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NMR characterization of Co sites in La+Co-doped Sr hexaferrites with enhanced magnetic anisotropy

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We investigated La+Co-doped $BaFe_{12}O_{19}$ and $SrFe_{12}O_{19}$, a recently discovered improved variant of the most popular hard magnetic *M*-type hexaferrites, with nuclear magnetic resonance at low temperature, and in magnetic fields up to 5 T. Two satellite lines were observed between 70 and 76 MHz in the zero-field powder spectra of ^{57}Fe. Satellites in Co+Ti-doped samples at the same frequencies have been assigned in the literature to *k*-Fe with a $f1$-Co neighbor, and *a*-Fe with a $f1$-Co neighbor. We report observation of a ^{59}Co-resonance in this structure. The signal is due to Co^{2+} in a low-spin state. Together with the field dependence of the hyperfine field this gives a very strong indication that Co^{2+} substitutes in the presence of La for $f2$-Fe, in contrast to the behavior assumed in Co+Ti-doped samples.

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I. INTRODUCTION

The hexaferrites $BaFe_{12}O_{19}$ (Ba*M*) and $SrFe_{12}O_{19}$ (Sr*M*) were discovered in the early 1950s and have been the working horse of the permanent magnet market for several decades (see, e.g., Ref. 1 and references therein). In view of the large volume of the market and over this long time, many attempts have been made to improve the key magnetic properties by various techniques, including doping on the Fe or Ba sublattices. It was found, however, that quite generally either the saturation magnetization M_s, or the anisotropy field H_A, or both decrease. A very early report of improved properties by simultaneous doping with La and Co went unnoticed.[2] The rediscovery of an anisotropy field enhancement by roughly 20% together with a constant saturation magnetization at room temperature few years ago[3] came, therefore, as a surprise and triggered considerable renewed interest in doped hexaferrites.[4–6]

Despite this research effort it turned out to be difficult to characterize the nature of the defect induced by La+Co doping and to identify the origin of the enhanced anisotropy. Mössbauer and preliminary neutron powder diffraction work resulted in conflicting assignments of the Fe site preferentially substituted by Co: The Fe-Mössbauer spectra indicate Co on $f2$, and probably on *a* and *b* sites, while the neutron work assigned a preferential Co occupation to the $f1$ site.[4,5] The complication arises because of the rather complex structure with five Fe sites in a unit cell that contains two formula units (see Fig. 1). There is a severe, temperature-dependent overlap of the absorption lines of the five Fe sites in the Mössbauer spectrum. In addition, a small distortion shifting *b*-Fe along the *c* axis to *e* sites makes a reliable evaluation of Mössbauer line intensities as a function of the doping concentration difficult.

In this situation the superior hyperfine field resolution of ^{57}Fe nuclear magnetic resonance (NMR) should be helpful. It is well known that NMR detects five well resolved lines at low temperature,[7–10] and resolved satellite lines in doped samples have also been investigated for considerable time.[11,12] In a preliminary study[13] we compared the ^{57}Fe-NMR spectra of $La_xSr_{1-x}Fe_{12-x}Co_xO_{19}$ powders with $x=0.0,0.1,0.2$ with the ones from Co+Ti-doped samples[11] and found evidence for $f1$-Co. Here, we extend this work to La+Co-doped Ba*M*, to $x\leqslant 0.4$, and to the La and Co resonances in external fields. Comparison of this resonance with the one in the Co spinel[14,15] lends very strong support to the assignment of this Co resonance to Co on the $f2$ site.

II. EXPERIMENTAL DETAILS

The powders used in this work were crushed to grain sizes of ≈ 1.0 μm and fired without sinter aids. The samples are single phase, as seen in this work as well as in previous and in ongoing neutron and Mössbauer studies[4] on similar powders.

