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^{57}Fe and ^{119}Sn Mössbauer studies on $La_{1.25}Nd_{0.6}Sr_{0.15}CuO_4$: Evidence for local magnetic ordering below $\simeq$ 32 K.

by

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Abstract

^{57}Fe - and ^{119}Sn Mössbauer effect studies on 0.5at%^{57}Fe (or ^{119}Sn) doped non-superconducting $La_{1.25}Nd_{0.6}Sr_{0.15}CuO_4$ in the temperature region 300 K $\geq$ T $\geq$ 4.2 K reveal an onset of local magnetic ordering occuring at $T_M \simeq$ 32 K for both ^{57}Fe - as well as ^{119}Sn-doped samples. The local magnetic ordering shows up in the presence of a very large transferred hyperfine field of $B_{thf} \simeq 11.0(5)$ T at the ^{119}Sn nuclei. Since such a large field is neither present in antiferromagnetic La_2CuO_4, nor in superconducting $La_{1.85}Sr_{0.15}CuO_4$ or overdoped $La_{2-x}Sr_xCuO_4$ (x = 0.4), the occurrence of such local spin correlations seems to be a signature of the non-superconducting low temperature tetragonal phase of $La_{1.25}Nd_{0.6}Sr_{0.15}CuO_4$.

Key-words: 74.70.Vy; Mössbauer; ^{119}Sn-doping in high T_c; ^{57}Fe-doping in high T_c.

The low temperature (LT) structural phase transition from the orthorhombic to a tetragonal (space group $P4_2/ncm$) phase occuring in $(La_{1-x}Nd_x)_{1.85}Sr_{0.15}CuO_4$ at a temperature T_{LT} seems to be in competition with the superconducting transition at T_c [1,2]. The compound remains in the LT orthorhombic (LTO) phase and is superconducting as long as $T_c > T_{LT}$, which is the case for $x \lesssim 0.18$. When T_{LT} becomes larger than T_c (extrapolated from the Nd-dependence of T_c), which is the case for Nd-concentrations $x \gtrsim 0.18$, the compound transforms in the LT tetragonal (LTT) phase, wherein there is no longer bulk superconductivity. The magnetic properties of this non-superconducting LTT phase are of great interest especially with respect to the Cu-moments. Susceptibility (χ) measurements [3] show that χ essentially is determined by the Nd-moments with a paramagnetic behavior down to the lowest measured temperature ($\simeq$ 2 K). There is no indication of any long-range magnetic ordering of the Nd- or Cu-moments for $T \gtrsim 2$ K in these experiments. Recent neutron diffraction studies [4] on single crystals of $La_{1.49}Nd_{0.39}Sr_{0.12}CuO_4$ also do not show long-range spin order in the LTT phase. The authors suggest a glassy state for the explanation of their observed results.

Mössbauer Effect (ME) spectroscopy, on the other hand is a microscopic method, which offers the possibility to study the local magnetic properties: one observes a magnetic hyperfine field at the Mössbauer nuclei (^{57}Fe or ^{119}Sn) if the system exhibits any static local magnetic order. It is for this reason that we have studied ^{57}Fe - as well as ^{119}Sn-doped $La_{1.25}Nd_{0.6}Sr_{0.15}CuO_4$ by means of ME spectroscopy. ME experiments on superconducting $La_{1.85}Sr_{0.15}CuO_4$ doped with ^{57}Fe as well as ^{119}Sn already have been performed by other groups [5-8]. Therein it was concluded that the dopant atoms occupy the Cu-site. This conclusion was drawn from the fact that both Fe- and Sn-doping lead to a strong reduction of T_c already at very low dopant concentration (T_c is decreased by $\simeq$ 10 K for both 0.5 at%Fe- and 0.5 at % Sn-doping [5,8]). ^{57}Fe- and ^{119}Sn-studies on non-superconducting $La_{1.25}Nd_{0.6}Sr_{0.15}CuO_4$, therefore, will give informations on the local magnetic order around the Cu-site in this compound.

Samples were prepared by standard solid state reaction. The stoichiometry of the samples was checked by energy dispersive X-ray (EDX) and chemical analysis. Powder X-ray diffraction showed the samples to be single phase. ME experiments were performed in a variable temperature liquid He cryostat in the temperature region $4.2 \leq T \leq 300$ K. The ^{57}Co:Rh- and $Ba^{119m}SnO_3$ -ME-source always was kept at room temperature.

