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Fe^{1+} TRANSIENT CHARGE STATE IN ZnS : ^{57}Co MÖSSBAUER SOURCES

by

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ABSTRACT

ZnS : ^{57}Co Mössbauer sources emit below 255 K a line attributed to Fe^{1+} ions in addition to the main Fe^{2+} spectrum. Above this temperature the Fe^{1+} charge state is either no longer generated, or more probably its life time becomes shorter than the nuclear life time of ^{57}Fe (14.4 KeV). Down to 100 K the Fe^{1+} contribution is present as a single line, and at lower temperatures this line broadens and splits into a doublet with large line widths.

1. INTRODUCTION

Most of the previous studies concerning the Mössbauer spectra of ^{57}Fe as substitutional impurities in ZnS blende have been related to the Fe^{2+} charge state.

The study of ZnS : ^{57}Fe absorbers as a function of the iron concentration [1] has shown that isolated Fe^{2+} impurities give a single line slightly broadened at low temperature by strain effects, and that Fe^{2+} ions associated in pairs of next nearest neighbors give a temperature dependant quadrupole doublet.

A comparative study of isolated Fe^{2+} impurities in ZnS: ^{57}Co sources and ZnS : ^{57}Fe dilute absorbers [2] revealed that source and absorber spectra are similar at room temperature, but that they are quite different at very low temperature. At these low temperatures the only noticeable feature for the dilute absorber experiments is the presence near 8 K of an anomaly of the Fe^{2+} absorption peak linewidth, which goes through a maximum due to relaxation effects between the two low lying electronic levels of this ion. On the other hand for the source experiments, a complex hyperfine structure of Fe^{2+} is observed below about 5 K, showing two quadrupole doublets in addition to the central line.

These quadrupole doublets have been attributed to the slow relaxation contributions of the excited spin-orbit triplets Γ_4 and Γ_5 of Fe^{2+}, whose populations appear to be out of the thermal equilibrium after the decay of the radioactive parent ^{57}Co [2,3].

The study of this structure, of which one doublet ("the external doublet") corresponds to the predictions of HAM [5], gave useful information about the Jahn-Teller coupling in the system ZnS : Fe^{2+}. [3]

In addition to the main contribution due to the Fe^{2+} ions, we have observed in the source spectra an extra contribution of much lower intensity, which we attribute to the charge state Fe^{1+} [2,4] . The detailed study of this small contribution forms the subject of the present note.

2. SAMPLE PREPARATION AND EXPERIMENTAL CONDITIONS

The activity of the various ZnS : ^{57}Co sources ranged between 1 and 3 mCi. The sources were prepared in the following different ways in order to examine the dependence of the Mössbauer spectra on the preparation method.

1a. ZnS blende powder was first prepared by heating the constituents under vaccuum at 900°C with about 2% excess sulphur. Then the powder was wetted with a solution of ^{57}CoCl$_2$ in 0.1N HCl. After drying under vaccuum at about 300°C, the powder was heated for a few hours near 900°C in a vaccuum sealed silica tube in order to allow the diffusion of the ^{57}Co into the ZnS lattice, and then it was slowly cooled.

1b. Same method as 1a, but the HCl solution was neutralized by the addition of NH$_4$OH in order to prevent a possible chemical attack of ZnS. ClNH$_4$ was then evaporated at about 300°C.

1c. Same method as 1a, but after wetting the ZnS powder with ^{57}CoCl$_2$ in HCl solution, a S(NH$_4$)$_2$ solution was added for precipitating ^{57}Co as a sulphide in order to avoid a possible formation of cobalt oxides during the doping process.

2. In order to eliminate the possibility of introducing additional defects into the ZnS lattice through the ^{57}Co doping process, we developed a second method of preparation where the synthesis of ZnS was made in the same way as in section 1a, but after doping the zinc constituent with ^{57}Co.

3. We used also a sample of ultra fine particles of blende powder prepared by precipitation from the disulphide according to the method described by Grillot [6], which was annealed for one hour near 930°C under a nitrogen flow in order to increase the number of sulphur vacancies. The ^{57}Co doping process was the same as described in section 1a.

4. Finally we used a natural single crystal of ZnS blende which we doped with ^{57}Co as described in section 1a. The sample was made of a 0.5 mm thick platelet parallel to the (100) plane. The amber colour of this crystal suggests that the impurity level was not negligeable.

Non active check samples were also prepared using the same methods as above, and were verified by X-ray diffraction. Only samples of the type 3 contained an appreciable proportion (about 10%) of the hexagonal phase of ZnS (Würtzite).