Figure 1 shows the crystal and magnetic structure of the *M*-type hexaferrites Ba*M* and Sr*M*. The unit cell contains two f.u. (expanded slightly in *c* direction in the figure). The oxygen ions form hexagonal close-packed layers, their positions are connected here in a way to emphasize the coordination of $f1$- and $f2$-Fe discussed below. Fe occupies five different interstitial sites in the oxygen structure, with octahedral coordination on the *k*, *a*, and $f2$ site; tetrahedral on $f1$; and trigonal bipyramidal on *b* sites. Magnetically, all Fe sites are Fe^{3+} with a saturation moment of $5\mu_B$. Transferred and dipolar fields lead to hyperfine fields ascending in the order of $2b$-, $12k$-, $4f1$-, $2a$-, and $4f2$-Fe^{3+} ions. The bonds between Fe neighbors in the figure indicate a strong superexchange coupling across oxygen.[16,17] The resulting collinear ferrimagnetic structure with eight Fe moments per unit cell on $f1$ and $f2$ antiparallel to 16 on *b*, *k*, and *a* sites corresponds to the experimental saturation magnetization at 0 K of $40\mu_B$ per unit cell.

All NMR data were taken at 4.2 K with a coherent, phase-sensitive pulse spectrometer. The spectra are measured point-

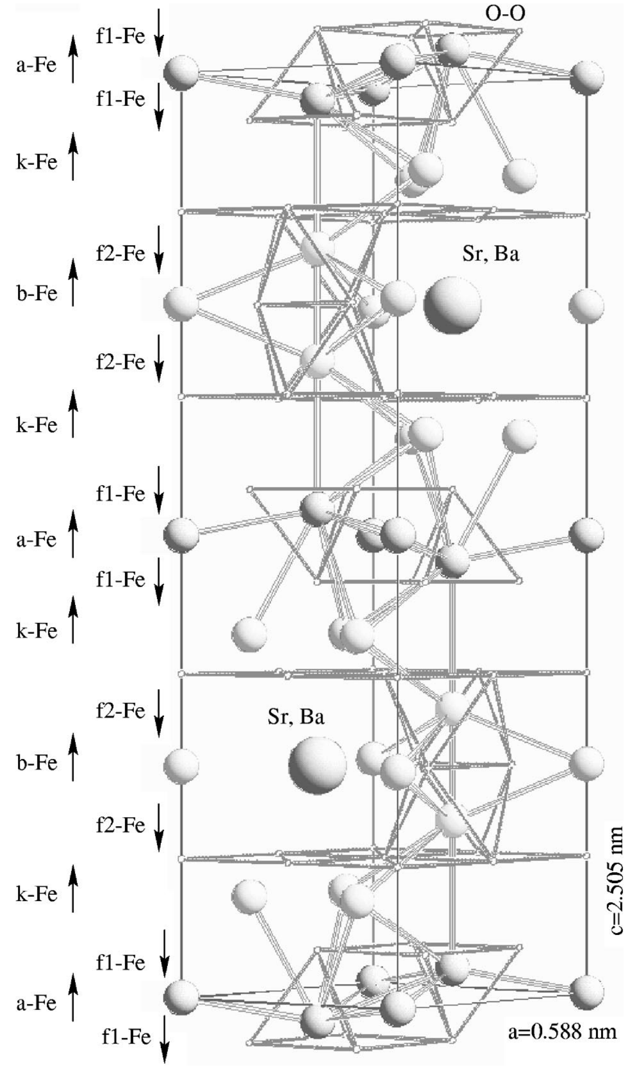

FIG. 1. Crystal and magnetic structure of the *M*-type hexaferrites. The thin lines indicate the unit cell of space group $P6_3mmc$ (dimensions for Ba*M*, Ref. 1). Oxygen occupies five sublattices in close-packed layers. The positions are connected to emphasize Fe coordinations; O ions are omitted for clarity. Connections between Fe neighbors ($d \leqslant 5$ Å) indicate strong superexchange coupling Ref. 16, showing the origin of the uncompensated collinear antiferromagnetic structure.