Fig. 1 shows the ^{57}Fe ME spectra for temperatures between 300 and 70 K. These spectra can be fitted with one quadrupole doublet [9-11], whose hyperfine (hf) parameters essentially are identical with those reported for ^{57}Fe-doped $La_{1.85}Sr_{0.15}CuO_4$ [5,6]. In fig. 2 the hf parameters (center shift δ, quadrupole splitting ΔE_Q) in the temperature region near the LTO → LTT phase transition are presented. The straight lines in this figure are drawn in such a way that they extrapolate to the <u>measured</u> hf-data at 300 K. From this we can conclude that the LTO → LTT phase transition at $T_{LT} \simeq 80$ K [1,2] has no measurable influence on these hf parameters. This is what one would expect, since there is no measurable volume change ($\Delta V/V \lesssim 10^{-6}$) between the LTO and LTT phase [12].

A drastic change of the ^{57}Fe-ME spectrum, however, occurs around 32 K: at this temperature the quadrupole doublet becomes strongly asymmetric [see fig. 3(a)], indicating the onset of local magnetic ordering or slow paramagnetic relaxation. The ^{57}Fe-ME spectrum is fully magnetically split at 4.2 K [see fig. 3.(b)]. The apparent asymmetry in the relative line intensities indicates that this spectrum is composed out of two sextetts with slightly different hf parameters. This is due to the already above mentioned fact that there are two Fe-sites with slightly different sourroundings in $La_{1.85}Sr_{0.15}CuO_4$ and $La_{1.25}Nd_{0.6}Sr_{0.15}CuO_4$, respectively. This point is not essential for the purpose of the paper, but it has to be taken into account in order to give a satisfactory fit to the 4.2 K-spectrum. The spectrum has been fitted taking the complete Hamiltonian (magnetic and quadrupole interaction) and assuming that the quadrupole interaction for both sextetts is given by the ΔE_Q values measured between 110 and 70 K and extrapolated to $T \to 0$ [$\Delta E_Q(0) \simeq 1.64$ mm/s]. The hf-data of these two sextetts are: $(B_{hf})_1 = 45.9(2)$ T, $(B_{hf})_2 = 46.7(2)$ T, center shift (relative to α-Fe at 300 K): $\delta_1 = 0.48(2)$ mm/s, $\delta_2 = 0.31(2)$ mm/s. The angles Θ_i between the direction of $(B_{hf})_i$ and the main component V_{ZZ} of the electric field gradient (EFG) tensor are small, namely $\Theta_1 \simeq 7(1.5)^\circ$ and $\Theta_2 \simeq 28(1.5)^\circ$. Our result on the local magnetic order in 0.5 at%^{57}Fe-doped $La_{1.25}Nd_{0.6}Sr_{0.15}CuO_4$ is in contrast to that found in 0.5at%^{57}Fe-doped superconducting $La_{1.85}Sr_{0.15}CuO_4$ [11]: there an onset of local magnetic ordering occurs at much lower temperature ($\simeq$ 8 K) and the angle Θ is $\simeq 90^\circ$, changing to $\Theta \simeq 0^\circ$ for Sr-concentrations $\gtrsim 0.2$ only. The magnitude of B_{hf} in $La_{1.25}Nd_{0.6}Sr_{0.15}CuO_4$, on the other hand, is slightly larger than that in $La_{1.85}Sr_{0.15}CuO_4$ ($B_{hf} \simeq 42$ T).

In order to check if the observed local magnetic ordering occuring at $T_M \simeq 32$ K is due to the Fe-moments, we additionally have performed ^{119}Sn-ME experiments on 0.5at%^{119}Sn-doped $La_{1.25}Nd_{0.6}Sr_{0.15}CuO_4$. Sn, in contrast to Fe, is diamagnetic and does not carry any magnetic moment. Fig. 4 shows the ^{119}Sn-ME spectrum at 300 K. This spectrum essentially is identical with that observed in 0.5at%^{119}Sn-doped $La_{1.85}Sr_{0.15}CuO_4$ [7,8]. It can be fitted with one quadrupole doublet with $\Delta E_Q = 0.72(3)$ mm/s, $\delta = 0.12(2)$ mm/s relative to $Ba^{119m}SnO_3$ at 300 K and linewidth $\Gamma = 0.97(2)$ mm/s. The 4.2 K - ^{119}Sn-ME-spectrum of $La_{1.25}Nd_{0.6}Sr_{0.15}CuO_4$, shown in fig. 5, is quite remarkable: it shows a large transferred magnetic hf field at the majority of the ^{119}Sn nuclei. The spectrum has been fitted using a magnetic and non-magnetic ($B_{thf} = 0$) component and assuming the same quadrupole interaction for both components. A broad hf field distribution for the magnetic component was simulated by introducing an additional line broadening proportional to the line position. The average hf field was found to be $B_{thf} \simeq$

11.0(5) T. The obtained quadrupole interaction is $\simeq$ -0.6 mm/s, close to the value observed above the magnetic ordering temperature. The fraction of the non-magnetic component was found to be $\simeq$ 7%.