In order to prevent a possible oxydation of our samples, we took the same precautions as for the absorber experiments [2] : namely the ZnS : ^{57}Co sources were kept either under vaccuum or in the presence of a deshydrating agent, and we used a non oxydant glue (Eastman 910) for sealing the source containers.

The Mössbauer spectra were recorded using a moving reference absorber made of Potassium ferrocyanide, containing about 0.1 mg ^{57}Fe by cm^2, and with a linewidth, as calibrated with a ^{57}Co source in Rhodium, of about 0.24 mm.s^{-1}.

3. EXPERIMENTAL RESULTS

Whatever the preparation method, the ZnS : ^{57}Co sources gave the same type of spectra, except for the relative intensities of the two charge states which are observed.

Source 2. The most detailed study has been made on the source 2, of which some spectra are represented in Fig. 1 in the temperature range (T >5K) where the Fe^{2+} line does not give any hyperfine structure.

As for the dilute absorbers of ZnS : ^{57}Fe, the room temperature spectrum consists of a single line due to Fe^{2+} whose isomer shift is 0.69 ± 0.02 mm.s^{-1} referred to K$_4$Fe(CN)$_6$,3H$_2$O, and whose width (0.26 mm. s^{-1}) is comparable to the minimum experimental width obtained with the same reference absorber (0.24 mm.s^{-1}).

Below 255 K a second line, about 0.3 mm.s^{-1} broad, appears to the right of the main Fe^{2+} line and its relative intensity (labeled P(Fe^{+1}), fig. 2a) increases rapidly at first, with decreasing temperature, and then reaches a quasi constant value below 190 K. The appearance and disappearance of this line is reversible, and no thermal hysteresis effect has been observed.

The difference between the isomer shifts of the new line and of the Fe^{2+} line is almost temperature independant, even in the transition region (190 - 255 K), and is equal to +0.34 0.02 mm.s^{-1} (fig. 3).

It should be mentioned that an alternative hypothesis could a priori be used when fitting the extra contribution between 77 and 255 K : instead of using a single line, a quadrupole doublet could be used with the left component being at the same place as the Fe^{2+} line, and the right component at the place of the previously admitted extra single line. However we eliminated this possibility, because it led to discrepancies with isomer shift and intensities measurements at lower temperatures .

Below about 100 K the new line broadens ; at lower temperature this contribution can be fitted to a first approximation by a doublet with large linewidths, whose separation increases rapidly up to 1.7 mm.s^{-1} between 50 and 20 K (fig. 4). Due to broadening the doublet is not clearly apparent on the spectra, but a careful computer analysis shows that it is present down to the lowest temperature examined.

Fig. 5 reproduces the spectrum of the source 2 at 1.35 K where the Fe^{2+} line itself splits into different contributions 2,3 . The corresponding fitted parameters are given in the table together with those for the other temperatures.

.   <u>Other sources.</u> Source 1a, 1b and 1c gave very similar spectra to those described above. This result shows that the direct doping process of ZnS with ^{57}Co did not introduce any significant alteration of the ZnS lattice, even when the HCl solution is not neutralized by NH_4OH when doping the ZnS powder (source 1a). As shown by the results of 1c, the characteristics and the relative intensity of the second line are not changed when special precautions are taken in order to prevent a possible formation of cobalt oxides during the doping process. As discussed in the section 5, this extra line cannot then be attributed to the presence of CoO.

The source 3, made of ultra fine particles, also gave the same type of spectra, but the relative intensity of the second line was at least 2 times larger than for the other samples (about 24%). The Fe $^{2+}$ linewidth, which is sensitive to small departures from local cubic symmetry, was slightly larger in this sample (0.36 mm.s^{-1} instead of about 0.30 at 77 K).

Finally, in the single crystal spectra (source 4), the second line is not detectable. The Fe^{2+} linewidth is particularly large in this natural sample (~ 0.56 mm.s^{-1} at 77 K) indicating large local strains probably due to impurities.

4. INTERPRETATION

1. Valence states

Whereas the isomer shift of the Fe^{2+} line is $+0.69 \pm 0.02$ mm.s^{-1} at room temperature, referred to $K_4Fe(CN)_6$, $3H_2O$, the isomer shift of the extra contribution, extrapolated to 295 K, is $+1.02 \pm 0.03$ mm.s^{-1} (fig.3).