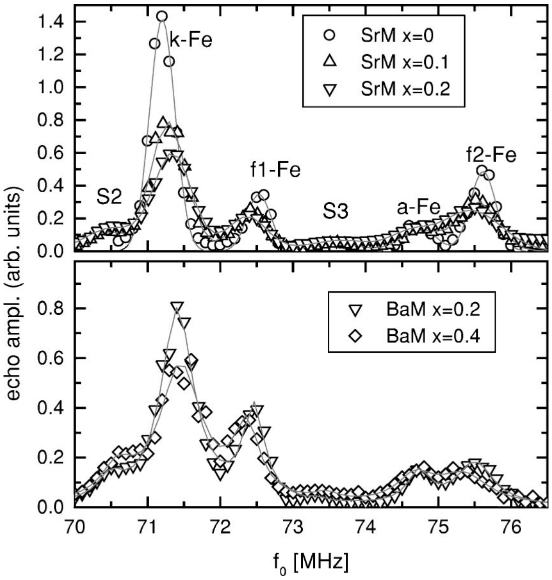

FIG. 2. Zero-field ^{57}Fe spectra of La+Co-doped Sr*M* (top), and BaM (bottom) at 4.2 K. The *b* site at 59.6 MHz with an unresolved satellite *S*1 is not shown, satellites *S*2 and *S*3 are discussed in the text.

by-point from Fourier-transformed spin echos with pulse sequence 1.0–50–2.0 μs and strong excitation field B_1, suitable for excitation of the domain signal. With this pulse distance, and at this temperature, no correction of the spectra for spin-spin relaxation is necessary, we only corrected for resonance frequency f_0^3, as explained in Ref. 13. The relative intensities of Fe and Co lines cannot be compared, because of the differences in the nuclear enhancement factors. External field was applied perpendicular to the rf field B_1. A field close above magnetic saturation had no significant influence on the excitation conditions of the Fe signal, indicating the observation of a domain signal in zero field. This behavior was expected in view of the small powder grain sizes favoring single domain particles. The Co signal, however, shows a broader distribution of enhancement factors and the details within the broad spectra were found to depend significantly on the excitation field and on magnetic saturation.

III. RESULTS AND DISCUSSION

In Fig. 2 we compare the zero-field Fe spectra of $\mathrm{La}_x\mathrm{Sr}_{1-x}\mathrm{Fe}_{12-x}\mathrm{Co}_x\mathrm{O}_{19}$ (see Ref. 13) with the ones of Ba*M* at $x = 0.2$ and 0.4, near the highest concentration allowing single phase samples. Clearly, the line positions do not depend strongly on the size of the divalent ion. The same holds for the satellites *S*2 and *S*3 (*S*1 near *b*-Fe was not investigated in Ba*M*), indicating that the local defect structure also is independent of the size of the divalent ion.

The dependence of the line positions on *x* is also seen to be the same for Ba*M* and Sr*M*: The hyperfine field of *a*-Fe is constant, that of *k*-Fe increases slightly, while those of the *f* sites decrease. If we assume that the hyperfine field is proportional to the Fe moments, we can conclude that saturation magnetization of La+Co-doped Ba*M* is independent of *x* to within 1%, as was found in Sr*M*,[13] and as observed in macroscopic magnetization measurements.

Resolved satellites as the ones shown in Fig. 2 are expected mainly from ions with a defect on a magnetic, exchange-coupled nearest neighbor. The position of a satellite line contains, therefore, information on the type of a particular defect; the intensity gives information on its concentration. Unfortunately, reliable calculations of hyperfine fields at defect sites in such a complex structure are not available up to now, so the identification of the defect structure in terms of the site of the resonating nucleus and the changes of its environment have to rely on comparison with results from reference materials, and on the dependence of the relative line intensities on the defect concentration. From the large relative intensities of the satellites, it is clear that Co does not substitute randomly on all Fe sites.