In order to determine the onset temperature of local magnetic ordering in 0.5at%^{119}Sn-doped $La_{1.25}Nd_{0.6}Sr_{0.15}CuO_4$ we have measured the area A of the central quadrupole doublet ($\hat{=} B_{thf} = 0$) as a function of temperature as shown in fig. 6. A sharp decrease of A is observed around $T_M \simeq 32$ K (Notice: the straight line for T > 32 K extrapolates to the <u>measured</u> value of A at T = 300 K). This temperature coincides with that observed for 0.5at%^{57}Fe-doped $La_{1.25}Nd_{0.6}Sr_{0.15}CuO_4$ [see fig. 3(a)]. We thus can conclude that the onset of local magnetic ordering in this compound is <u>not</u> caused by the Fe-moments but must be an intrinsic temperature of the system.

Our ^{119}Sn-ME results at 4.2 K on 0.5at%-^{119}Sn-doped <u>non</u>-superconducting $La_{1.25}Nd_{0.6}Sr_{0.15}CuO_4$ are quite in contrast to those found in 0.5at%-^{119}Sn-doped superconducting $La_{1.85}Sr_{0.15}CuO_4$ by Abd-Elmeguid et al. [8]: no indication of any static local magnetic order has been seen by these authors. Shinjo et al. [7], on the other hand, report on a large transferred hf field of $B_{thf} \simeq 10$ T at the majority of the ^{119}Sn nuclei in $La_{1.85}Sr_{0.15}CuO_4$ doped with 1at% and 2at% ^{119}Sn, respectively. An additional weak, non-magnetic component with $B_{thf} = 0$, similar to our finding in $La_{1.25}Nd_{0.6}Sr_{0.15}CuO_4$ also was seen in these experiments. The seemingly contradictionary results of Abd-Elmeguid et al. and Shinjo et al., together with our results on <u>non</u>-superconducting $La_{1.25}Nd_{0.6}Sr_{0.15}CuO_4$, can be explained in the following way: high Sn-doping ($\gtrsim$ 1at%) of superconducting $La_{1.85}Sr_{0.15}CuO_4$ leads to inhomogenous samples, where most of the sample is in a <u>non</u>-superconducting state with a large B_{thf} at the ^{119}Sn nuclei. The remaining superconducting phase gives the non-magnetic part of the ^{119}Sn-ME spectrum. The fact that the 4.2 K - ^{119}Sn-ME spectrum of our <u>non</u>-superconducting $La_{1.25}Nd_{0.6}Sr_{0.15}CuO_4$ sample also contains a non-magnetic component ($\simeq$ 7% of total intensity, see fig. 5) is an indication for a non-complete LTO →

LTT phase transition. The superconducting LTO fraction, as obtained from X-ray analysis is $\lesssim 5$ %. This discrepancy between ME and X-ray results can be explained if we assume that the remaining ($\simeq 7\%$) LTO phase, seen in ME experiments, mainly is present in form of microcrystalline domains not detectable by X-ray diffraction.

We thus come to the conclusion that local magnetic ordering of Cu-moments occurs at $T_M \simeq 32$ K in the non-superconducting LTT phase of $La_{1.25}Nd_{0.6}Sr_{0.15}CuO_4$. The coincidence of T_M with the superconducting transition temperature T_c of the LTO phase at the critical Nd-concentration $x \simeq 0.18$ where bulk superconductivity dissappears may be just accidental. Additional experiments with different Nd-concentrations in the region $0.18 < x < 0.6$ are planned in order to check if T_M depends on x.

Local magnetic ordering of the Cu-moments also has been found in $La_{2-x}Ba_xCuO_4$ around $x = 0.12$ by positive muon rotation [13,14]. In the region $0.11 \leq x \leq 0.135$ a structural phase transition from the LTO to the non-superconducting LTT phase, exactly like that in $(La_{1-x}Nd_x)_{1.85}Sr_{0.15}CuO_4$ for $x > 0.18$, takes phase in $La_{2-x}Ba_xCuO_4$ [15]. Magnetic ordering of the Cu-moments appears in the LTT phase of $La_{1.88}Ba_{0.12}CuO_4$ below $T_M \simeq 35$ K. Other evidence for local magnetic ordering of Cu-moment in the LTT phase of $La_{1.88}Ba_{0.12}CuO_4$ has been obtained through NMR studies [16].