Following the diagram due to Walker, Werthein and Jaccarino as modified by Danon [7], which corresponds to a ^{57}Fe isomer shift calibration constant $\alpha = -0.21 \, a_o^3$ mm.s^{-1} [8], we find that these two isomer shift values correspond respectively to the configurations $3d^6 4s^{0.6}$ and $3d^7 4s^{0.6}$ which differ exactly by one 3d electron.

The extra contribution can thus be assigned to the formation of Fe^{1+} ions in substitutional positions at the ZnS lattice. Other evidence that these ions are really located in the ZnS lattice and not in some distinct chemical phase is given in Section 4.3 and is discussed in section 5.

An abnormal Fe^{1+} valence state has already been observed following radioactive decay in Mössbauer sources, in for example MgO [9] and CaO [10].

However, in contrast to the case of MgO and CaO, no Fe^{3+} contribution is present in the spectra of the ZnS sources.

2. Thermal dependence of the line intensity.

Let $P(Fe^{1+})$ and $P(Fe^{2+})$ be the relative areas of the contributions Fe^{1+} and Fe^{2+} in the spectra, and $p(Fe^{1+})$ and $p(Fe^{2+})$ the relative proportions of the Fe^{1+} and Fe^{2+} ions in the lattice. We have :

$$P(Fe^{1+}) + P(Fe^{2+}) = p(Fe^{1+}) + p(Fe^{2+}) = 1 \quad \text{and}$$

$$\frac{P(Fe^{1+})}{P(Fe^{2+})} = \frac{p(Fe^{1+}) \, f(Fe^{1+})}{p(Fe^{2+}) \, f(Fe^{2+})} \, ,$$

where $f(Fe^{1+})$ and $f(Fe^{2+})$ are the Debye-Waller factors relative to Fe^{1+} and Fe^{2+}. It follows that :

$$f(Fe^{1+}) = \frac{p(Fe^{2+})}{p(Fe^{1+})} \times y(T)$$

$$\text{with } y(T) = \frac{P(Fe^{1+})}{1-P(Fe^{1+})} \times f(Fe^{2+})$$

If we suppose first that the actual ionic proportions $p(Fe^{1+})$ and $p(Fe^{2+})$ are temperature independant, $f(Fe^{1+})$ should be proportional to $y(T)$. The curve $y(T)$ has been calculated (fig. 2b) from the experimental thermal variation of $P(Fe^{1+})$ (fig. 2a), taking also into account the slight thermal variation of $f(Fe^{2+})$ deduced from the Debye temperature $\Theta_D \simeq 315$ K of the ZnS lattice [11].

It is clear on fig. 2b that the curve $y(T)$ cannot be accounted for by a variation following the usual Debye-Waller factor $f(T)$, as shown by the dashed curves calculated from various Debye temperatures. Therefore the actual ionic proportions $p(Fe^{1+})$ and $p(Fe^{2+})$ depend on the temperature, and the disappearance of the Fe^{1+} line near 255 K is due to a vanishing proportion $p(Fe^{1+})$, and not to a vanishing Debye-Waller factor $f(Fe^{1+})$. So the hypothesis of a weakly bound Fe^{1+} ion, which was made in order to explain the thermal variation of the Fe^{1+} contribution in the source spectra in MgO and CaO [9,10] does not apply to Fe^{1+} in ZnS.

The variable proportion of the Fe^{1+} ions between 190 and 255 K can be attributed either to a temperature dependant proportion of monovalent iron produced by the decay of ^{57}Co in ZnS , or to a temperature dependant life time of these Fe^{1+} ions. Following this last interpretation, the life time of the transient Fe^{1+} charge state would become much shorter than the nuclear life time $\tau = 1.41 \ 10^{-7}$s of ^{57}Fe (14.4 KeV) above 255 K and the transformation into Fe^{2+} would then occur before the emission of the Mössbauer γ rays. At lower temperatures Fe^{1+} would be a metastable charge state with a life time greater than τ.

Temperature dependant proportions of different charge states (Fe^{2+} and Fe^{3+}), which cannot be attributed to different Debye-Waller factors, have already been observed following the ^{57}Co decay in CoO [12], where it is thought that Fe^{3+} presents a metastable character at low temperature.

In order to obtain further information about the stability of the Fe^{1+} ions in ZnS, we tried to generate them in another way. It has been shown [13] that the same stable charge states of ^{57}Fe are formed either as a consequence of the ^{57}Co electron conversion or by electron irradiation of the corresponding iron compound. Thus, if a stable Fe^{1+} state is observed in the decay of ZnS : ^{57}Co sources one would expect to be able to detect the same species after electron bombardment of ZnS : ^{57}Fe absorbers. We have performed electron irradiation studies of ZnS : ^{57}Fe absorbers in a 2 MeV electron linear accelerator, the samples being placed in a cryostat at liquid nitrogen temperature. Mössbauer spectra were recorded in the same cryostat, which means that either during or after irradiation the absorbers were kept at temperatures at which any Fe^{1+} formed could be detected.