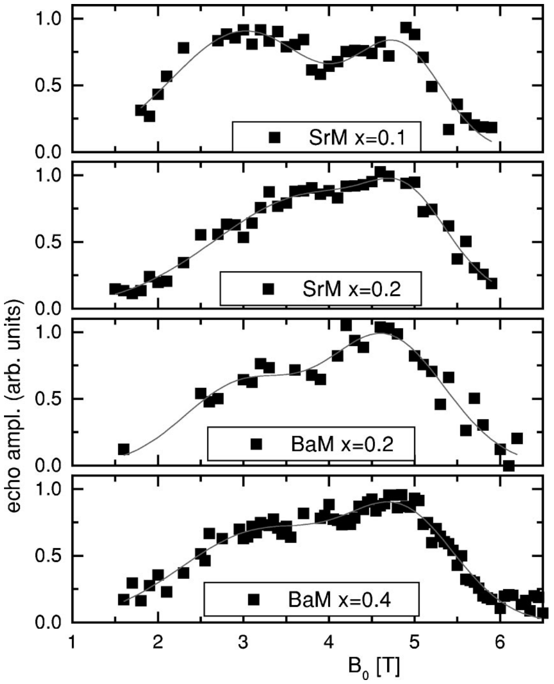

FIG. 3. Field sweep spectra of ^{139}La in La+Co-doped Sr*M* (two top panels), and Ba*M* (bottom panels) at 6.0 K and 32.8 MHz ($^{139}\gamma/2\pi = 6.0146$ MHz/T). The lines are fits using two Gaussians.

In particular, $S2$ at 70.5 MHz corresponds to *k*-Fe with a neighboring defect, because the sum of the contributions of $S2$ and *k*-Fe to the total spectrum is constant. Inspection of Fig. 1 shows that *k*-Fe is coupled to $f1$- and $f2$-Fe, so the large relative intensitiy of $S2$ is a clear indication that Co enters preferentially on one or both f sites. In Sr*M* we assigned $S2$ to *k*-Fe with a $f1$-Co neighbor, and S3 at 73.65 MHz to *a*-Fe with a $f1$-Co neighbor. In view of the great similarity in the position of the satellites in Co+Ti-doped samples this assignment was simply taken from Stepankova *et al.*,[11] but $f2$-Co would obviously be just as compatible with our data on the concentration dependence of the satellite intensities. It has to be noted that Stepankova *et al.* arrived at their assignment with the *assumption* that Co does not enter the $f2$ site. This assumption of a site preference is based on the Pauling valence rules only, which might not apply in the present case.

The similarity in the local defect structure of Ba*M* and Sr*M* is underlined by the comparison of the ^{139}La spectra shown in Fig. 3. The La signal is severely broadened by inhomogeneous internal fields and, therefore, is very small. The La spectrum of doped Ba*M* and Sr*M* do not differ, and the influence of the concentration also is small with a somewhat better resolved second peak at low external field for $x = 0.1$. In all cases a fit with two Gaussian lines shows one line at $B_0 = 4.8$ T with a full width at half-maximum of ≈ 1.1 T, and a second, even broader one at $B_0 = 3.0$ T. The ^{139}La resonance in a diamagnetic reference at this frequency would occur at $B_0 = 5.453$ T, so there is an internal field of $B_{\mathrm{La}} \approx 0.6$ and 2.4 T present at the corresponding La sites. B_{La} is parallel to the external field, which is parallel to the neighboring *b*- and *k*-Fe moments, indicating that this field is not of dipolar origin but a transferred hyperfine field. In view of the discussion of the Fe above, it is tempting to assign the two La lines to La with and without Co on a neighboring $f2$ site, but in the absence of reference spectra from samples doped only with La it is impossible to assign the resonances to a particular environment.