The fact that a large transferred hf field B_{thf} at the ^{119}Sn nuclei only is observed in metallic, non-superconducting $La_{1.25}Nd_{0.6}Sr_{0.15}CuO_4$ and Sn-overdoped $La_{2-x}Sr_xCuO_4$ but not in the insulating antiferromagnet La_2CuO_4 [7,8,17] might suggest that a large B_{thf} is typical for the metallic, non-superconducting state. However, the additional finding by Shinjo et al. [6] that there is no large B_{thf} in overdoped metallic $La_{1.6}Sr_{0.4}CuO_4$ shows that the situation is not that simple. The reason for the dissappearance of superconductivity in $La_{1.25}Nd_{0.6}Sr_{0.15}CuO_4$ is the occurence of the LTT phase transition [2]. In contrast to this, the suppression of superconductivity in overdoped

$La_{2-x}Sr_xCuO_4$ definitely is not due to the occurence of the high-temperature tetragonal (HTT) phase as concluded by Takagi et al. [18] but caused by a doping effect of the CuO-planes [19]. The latter conclusion is drawn by experiments on $(La_{1-x}Pr_x)_{1.85}Sr_{0.15}CuO_4$, where the HTT phase transition is shifted towards much higher Sr-concentrations, while the dissappearance of superconductivity is not influenced by the Pr-substitution. A consequence of this is, that the Cu-moments essentially dissappear in overdoped $La_{2-x}Sr_xCuO_4$, while this is not the case for the LTT phases of $(La_{1-x}Nd_x)_{1.85}Sr_{0.15}CuO_4$ and $La_{2-x}Ba_xCuO_4$, respectively. Strong short range Cu-moment correlations apparently exist in the latter compounds below T_M, leading to a large B_{thf} as experimentally observed in $La_{1.25}Nd_{0.6}Sr_{0.15}CuO_4$. The existence of a large B_{thf} in the LTT phase of $La_{2-x}Ba_xCuO_4$ has not yet been proven. ^{119}Sn-doped $La_{1.88}Ba_{0.12}CuO_4$ are under way to show that a large B_{thf} is a general signature of the non-superconducting LTT phases.

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Fig. 1: ^{57}Fe-ME spectra of $La_{1.25}Nd_{0.6}Sr_{0.15}CuO_4$ doped with 0.5at%^{57}Fe at various temperatures ($70 \leq T \leq 300$ K). The spectra have been fitted with one quadrupole doublet.

Fig. 2: Hyperfine parameters (quadrupole splitting ΔE_Q, center shift δ) of quadrupole doublet shown in fig. 1 in the temperature region around the LTO → LTT phase transition. The straight lines through the data point are extrapolated to the measured hf parameters at T = 300 K.

Fig. 3: ^{57}Fe-ME spectra of $La_{1.25}Nd_{0.6}Sr_{0.15}CuO_4$ doped with 0.5at%^{57}Fe at T = 32 K [fig. (a)] and T = 4.2 K [fig. (b)]. The 32 K-spectrum has been fitted with an asymmetric quadrupole doublet, the 4.2 K-spectrum with a combined magnetic and quadrupole interaction as described in the text.

Fig. 4: ^{119}Sn-ME spectrum of $La_{1.25}Nd_{0.6}Sr_{0.15}CuO_4$ doped with 0.5at% ^{119}Sn at T = 300 K. The spectrum has been fitted with one quadrupole doublet.

Fig. 5: ^{119}Sn-ME spectrum of $La_{1.25}Nd_{0.6}Sr_{0.15}CuO_4$ doped with 0.5at% ^{119}Sn at T = 4.2 K. The spectrum has been fitted with a non-magnetic and magnetic component as described in the text.

Fig. 6: Resonance absorption area A of non-magnetic part in ^{119}Sn-ME spectra as a function of temperature around $T_M \simeq 32$ K. The line through the data points for T < 32 is guide to the eyes. The straight line for T > 32 K is drawn in such a way that it extrapolates to the measured value of A at T = 300 K.

