

HYPERFINE INTERACTIONS IN THE INTERMETALLIC SYSTEM

$Ce(Fe_{1-x}Al_x)_2$ Al-RICH SIDE

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ABSTRACT

Investigations of the hyperfine interactions of the $Ce(Fe_{1-x}Al_x)_2$ system in the Al rich side for $0.60 \leq x \leq 1.0$ have been performed using Mössbauer spectroscopy at room temperature (RT) and 4.2K, under applied magnetic fields $B_a \leq 4.5T$. The spectra can be analyzed in terms of two components, D1 and D2; the former one is associated to the Fe in $Ce(Fe_{1-x}Al_x)_2$ and D2 to the spurious phase $Ce_2(Fe_{17-x}Al_x)$ that appears in small amounts, but is strongly magnetic.

Key-words: $Ce(Fe_{1-x}Al_x)_2$; Mössbauer effect; Magnetism.

Introduction

The intermetallic compound CeFe_2 with cubic C15 structure (Laves phase) exhibits some anomalous properties: the magnetic ordering temperature (230 K) and the magnetic moment per unitary formulae ($2.4\mu_B$) are considerably lower compared to others RFe_2 (R = rare earth) with average values around 600 K and $3.4\mu_B$ [1]. These anomalies are attributed to the high hybridization of the 4f electrons of the Ce with the 3d electrons of the Fe.

On the other hand, the C15 compound CeAl_2 displays a quite distinct behavior relative to the others RAl_2 (R with moment) that are ferromagnetic . This compound is a magnetic concentrated Kondo system with $T_K = 7$ K and $T_N = 3.8$ K. From neutron diffraction studies it has been known that CeAl_2 orders in a sinusoidally modulated antiferromagnetic structure with a period incommensurate with the crystalline structure [2,3]. The antiferromagnetic order results from a competition between the Kondo effect, which reduces the Ce moments at low temperatures, and the RKKY interaction, which pushes the system towards magnetic order.

Electrical and magnetic measurements performed in the pseudo-binary intermetallic compounds $\text{Ce}(\text{Fe}_{1-x}\text{Al}_x)_2$ show new interesting behaviors in the Fe-rich and Al-rich side of the system. At the Fe-rich side, the Fe substitution for Al, for concentrations as low as $x = 0.01$ [4,5], brings instability to the magnetic order of CeFe_2 and induces a first order second transition at lower temperatures to a non collinear state[6]. The existence of spin-canted phase was discussed by da Cunha et al.[7] in terms of competing exchange and anisotropy for $x < 0.10$. For $0.10 \leq x \leq 0.20$ a small amount of other phase is present and spin glass magnetic behavior is observed.

In contrast with the Fe-rich side, only few investigations have been done at the Al-rich side of the $\text{Ce}(\text{Fe}_{1-x}\text{Al}_x)_2$ series [8-10]. The experimental results of magnetic studies show that the effect of introducing Fe in CeAl_2 is drastic. Initially is observed that the antiferromagnetic ordering temperature T_N has a gradual decrease with the addition of Fe. For Fe concentration higher than 8% ($x \leq 0.92$) a new magnetic phase

transition appears at higher temperatures with ferromagnetic-like characteristic. The nature of this magnetic ordering is not easy to explain, mainly because the transition temperature is higher than the Curie point of pure CeFe_2 [8-10]. At temperatures below this transition, the magnetization curves present distinct behavior for zero field cooled (ZFC) and field cooled (FC) samples indicating the presence of some kind of magnetic freezing. This variety of magnetic behaviors, observed when Fe is substituted for Al in CeAl_2 are not well understood.

The purpose of this work is to study the magnetic properties of Al-rich side of the $\text{Ce}(\text{Fe}_{1-x}\text{Al}_x)_2$ system through the experimental investigation of the hyperfine interactions by ^{57}Fe Mössbauer spectroscopy. We consider that this investigation may be an important contribution to the understanding of the magnetic behavior of the $\text{Ce}(\text{Fe}_{1-x}\text{Al}_x)_2$ system since no explanation of the anomalous behaviors was found up to the moment to our knowledge.

Experimental

Polycrystalline samples of the $\text{Ce}(\text{Fe}_{1-x}\text{Al}_x)_2$ system for $0.60 \leq x < 1.0$ and $0.00 \leq x \leq 0.20$, were prepared by arc melting, in purified argon atmosphere, from stoichiometric amounts of Ce, Fe and Al, with subsequent annealing for one week at 800 C. The sample with $x = 0.98$ was prepared using iron metal enriched in the ^{57}Fe Mössbauer isotope. All the compounds used in this study, except that with 98% of Al, are those on which the magnetic and electrical properties were investigated by two of the authors (da Cunha and Takeuchi) including samples of the Fe - rich side. Recent X-ray diffraction and magnetic measurements indicated that the features of these samples are preserved and that the sample with $x = 0.98$ displays the properties characteristics of this concentration range in the phase diagram.

The Mössbauer measurements were done using a conventional Mössbauer spectrometer, operating in a sinusoidally modulated mode. A ^{57}Co in Rh foil was used as γ -ray source. The system was regularly calibrated using α -Fe foil. The Mössbauer spectra

were recorded at room temperature (RT), 4.2 K and in some cases at 10 K with applied field up to 4.5 T parallel to the γ -ray direction. The Mössbauer absorbers were prepared with fine powder obtained after crushing the samples.