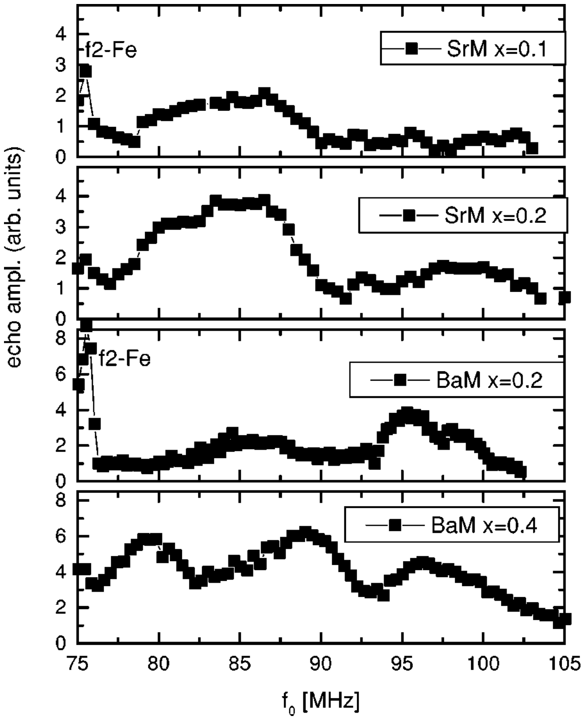

FIG. 4. ^{59}Co spectra for La+Co-doped Sr*M* (top panels) and Ba*M* (bottom panels) at 4.2 K in zero field. The spectra of Sr*M* $x = 0.1$ and Ba*M* $x = 0.2$ were taken with pulse amplitude B_1 optimized for the $f2$-Fe signal at 75.5 MHz (left). For the other two spectra B_1 was reduced by 16 dB.

We now turn to the ^{59}Co signal. It may be noted that in Fig. 2 the signal intensity for the doped samples does not vanish above the line of $f2$-Fe. In Fig. 4 we compare the high-frequency parts of these spectra. From Mössbauer studies in the same samples, it is clear that this signal cannot be due to Fe, the hyperfine fields would be much too large. The integrated signal intensity in this high-frequency part is, however, roughly proportional to x. Furthermore, Fig. 5 shows that the broad spectrum shifts with the applied field according to $^{59}\gamma/2\pi = 10.01$ MHz/T, so we can safely assign this signal ^{59}Co. The detailed shape of this Co spectrum depends on the excitation conditions. At $x \geqslant 0.2$ we always observed the maximum between 95 and 100 MHz, but the peak next to the $f2$-Fe line is more pronounced at smaller rf amplitude B_1 (second and bottom panel), at amplitudes too small for a proper excitation of the Fe signal. The individual linewidths of the peaks vary between 0.5 and 1.5 T for the internal field.

We emphasize that, to the best of our knowledge, no such signal has been reported in Co-doped samples in the literature, indicating that the Co sites responsible for this signal in the La+Co-doped ferrites are rather unique. Fortunately, we can derive a detailed characterization of this site from the

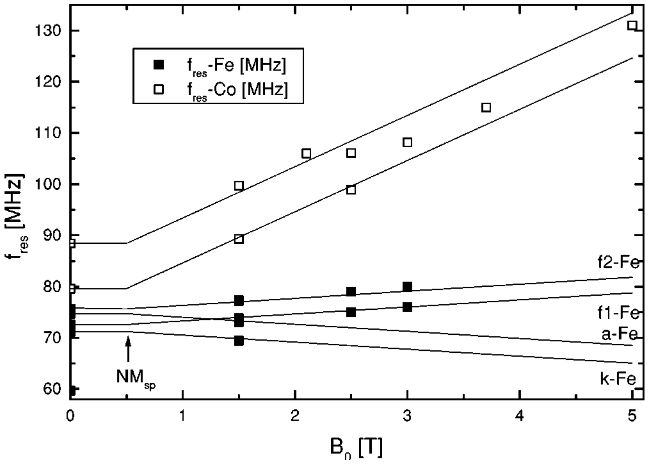

FIG. 5. Field dependence of the resonance frequencies of ^{57}Fe and ^{59}Co in La+Co-doped Ba*M* and Sr*M*. The lines are calculated for the collinear ferrimagnetic structure of Fig. 1 in a field along the *c* axis. The demagnetization field keeps the internal field constant up to $B_0 = NM_{sp}$, where *N* is the demagnetization factor, and M_{sp} the spontaneous magnetization. At higher fields the slope of the lines is equal to the gyromagnetic ratio of the resonating nucleus.

field dependence of the resonance frequency.