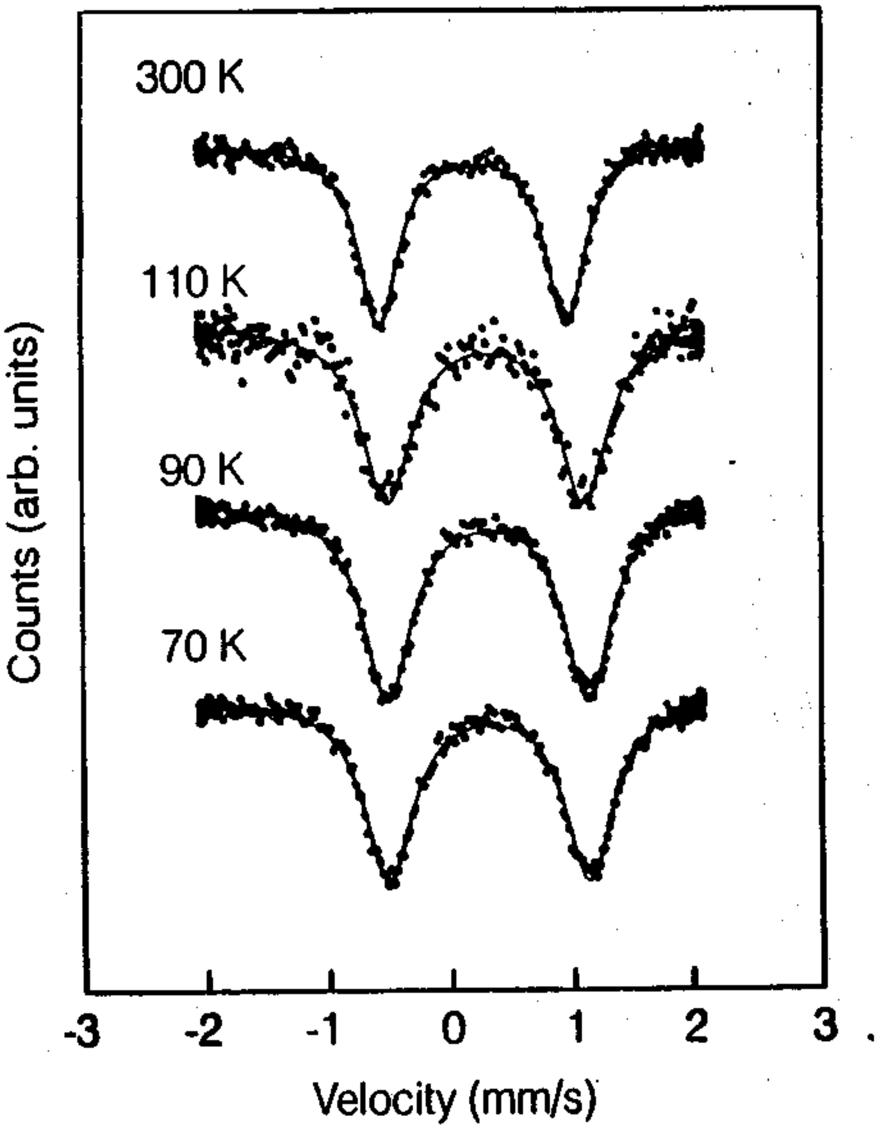

Fig. 1

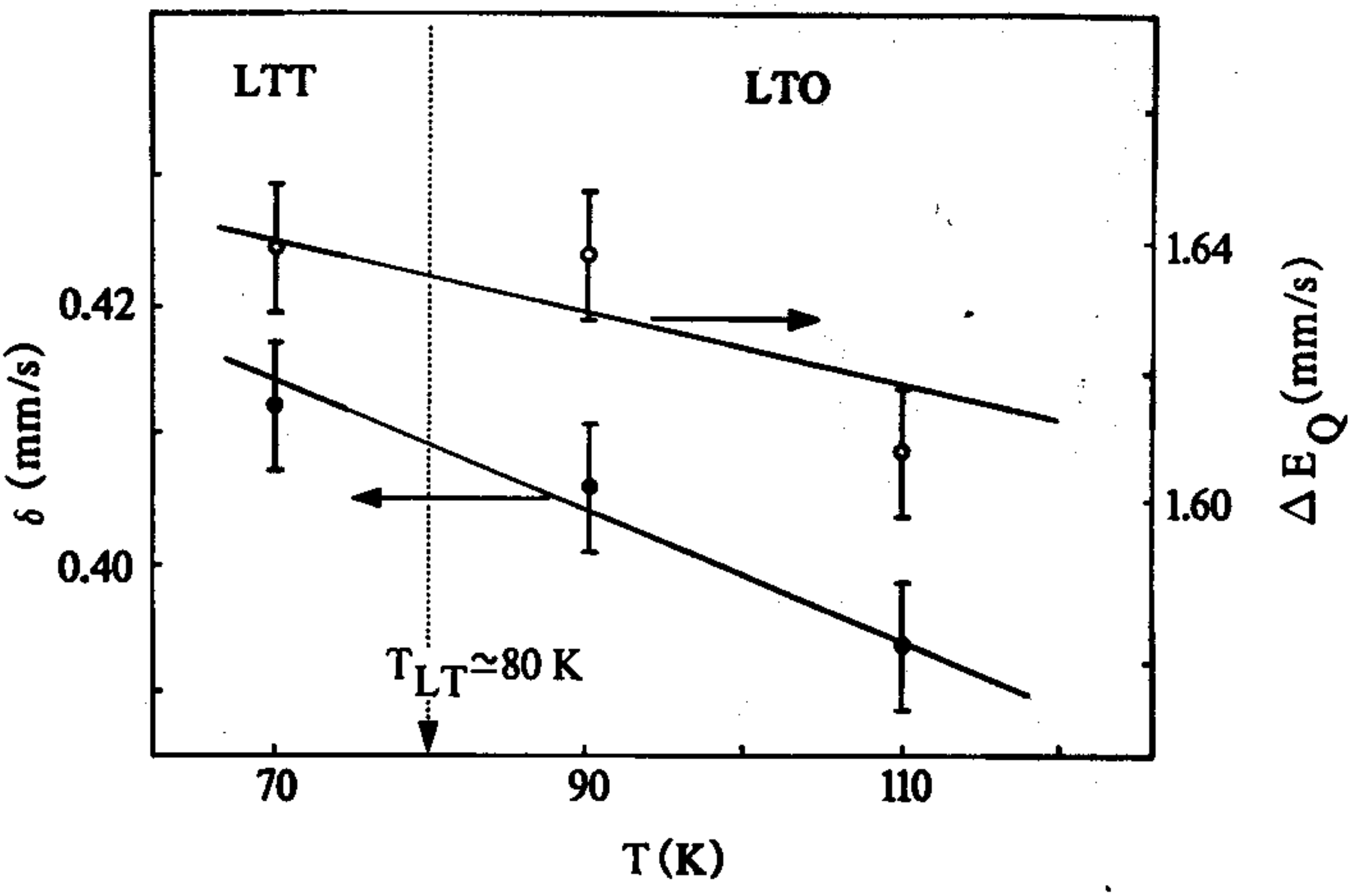
LTT
LTO
$T_{LT} \simeq 80$ K
0.42
0.40
δ (mm/s)
1.64
1.60
ΔE_Q (mm/s)
70