As required to interpret the Mössbauer results, metallographic examinations were performed.

Results and Discussion

Spurious phases in the system under investigation, has been observed by Coles et al (10) and assigned to Ce_3Al_{11} , which is paramagnetic at 12K. In our samples, the X-ray diffraction pattern display some additional lines to the $MgCu_2$ cubic structure, but due to their low intensity, no clear identification was achieved.

The Mössbauer spectra for some samples of the system $Ce(Fe_{1-x}Al_x)_2$ at RT are shown in Fig.1. All the spectra are characteristic of electric hyperfine interactions and present a clear asymmetry for negative velocities. In general, in the Laves phase compounds with cubic C15 structure (for example: $Y(Fe_{1-x}Al_x)_2$ system [11,12]), this shape of the spectra is ascribed to the different environments of the Fe atoms produced by the random substitution of Fe by Al. The spectra could be fitted then, with a set of subspectra associated to each of the possible neighborhood of the Fe with intensities determined by the binomial distribution. Our attempt to fit the spectra using this model do not give consistent results. This fact probably indicates that the samples have some problem related either to the lack of homogeneity in the distribution of the Fe atoms, or to the formation of other phases not detected by X-ray analyses. In principle, the RT spectra should be fitted with a quadrupole distribution. However, two quadrupole doublets gave already satisfactory fits, as can be seen in Fig. 1. In this case, the doublet with the smaller electric quadrupole splitting (QS) and more positive isomer shift (IS), D1, explains the positive region of the spectrum. The other one with bigger QS and more negative IS, D2, determines the asymmetric part of the spectrum.

The Al concentration dependence of IS, relative to the α -Fe, of both doublets show similar behavior: increases linearly with x , Fig. 2. This indicates that the electronic charge density at the Fe nucleus decreases with Al concentration, probably due to a combination of volume effect and variation of the number of Fe first neighbours. In contrast, the concentration dependence of QS displays different behavior: QS(D1) decrease linearly with x and QS(D2) first increases and then decreases (Fig.2).

Mössbauer spectra were obtained at 4.2 K for some samples, as shown in Fig. 3. These low temperature spectra are formed by the superposition of a broad hyperfine field distribution (HFD) with paramagnetic part and were initially analyzed using a unique sextet and a quadrupole doublet. For this fits the line ratios of the sextet were kept fixed in the ratio 3:2:1 and its line widths were free to represent the HFD. The results show that, for $x \geq 0.84$, the relative intensity and the hyperfine parameters of the paramagnetic component are, within the experimental error, the same as obtained at RT, indicating that, for this concentration range, the HFD is due only to the magnetic ordering of the Fe associated to the D2 component. However, for $x < 0.84$ there is also a contribution of a fraction of the D1 component (named S1) to the HFD and it was necessary to use a second sextet to fit these spectra, Fig. 3. The mean hyperfine field, \overline{B}_{hf} , obtained from the fits are shown in Fig. 4. \overline{B}_{hf} associated to the D1 component (named S1) decreases gradually with the Al concentration. At the same time the relative area of the corresponding subspectrum decreases from 35% ($x = 0.65$) to 0% ($x = 0.84$) showing that the Al dilution process has a big influence on \overline{B}_{hf} due to various nearest neighbors configuration. On the other hand, \overline{B}_{hf} associated to the other component, D2 (S2), shows a more complicated behavior: first it is nearly constant, increases abruptly in $x = 0.84$ and then decreases with x , while the relative area is maintained around 50%. This type of behavior is very difficult to explain since there is no indication of segregation of a different phase from the X-ray diffraction investigation of the samples.

In order to obtain further information about the magnetic features of the different types of Fe, two samples with Al concentration of $x = 0.65$ and 0.75 were measured at 10 K in various applied magnetic field (B_a), always cooling the sample in zero applied

field. The spectra, Fig.5, were fitted with three sextets named as S_A , S_B , and S_C ; S_A and S_B represent the paramagnetic and magnetic Fe fractions, respectively, observed at low temperatures with zero applied field. They are associated to D1 component, and S_C represents the hyperfine field distribution associated to D2. The fits indicate that the \bar{B}_{hf} of each subspectra, $\bar{B}_{\text{hf}}(S_A)$, $\bar{B}_{\text{hf}}(S_B)$ and $\bar{B}_{\text{hf}}(S_C)$, displays different B_a dependence, as can be seen in Fig. 6. $\bar{B}_{\text{hf}}(S_A)$ increases linearly with a slope around $(\bar{B}_{\text{hf}}(S_A)/B_a)$, $\bar{B}_{\text{hf}}(S_B)$ decreases linearly and $\bar{B}_{\text{hf}}(S_C)$ remains constant for different values of B_a . The Mössbauer spectra taken after FC or ZFC gave essentially the same result.

