has lower anisotropy than Co and substitutes preferentially at the dumbbell sites would be expected to increase the axial anisotropy of the entire structure. This rather simplistically explains the fact that many elements have been determined to have beneficial effects on H_A. Alternatively, Perkins and Strässler[4] have concluded from their calculations that a large part of the anisotropy change must arise from the reduced occupation of the electron bands associated with a decreased electron concentration.

Experimental verification of preferential occupation of substituents at the dumbbell sites is not well established for most of the ternary and quaternary systems whose anisotropy has been measured. A few such studies are available, but the results are not comprehensive being mainly confined to the case of Fe on the 2:17 lattice. For example, neutron scattering experiments have shown[5] that Fe occupies the mixed planes (which include the dumbbell sites) in $Sm_2(CoFe)_{17}$ and that Fe favors the dumbbell sites[6] in hyperstoichiometric $Y_2(CoFe)_{19}$. NMR studies[3] of $Y_2(CoCuAl)_{17}$ indicate that Al prefers the dumbbell sites but Cu substitutes randomly on the 4 Co sublattices; the Fe in $Y_2(CoFe)_{17}$ also prefers the dumbbell sites.[7] Analyses of Mössbauer spectra from $Tm_2(CoFe)_{17}$ also indicate that small amounts of Fe favor the dumbbell sites in that system.[8] Although it is relatively well-established that Fe tends to occupy the dumbbell sites in 2:17 compounds, very little experimental evidence is available for the other possible substituents.

Recently it has been shown that for certain favorable crystal structures, the orientation dependence of the inelastic scattering of electrons can be used to obtain information about the chemical occupation of specific atomic planes.[9] A modification[10] of this technique can be easily applied to the problem of site occupation in $RE_2(CoTM)_{17}$ systems. It is the purpose of this paper to show how this has been done for the case of a $Sm_2(CoFeMn)_{17}$ alloy.

Technique

The technique used in this investigation involves the use of a transmission electron microscope equipped with an energy-dispersive x-ray spectrometer for microanalysis. The diffraction and tilting capabilities of the electron microscope are used to accurately orient a thin-foil specimen in a series of diffracting conditions. The x-ray spectrum produced by the interaction of the electron beam with

the specimen is monitored as a function of orientation of the incident electron beam. Comparison of spectra arising from beams channelled between specific planes and those arising from beams blocked by those planes gives a chemical microanalysis of those crystal planes.

The physical principles involved in this technique are well understood but it is only recently that it has been applied on a routine basis. In 1949, von Laue[11] explained Borrmann's discovery of the orientation effects of x-ray absorption in terms of the standing waves which are set up by the x-ray beam as it propagates along specific crystal directions. If the intensity maxima of these Bloch waves coincide with the atomic planes in the crystal, the wave will be anomalously absorbed, the absorption generating enhanced x-ray fluorescence and vice versa. This basic concept has been adapted and expanded for the case of dynamical electron diffraction and its implication discussed both as a potential probe of parallel but unequal crystal planes[12] and as a possible detrimental effect in x-ray microanalysis techniques.[13]

To apply this Borrmann effect as a probe requires, in the general case, a knowledge of the dynamical electron wave function including inelastic effects as well as a complete calibration of all the instrumentation. These stringent experimental requiements have, until recently, discouraged application of this technique. However, Spence and Taftø[9] have shown that for certain layered crystal structures, and a priori knowledge of some aspects of the structure, it may be possible to effect an extreme simplification of the data analysis. In other words, a knowledge of the occupancy of one sublattice may be used as an internal standard in the interpretation of results concerning another sublattice. The data analysis then reduces to a comparison of ratios of x-ray intensities and all instrumental parameters can be cancelled out of the analysis.

For the case of substitutions on the Co sublattices in $Sm_2(CoTM)_{17}$, the analysis due to Spence and Taftø must be modified.[10] In this case, planes containing only Co sites alternate along [0001] with planes containing both Co and Sm sites. This requires retention of more terms in the analysis. Furthermore, for cases of interest for permanent magnets, the level of substitutional impurities is a significant fraction of the total number of available Co sites and this must also be accounted for.