First, from the fact that the Co frequencies increase in external field we can ascribe this resonance to Co on a $f1$ or $f2$ site. This follows because the hyperfine coupling constant has the same (negative) sign as for Fe, so the hyperfine field B_{hf} and the external field add up for the sublattices antiparallel to the total moment (see Fig. 5), while they subtract in the case of majority sublattices. This is the reason for the well-known fact that the *k*-Fe and *a*-Fe resonance frequencies decrease with increasing external field, while $f1$- and $f2$-Fe increase.[12]

Second, Co is known to have a hyperfine coupling constant of ≈ -12 T/μ_B, quiet independent of valency and metallic or insulating environment. Especially in the closely related spinel $CoFe_2O_4$ the $Co^{2+,3+}$ resonances were observed above 350 MHz, corresponding to the high-spin state of both valences with this coupling constant.[14] 350 MHz corresponds to 35 T hyperfine field, which clearly outweighs any transferred hyperfine field contributions from neighboring Fe ions. We can conclude, therefore, that the Co site with a hyperfine field of at most $B_{hf} = 10$ T (100 MHz) observed here is due to low-spin Co with $\approx 0.8\mu_B$ or less at 4.2 K. Since $S = 0$ for low-spin Co^{3+}, and 10 T is still too high for transferred fields, we can assign the resonance to low-spin Co^{2+}. Therefore, the charge compensation from the La substitution on the Sr sublattice takes place at the Co defects, as expected.

The observation of a low-spin state allows us to decide whether Co substitutes $f1$- or $f2$-Fe. There is a general rule that the crystal field in a tetrahedral coordination like $f1$ is too small to dominate the intra-atom exchange and induce a low-spin state.[18] A low-spin state could be induced by a severe distortion of the tetrahedral symmetry, and one might guess that this distortion is the crucial contribution of La in arriving at the improved hard magnetic properties of the samples. Figure 1 shows, however, that the La substitution takes place on a rather distant site from $f1$-Fe. In addition, the size mismatch between La^{3+} and Sr^{2+}, and the close match to Ba^{2+} does not lead to any significant differences in the Fe, La, or Co spectra, as pointed out above, indicating that lattice distortions do not play a major role in the effect.

This leaves us with $f2$-Co as the most natural assignment of this resonance. With the crystal field splitting larger by a factor of ~9/4 than in the tetrahedral symmetry, the low-spin state is a common phenomenon in octahedral $(f2)$ coordination. A La substitution on a Sr site is expected to have a larger influence on a neighboring $f2$-Co site (and vice versa) than on the distant $f1$, which might also account for the large inhomogeneous linewidths of the La and Co resonances. We note that $f2$-Co^{2+} is in contrast to the strong site preference of Co^{2+} for tetrahedral, and of Co^{3+} for octahedral sites in the structurally closely related spinels,[18] and to the above-mentioned assignment of Fe satellites in Co+Ti-doped Ba*M*.[11] In the absence of comparable studies of the Co resonance in hexaferrites without La doping we are unable to decide whether this contradiction is due to a failure of the simple Pauling rules leading to a wrong line assignment by Stepankova *et al.*, or due to Co entering $f2$ sites only in the presence of La, as is suggested by the absence of this resonance in Co+Ti-doped Ba*M*.

IV. CONCLUSION

We investigated La+Co-doped $SrFe_{12}O_{19}$ and $BaFe_{12}O_{19}$ with Fe, La, and Co NMR at low temperatures and in fields up to 5 T. The satellite structure we observed in the ^{57}Fe spectra is similar to the one reported for Ti+Co-doped Ba*M* in the literature and can be explained by the presence of Co on the $f1$ or on the $f2$ sites. Substitution on other sites cannot be excluded, but the relative satellite intensities are much too large to be compatible with a random substitution on all Fe sites. The La spectra are almost independent of *x* and of the divalent ion. They are described by two broad Gaussian lines at positive internal fields of 0.6 and 3.0 T, respectively. The zero-field resonance in the frequency range from 75 to 100 MHz has not been reported before in doped hexaferrites. Experiments in external field show that this line is due to ^{59}Co on a $f1$ or $f2$ site. The zero-field hyperfine field corresponds to a low-spin state of Co^{2+} with $\approx 0.8\mu_B$. Crystal-field arguments strongly suggest that this low-spin state is localized on the octahedral $f2$ site.

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