The magnetic field dependence of \bar{B}_{hf} gives some information about the magnetic properties of the Fe related to the different sextets. From the curve of $\bar{B}_{\text{hf}}(S_A)$ it is possible to assume that the Fe atoms have no magnetic moments, since the mean hyperfine field is found to be equal to B_a . On the other hand, the field dependence of $\bar{B}_{\text{hf}}(S_B)$ is characteristic of a magnetic saturate state with collinear order of the Fe magnetic moments. And finally, the $\bar{B}_{\text{hf}}(S_C)$ behavior is typical of a state with non collinear magnetic moments and high anisotropy.

From the low temperature and field applied Mössbauer measurement results it can be seen that, in the samples of the Al-rich side there are three different types of Fe, A, B and C as defined above. Since the Fe sites on the cubic C15 structure are, in principle, crystallographically equivalent it is very difficult to justify the existence of all these types of Fe. However, in order to interpret the Mössbauer data it is possible, as a main hypothesis, to take into account the different environments of the Fe atoms.

A and B types of Fe are associated to the D1 component obtained at RT. The concentration dependence of Mössbauer hyperfine parameters of the subspectra related to D1 ($IS(D1)$, $QS(D1)$ and $\bar{B}_{\text{hf}}(S1)$) is reminiscent of the behavior of the Fe rich side of the system, fact that is consistent with a dilution process. Then, as qualitative explanation, the A and B types of Fe associated to D1 can be attributed to the occurrence of two, even more, environments around the Fe in the cubic C15 structure for this range of concentration: the Al-rich and Fe-rich environments, respectively. According with this

explanation the C type of Fe, Fe(C), (associated to D2) should be out of the (Fe,Al) sublattice of the C15 structure.

In this case, it is possible to assume that the Fe(C) atoms reside on wrong (Ce) lattice site (antistructure (AS) atoms [13,14]). An Fe atom, which occupies on C15 AS sites, is surrounded by 4 first nearest Ce atoms and 12 second nearest neighbors, Fe or Al atoms. For the high Al concentration of our samples ($x > 0.60$), it is difficult to explain the predominantly high local moment shown by this Fe, as suggested by the concentration dependence of $\overline{B}_{\text{hf}}(\text{S2})$ compared to the hyperfine field in CeFe_2 . Moreover, the high relative fraction of the subspectrum related to this Fe(C) ($\approx 50\%$) lead us to discard this possibility.

An alternative explanation, that can justify the observation of the D2 component in our samples, may be the presence of another structural phase even though the X-ray diffraction measurements show only the typical lines of the cubic C15 structure of the MgCu_2 type. To analyze this possibility pieces of several samples ($x = 0.75, 0.84, 0.88$ and 0.98) were polished and etched with adequate reagent for metallographic examinations using standard techniques.

The metallographic investigations revealed that the samples have different amounts of a second spurious phase. The quantity of this second phase increases with the Fe concentration. At this stage of the work, the spurious phase has not been completely identified. However, there exists some evidences that allow to suggest the type of structure of this phase.

The structural phase diagram of the ternary system Ce-Fe-Al, for Fe and Al concentration from 0 up to 100 at % and for Ce up to 33.3 at %, was proposed by Zarechnyuk et al [15]. This phase diagram shows two intermetallic compounds with defined structure $\text{Ce}_2(\text{Fe}_{17-x}\text{Al}_x)$ formed by the Al substitution in $\text{Ce}_2\text{Fe}_{17}$ and the $\text{Ce}(\text{Fe}_{1-x}\text{Al}_x)_2$ system under study.

The $\text{Ce}_2(\text{Fe}_{17-x}\text{Al}_x)$ series of compounds has the rhombohedral $\text{Th}_2\text{Zn}_{17}$ type structure preserved for Al concentration $x \leq 11$. For this series there exist in the literature only one study related to their magnetic properties [16]. When the magnetization curves

shown in this work are compared to the similar ones of the samples with $x < 0.9$ of the system $\text{Ce}(\text{Fe}_{1-x}\text{Al}_x)_2$ published [9], it is possible to observe a high similarity between them. Moreover from the magnetic phase diagram presented in [9] a high transition temperature was found for the $\text{Ce}(\text{Fe}_{1-x}\text{Al}_x)_2$ system, with $0.70 \leq x < 0.90$, which coincide very well with those of the $\text{Ce}_2(\text{Fe}_{17-x}\text{Al}_x)$ system for $0.6 \leq x \leq 0.8$ reported in [16]. All these observations lead us to suggest that the type of structure of the spurious phase which occurs in our samples, in small amounts but with a strong magnetic signal, is of the $\text{Ce}_2(\text{Fe}_{17-x}\text{Al}_x)$ kind.

Neutron diffraction experiments performed in $\text{Ce}_2\text{Fe}_{17}$ by Givord and Lemaire[17] indicated that the Fe moments define a fan structure in zero field at 4.2K. This fan structure is broken when magnetic fields larger than about 1T are applied [16]. According to Middleton et al. [16] the Al substitution for Fe in $\text{Ce}_2(\text{Fe}_{17-x}\text{Al}_x)$ leads to normal ferromagnetism at low temperatures for $x \leq 7$. For higher Al concentration ($x = 8$, for example) the magnetization curves show sharp cusp, suggesting a spin glass or cluster glass ordering. This type of ordering may arise as a consequence of Al concentration fluctuations. With these properties, the presence of a spurious phase of $\text{Ce}_2(\text{Fe}_{17-x}\text{Al}_x)$ type, having Al concentration distribution, in samples of $\text{Ce}(\text{Fe}_{1-x}\text{Al}_x)_2$ with $x \leq 0.92$, may help to explain the nature of the magnetic phase transition with ferromagnetic like characteristics observed in the magnetization curves at higher temperatures [9,10]. Moreover, the increase of the magnetization observed for our samples with $1.0 > x > 0.92$ can be attributed to precipitates of this phase, that appears in different ways of preparations [9,10].