One expresses the rate of characteristic x-ray counts (N) for specific element (Z) in a given incident beam orientation (η) as a summation of the count rate arising from each plane (A,B,...) in a series of parallel but inequivalent crystal planes within a unit cell

$$N_Z^{(n)} = \sum_{A,B,...}^{unit\ cell} P_Z m_Z I_A^{(n)} f_A^Z C_Z$$

where P_Z is a rate factor for production of x-rays from element Z

m_Z is the total number of sites which a Z atom may occupy per unit cell.

$I_A^{(n)}$ is the effective Bloch wave intensity at plane A in orientation .

f_A^Z is the fraction of the sites available to a Z atom which occur on plane A.

C_Z is the fraction of the Z atoms which occupy plane B.

This produces two terms for each beam orientation for each transition metal which occupies a Co site:

$$N_Z^{(1)} = P_Z m_Z I_A^{(1)} f_A^{Co}(1-C_Z) + P_Z m_Z I_B^{(1)} f_B^{Co} C_Z$$

and

$$N_Z^{(2)} = P_Z m_Z I_A^{(2)} f_A^{Co}(1-C_Z) + P_Z m_Z I_B^{(2)} f_B^{Co} C_Z$$

For the Sm sublattice, this simplifies to:

$$N_{sm}^{(1)} = P_{sm} m_{sm} I_A^{(1)} \quad \text{and} \quad N_{sm}^{(2)} = P_{sm} m_{sm} I_A^{(2)}$$

It is possible to define

$$\beta \equiv I_B^{(1)}/I_A^{(1)}$$

$$\gamma \equiv I_B^{(2)}/I_A^{(2)}$$

and

$$\mathcal{R}\left(\frac{sm}{Z}\right) = \frac{N_{sm}^{(1)}/N_Z^{(1)}}{N_{sm}^{(2)}/N_Z^{(2)}} =$$

$$\frac{f_A^{Co}(1-C_Z) + \gamma f_B^{Co} C_Z}{f_A^{Co}(1-C_Z) + \beta f_B^{Co} C_Z}$$

which can be inverted to give

$$C_Z = \frac{\mathcal{R}\left(\frac{sm}{Z}\right) - 1}{\left(\dfrac{f_B^{Co}}{f_A^{Co}}\right)\left(\gamma - \beta\mathcal{R}\left(\frac{sm}{Z}\right)\right) + \left(\mathcal{R}\left(\frac{sm}{Z}\right) - 1\right)}$$

which is an expression for the fraction of the Z atoms on the mixed planes in terms of the experimental data and the two parameters γ and β.

To determine γ and β, it is necessary to obtain an experimental spectrum in which no channeling occurs: $I_A \approx I_B$. Then, for such a no-channeling condition, (n)

$$\frac{N_{Co}^n}{N_{sm}^n} = k[f_A^{Co}(1-C_{Co}) + f_B^{Co} C_{Co}]$$

where

$$k = \frac{P_{Co} m_{Co}}{P_{sm} m_{sm}}$$

Then for the original conditions 1 and 2

$$\beta = \frac{1}{f_B^{Co} c_{Co}} [\frac{1}{k} \frac{N_{Co}^{(1)}}{N_{sm}^{(1)}} - f_A^{Co}(1 - c_{Co})]$$

$$\gamma = \frac{1}{f_B^{Co} c_{Co}} [\frac{1}{k} \frac{N_{Co}^{(2)}}{N_{sm}^{(2)}} - f_A^{Co}(1 - c_{Co})]$$

This gives an expression for the fraction of each transition metal component on the Co plane in terms of the concentration of Co on the Co plane and the experimental results $N_Z^{(\eta)}$. To complete the analysis, an expression for the C_Z in terms of C_{Co} must be obtained from the overall composition of the compound.

This analysis allows a straightforward determination of the chemical composition of parallel crystal planes to be made. Its validity rests on the assumptions that: (1) there are no antisite defects; (2) the rate of characteristic x-ray production is not a function of the environment of an atom, (3) the condition of no channeling is well approximated, (4) the production of the characteristic x-rays is a sufficiently localized process, and (5) for RE_2Co_{17} compounds, the dumbbell sites can be taken as part of the mixed planes.