90
110
T (K)

Fig. 2

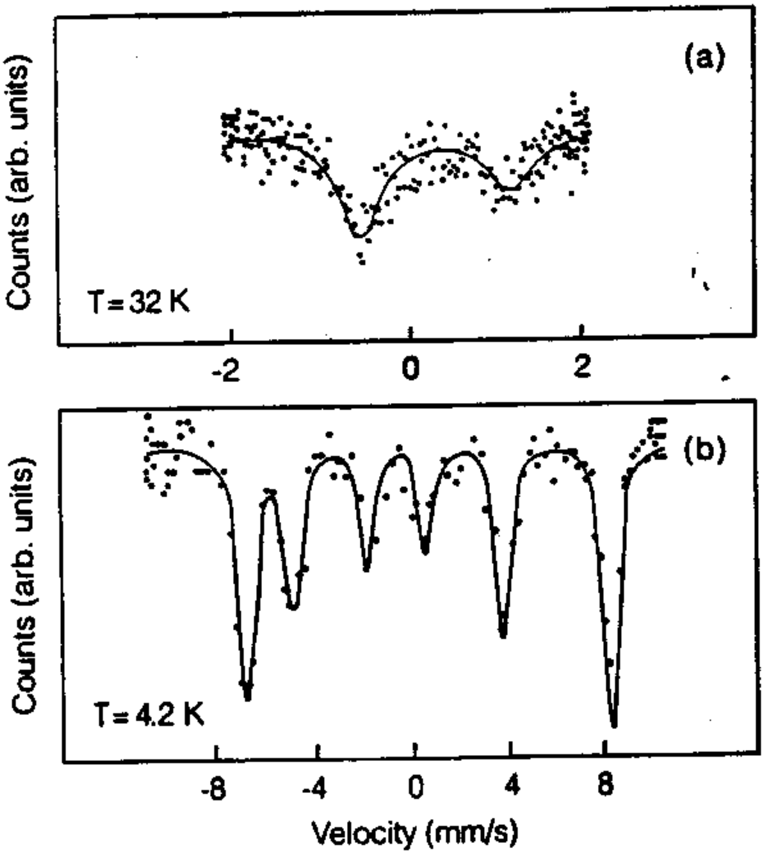
(a)
Counts (arb. units)
T=32 K
-2
0
2
(b)
Counts (arb. units)
T=4.2 K
-8
-4
0
4
8
Velocity (mm/s)