Fits allowing hyperfine field distributions obtained at RT on samples of $\text{Ce}_2(\text{Fe}_{17-x}\text{Al}_x)$ have shown that the weighted average quadrupole splitting decreases from 0.52 mm/s in $x = 7.2$ to 0.32 mm/s in $x = 10.6$ [18]. This behavior is consistent with that observed for QS(D2) on the samples of $\text{Ce}(\text{Fe}_{1-x}\text{Al}_x)_2$ system with $0.8 < x \leq 0.98$ and likely confirm the presence of spurious phase of $\text{Ce}_2(\text{Fe}_{17-x}\text{Al}_x)$ type in our samples. No Mössbauer measurements at 4.2K, for samples of the $\text{Ce}_2(\text{Fe}_{17-x}\text{Al}_x)$ series with $6 \leq$

$x \leq 8$, were reported up to the moment, to our knowledge. So it is difficult to extend the comparison with our results further on.

We conclude that all the complex magnetic properties observed at high temperature, in samples of the $\text{Ce}(\text{Fe}_{1-x}\text{Al}_x)_2$ system with $0.8 < x \leq 0.92$ are associated to the precipitation of spurious phase of $\text{Ce}_2(\text{Fe}_{17-x}\text{Al}_x)$ type. Therefore, to continue the study of the magnetic properties of the Al-rich side of the system it is necessary, initially, to performe a systematic work in order to improve the method of samples preparation .