Experimental

Samples of a $Sm_2(CoFeMn)_{17}$ magnet of nominal composition 23.3wt%Sm, 7.4%Fe, 7.2%Mn, remainder Co were obtained from General Motors Research Laboratories. The magnet had a remanent magnetization of 8500G and an intrinsic coercivity of 5800G.

Electron transparent foils were obtained by sectioning, followed by ion beam milling. In the microscope, thin foils were oriented for strong diffraction along the [0002] systematic row. Characteristic x-ray spectra were recorded from foils in three distinct orientations:

1) Positive deviation from the exact $[0006]_{2:17} = [0002]_{1:5}$ Bragg condition. (s > 0)

2) Negative deviation from the exact $[0006]_{2:17} = [0002]_{1:5}$ Bragg condition, and

3) A non-channeling condition in which there were no strong low-order diffraction maxima.

In each case, collection of x-rays continued for 300 seconds with an average counting rate for the entire spectrum between 2500 and 3000 counts per second. A "hole" (no specimen) count was taken to detect spurious x-rays and subtracted along with the continuous background from each spectrum.

Results

The results of the spectral analysis after background subtraction appear in Table I.

TABLE I

Characteristic X-ray Intensity

(x 10^3 counts in peak)

	s < 0	s > 0	non-channeling
$Sm(L_\alpha)$	110.7	87.1	156.9
$Mn(K_\alpha)$	77.5	64.2	105.6
$Fe(K_\beta)$	81.2	68.4	109.8
$Co(K_\alpha)$	654.4	690.7	920.0

For the $Sm_2(Co_{0.8}Fe_{0.1}Mn_{0.1})_{17}$, magnet of this investigation, an average unit cell contains 40.8Co, 5.1Fe, and 5.1Mn atoms. There are 27 available sites in the Co plane; the following relationship applies

$$40.8C_{Co} + 5.10(C_{Fe} + C_{Mn}) = 27$$

Also

$$f_A^{Co} = 24/51 \qquad f_B^{Co} = 27/51$$

Combining these relationships with those established previously, and applying the data of Table I, one immediately generates the following results

$$C_{Co} = 0.629$$
$$C_{Fe} = 0.149$$
$$C_{Mn} = 0.115$$

That is, 62.9% of the Co atoms, 14.9% of the Fe atoms and 11.5% of the Mn atoms lie in the Co plane.

Discussion

The technique used in this investigation gives quantitative information about the chemical occupation of the two different crystal planes perpendicular to [0002] in $(RE)_2Co_{17}$ compounds. It is easy to apply and is not limited to any specific element or elements. It readily distinguishes elements of similar atomic

number and can detect most elements ($Z \geq 11$) for concentrations as small as 0.1%. It can be applied on a routine basis, easily generating relationships between occupation and magnetic properties.

The major limitation of this technique is that it cannot in general distinguish crystallographically different sites within an atomic plane. The results reported here indicate that almost 90% of the Fe and Mn atoms occupy sites in the mixed planes, but it is impossible to determine whether the dumbbell (6c) or the adjacent 18j sites are favored. Because the number of Fe and Mn atoms on the mixed planes (~8.85 per unit cell) is well in excess of the number of dumbbell sites (6 per unit cell), it can be concluded that Fe and Mn favor the 18j sites over either Co plane site (18h or 9d). Nevertheless, it would be desirable to locate these elements more exactly.

The inability to distinguish sites within planes can be partially eliminated by performing a series of experiments using linearly independent diffraction vectors. If it were possible to find three different sets of parallel planes in the crystal, experiments could be performed for each family of planes, allowing complete determination of the occupation of each site in the structure. For RE_2Co_{17} compounds, only two parallel but unequal families of planes exist; this type of experiment could be performed using $[11\bar{2}0]$ as well as the $[0002]$ diffraction vectors. A combination of these two would still allow one degree of freedom within the limitations imposed by the overall composition and the number of available sites.

Conclusion

It has been shown that ternary and quaternary substituents in RE-Co based permanent magnets can be readily located in the crystal structure using electron channelling techniques. By using the Sm sublattice as an internal standard, it is possible to simplify the data analysis to a comparison of ratios of intensities,

allowing routine application of this technique. The results of this type of investigation can lead to a better understanding of magneto-crystalline anisotropy in these compounds.

Acknowledgement

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