Fig. 3

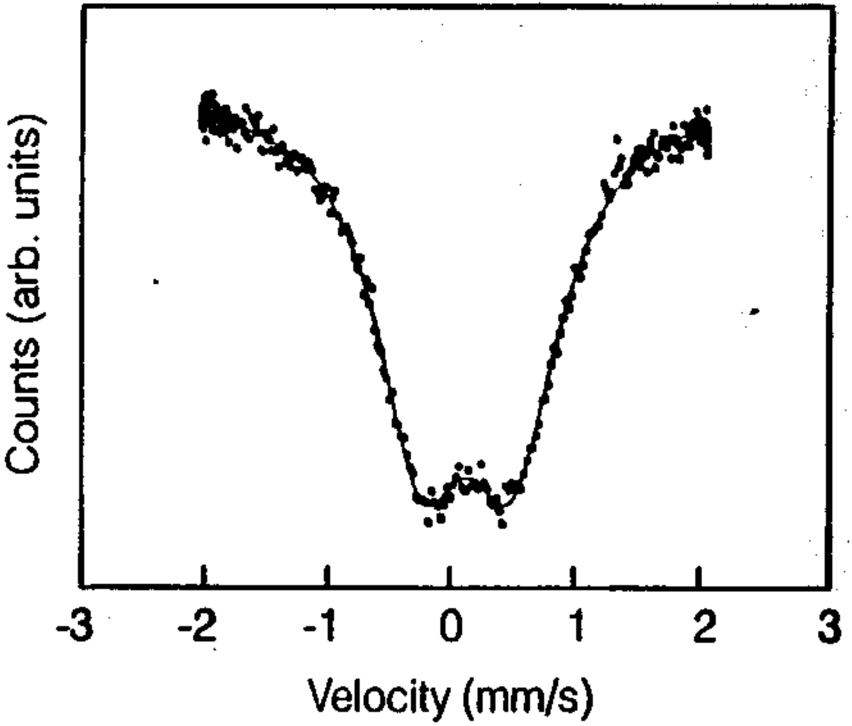

Fig. 4

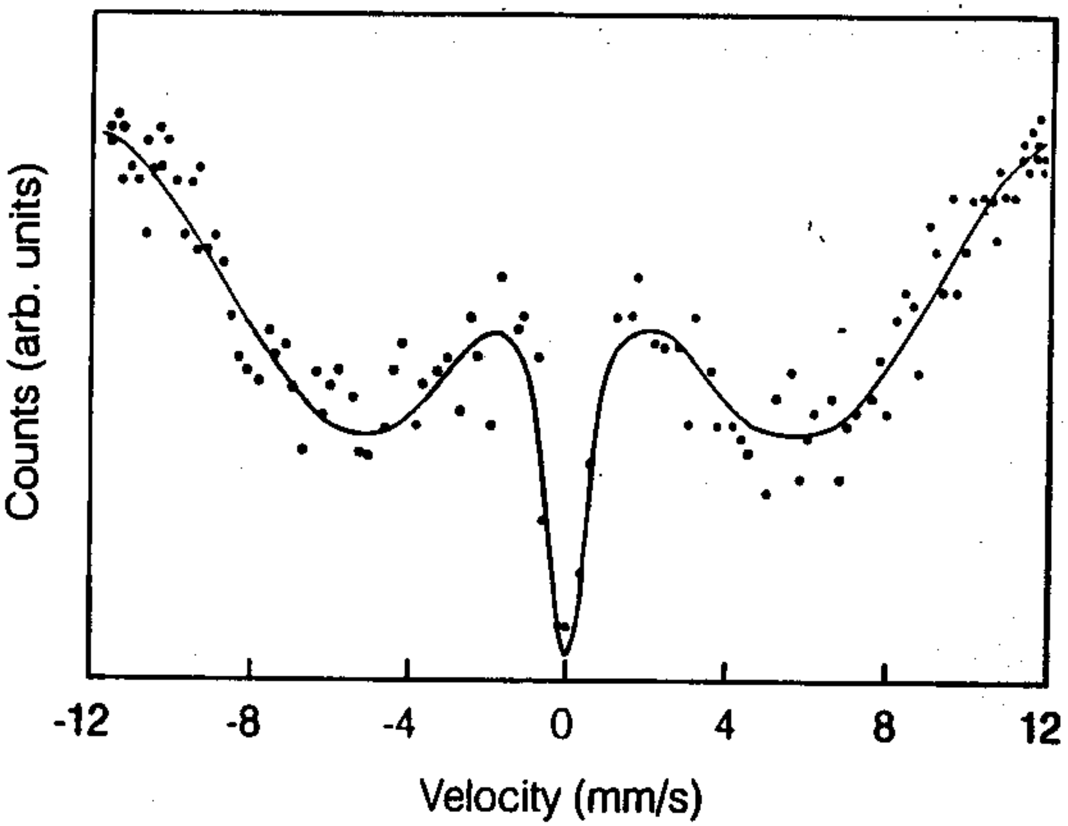

Fig. 5