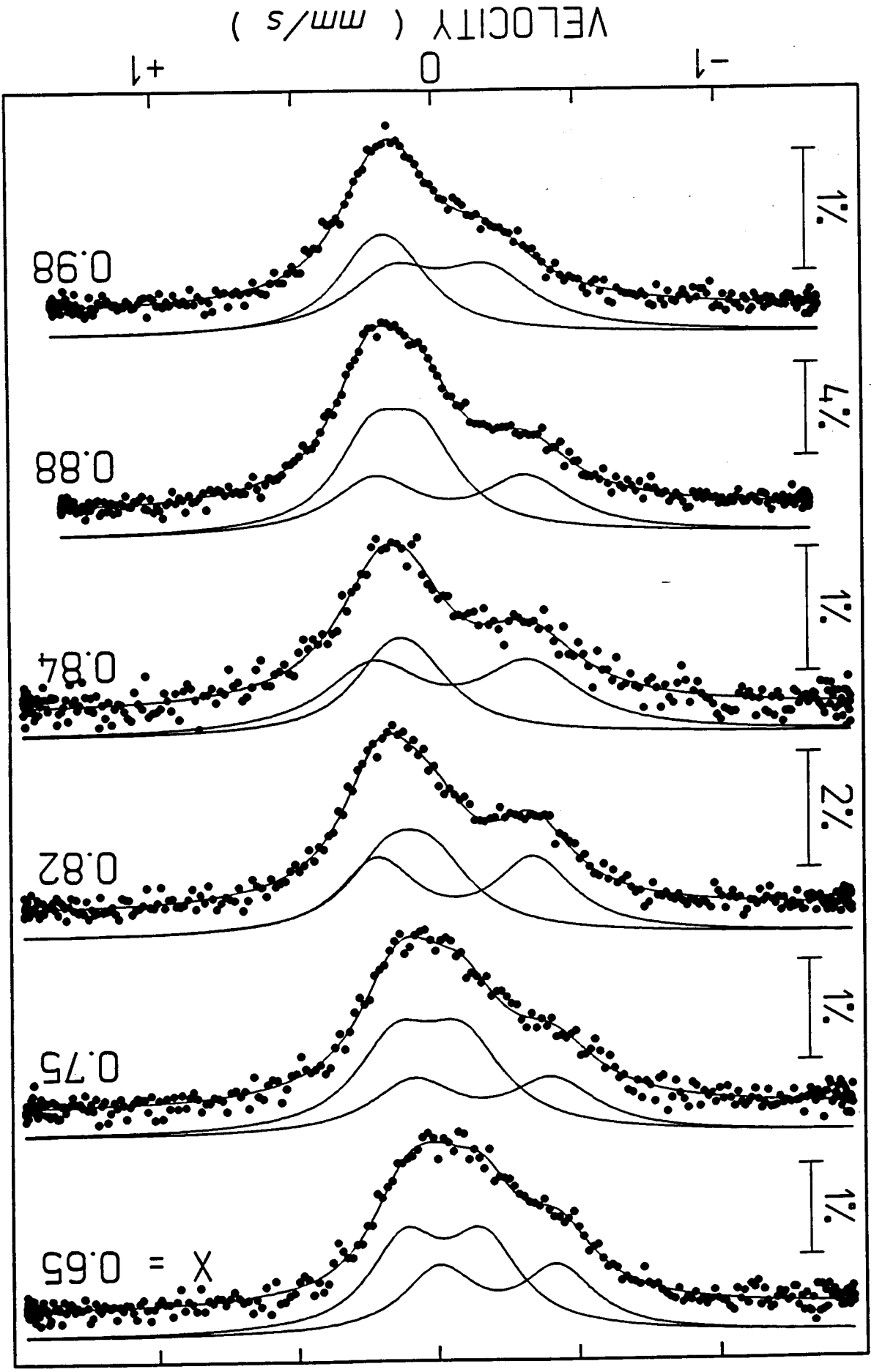
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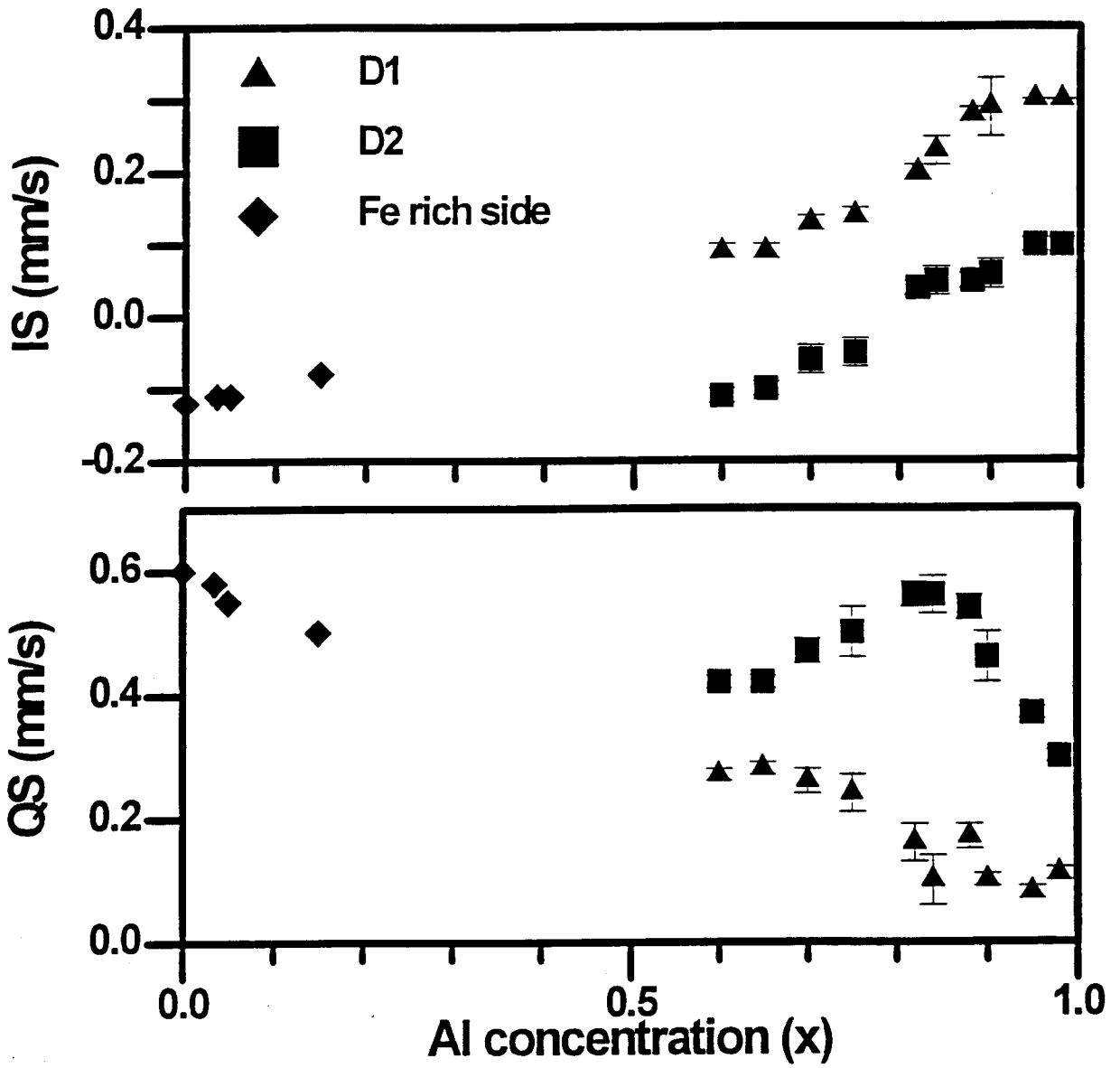
We thanks Dr. A. Fernandes from Instituto Militar de Engenharia for the metallographic analysis of our samples.

Figure Captions

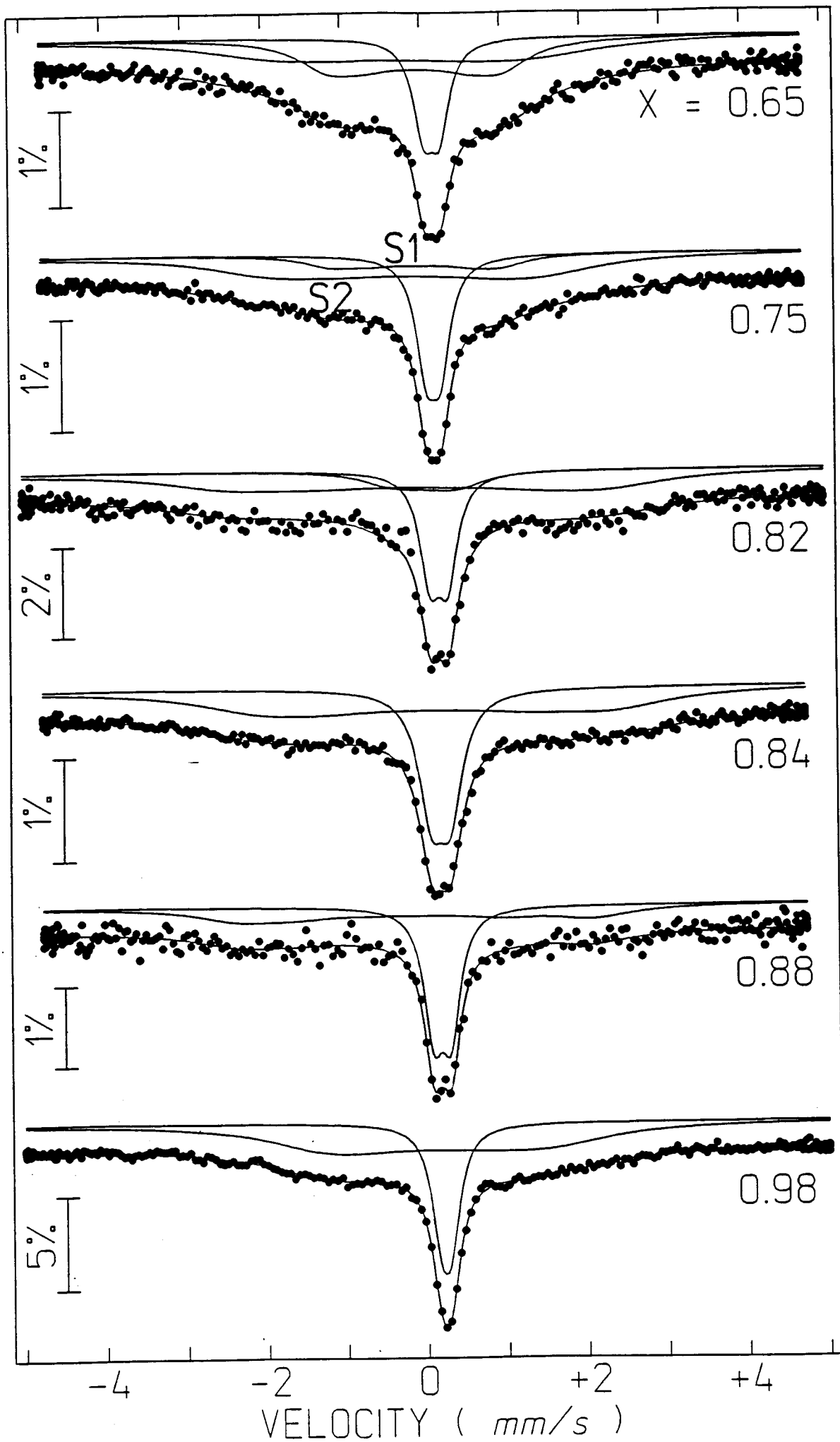
- Fig. 1. Mössbauer spectra for some samples of the Al-rich side of the system $\text{Ce}(\text{Fe}_{1-x}\text{Al}_x)_2$ at RT.
- Fig. 2. Al concentration dependence of IS and QS of both doublets, D1 and D2, observed at RT.
- Fig. 3. Mössbauer spectra for some samples of the Al-rich side of the system $\text{Ce}(\text{Fe}_{1-x}\text{Al}_x)_2$ at 4.2K.
- Fig. 4. Al concentration dependence of the mean hyperfine field, \overline{B}_{hf} , associated to the both magnetic components at 4.2K.
- Fig. 5. Mössbauer spectra of the $\text{Ce}(\text{Fe}_{0.25}\text{Al}_{0.75})_2$ sample at 10K in various applied fields (B_a).
- Fig. 6. B_a dependence of the mean hyperfine field associated to each component of the spectra obtained at 10K.