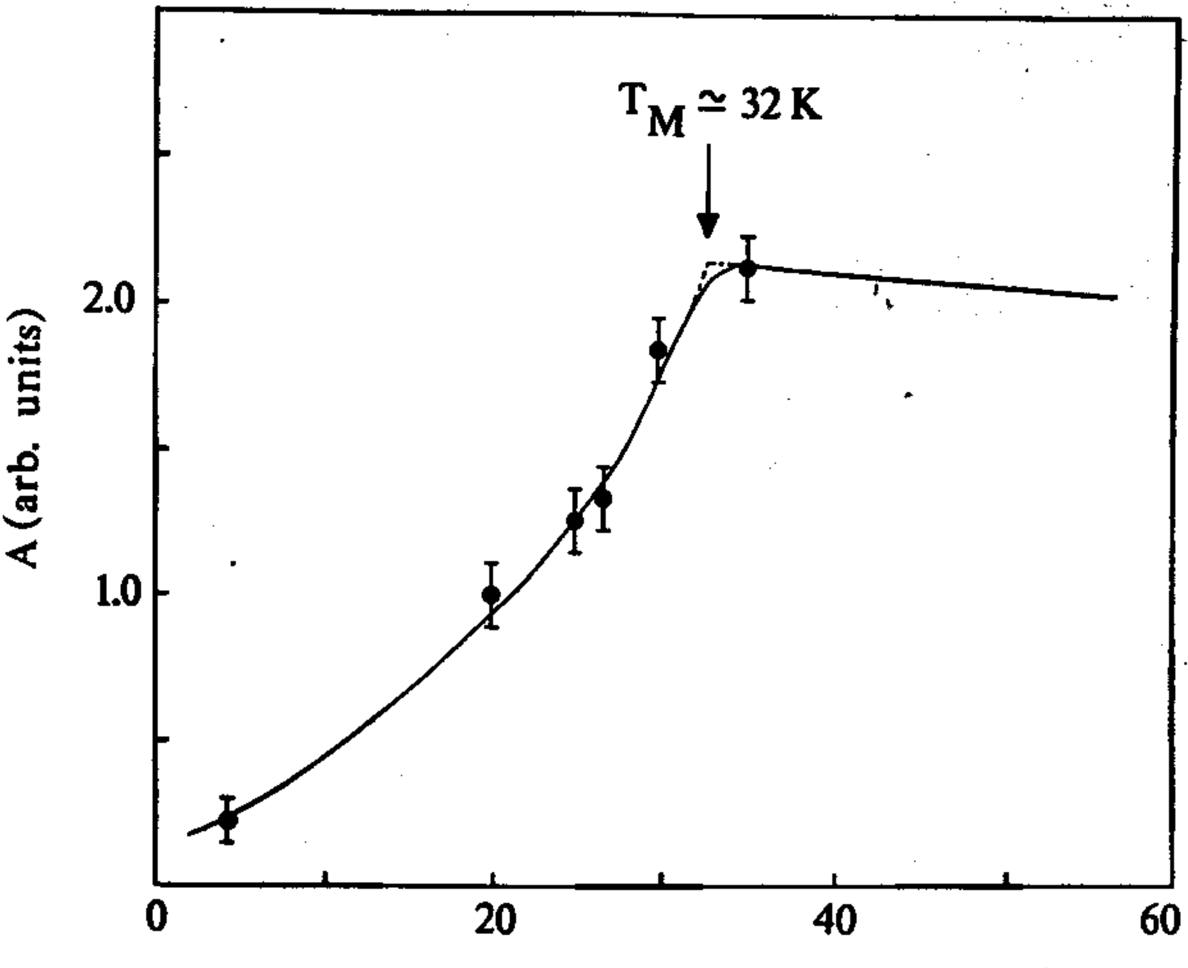

Fig. 6

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