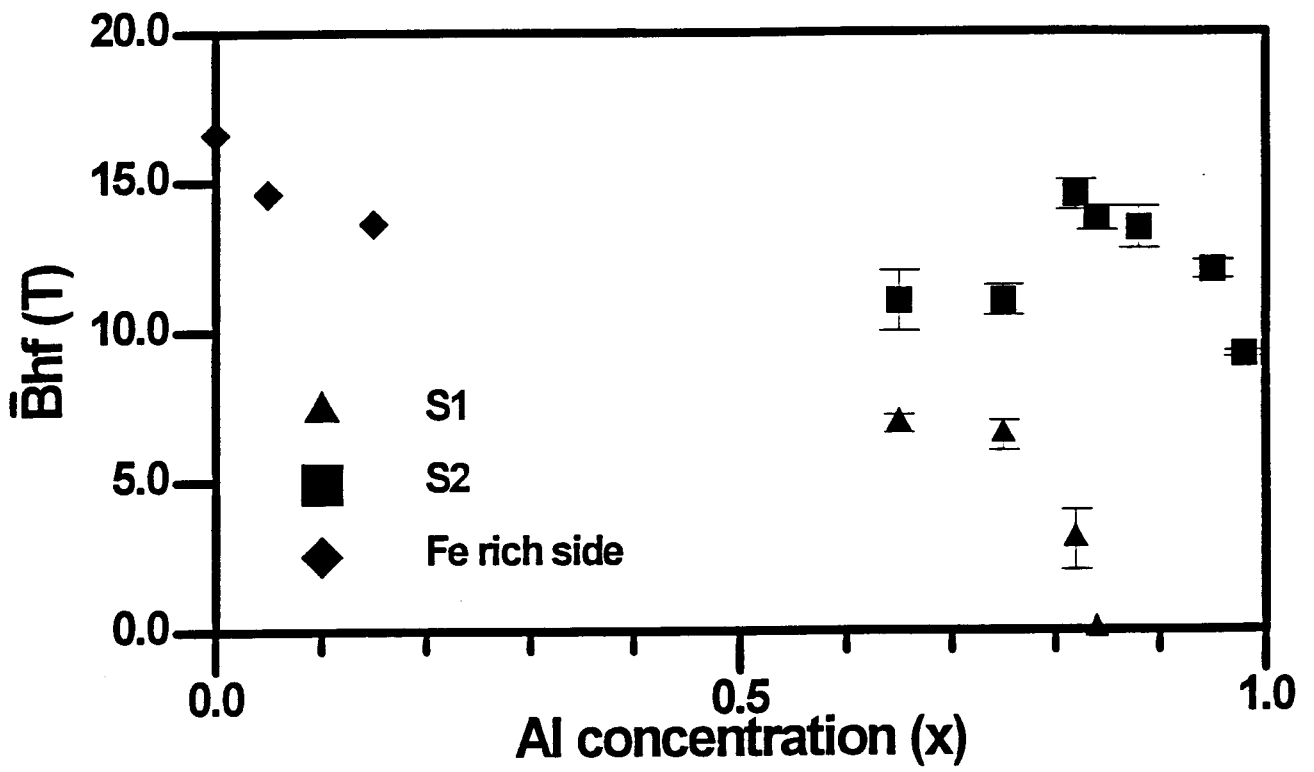
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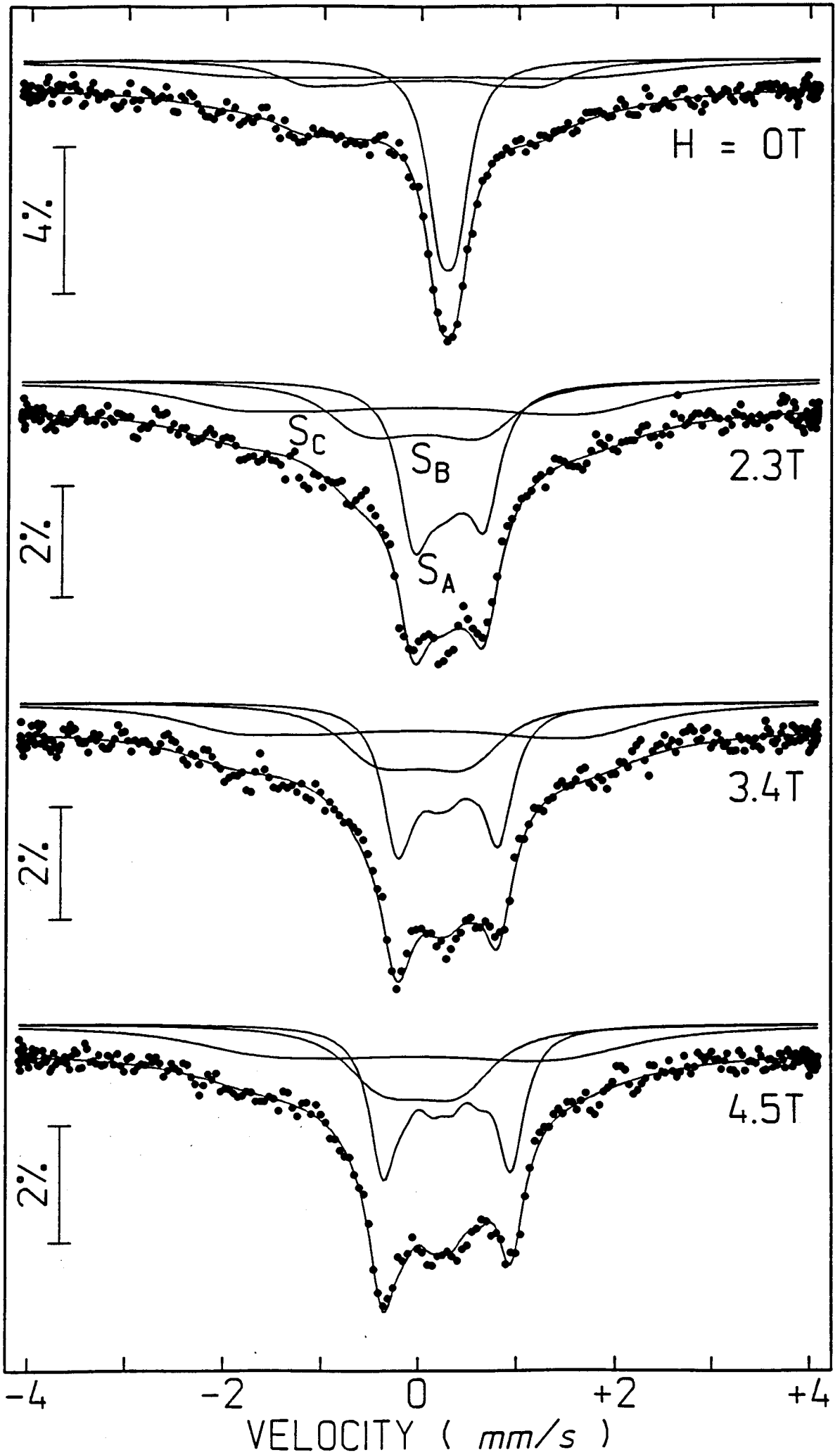


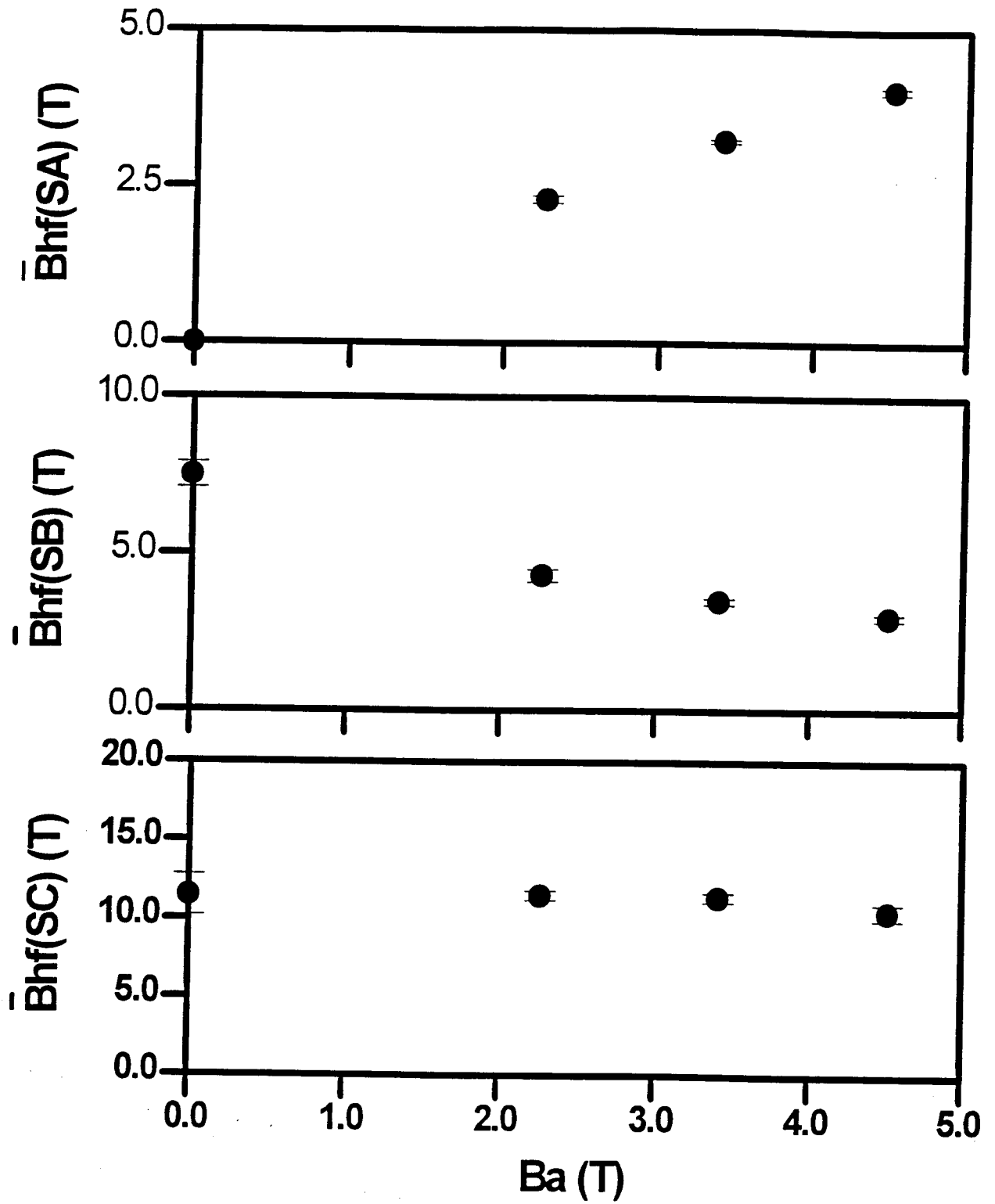
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