However, we did not observe in the irradiation experiments the Mössbauer line assigned to Fe^{1+} even with doses as high as 1,000 megarads, which tends to support the interpretation in terms of the transient character of the Fe^{1+} species formed in the ZnS : ^{57}Co sources.

3. Location of the Fe^{1+} ions

Above 255 K the source spectrum does not contain any contribution other than the single line of Fe^{2+} in ZnS. This means that all the radioactive parents ^{57}Co are located at substitutional sites in the ZnS lattice. Therefore the Fe^{1+} ions themselves, which are observed below 255 K, are necessarily generated by the decay of ^{57}Co in the same sites of ZnS, and not in some different chemical phase. As shown by the absence of quadrupole splitting - or broadening - of the Fe^{1+} line above 100 K, the local symmetry is cubic between 100 and 255 K. The splitting of the Fe^{1+} line at lower temperature seems to indicate the appearance of an electric field gradient (EFG), but the large width of the two components of the doublet might suggest some dynamical behaviour.

4. A possible model

In order to account for these different observations a plausible model can be proposed.

Since the amount of energy which is dissipated in the lattice during the ^{57}Co decay is much larger than that required for a charge transfer of an electron from a S^{2-} neighbour to the Fe^{2+} ion, we suppose that an electronic

defect is formed simultaneously with each Fe^{1+} ion. Above 100 K this electronic vacancy would be delocalized between each of the four S^{2-} neighbours of the Fe^{1+} ion, giving a zero effective EFG. Below this temperature the electronic motion would slow down and an EFG would appear at the Fe^{1+} site. The defect (Fe^{1+} + electronic vacancy) would be metastable, and its life time would decrease with increasing temperature, becoming comparable to the nuclear life time around 240 K and much lower above 255 K, where the reverse charge transfer process from the Fe^{1+} ion to S^- would give back the normal Fe^{2+} before the Mössbauer emission. Although this model seems to give a qualitative explanation of the observed behaviour of the Fe^{1+} contribution, it must be regarded as hypothetical in the absence of more direct evidence for its existence.

5. DISCUSSION

In the previous section we have interpreted the extra line as being due to Fe^{1+} ions which are located in the ZnS lattice, and whose proportion varies with temperature.

We discuss here in more detail the alternative possibility namely that this line originates from ^{57}Co atoms located in a distinct chemical phase, which could result for example from some superficial alteration of ZnS, as observed in MgO and CaO [9] [10]. The fact that the most finely divided powder (sample 3) present the most intense extra line could give some support to such a hypothesis.

The iron atom resulting from the decay of ^{57}Co in this extraneous phase would have to show a dynamical behaviour very similar to that of Fe^{2+} in ZnS between zero and 150 K, because the relative intensities of the two contributions are constant in this temperature range (Fig. 2a). But above 150 K this behaviour would have to strongly differ from the Debye model, as shown by fig. 2b, leading to a vanishing recoil free fraction at 255 K. Such a sudden delocalization of the iron atom is hardly imaginable, specially in a site of cubic symmetry, as shown by the lack of EFG at these temperatures.

The only chemical phase containing ^{57}Co which could exist with a non negligeable proportion in the sources 1a, 1b, 2 and 3, apart ZnS : ^{57}Co, is CoO. This cubic oxide is antiferromagnetic with a Neel Temperature T_N = 291 K, and

the isomer shift of Fe^{2+} in CoO is O.87 ± O.O4 mm.s^{-1} at 298 K referred to potassium ferrocyanide [14]. Even admitting that ultra fine particle of ^{57}CoO have dynamical and magnetic properties distinct from the bulk material, the extra line existing in the spectra of sources 1a,1b, 2 and 3 cannot be attributed to Fe^{2+} in CoO, because this line also exists with the same intensity in the source 1c where the presence of cobalt oxides is unlikely (see section 2).

For all these reasons we think that the interpretation given in the section 4 in terms of Fe^{1+} ions in ZnS is much more probable than the existence of an impurity phase.

Whereas the thermal behaviour of the Fe^{1+} contribution is the same in the various samples where it exists, the corresponding proportion varies considerably depending on which ZnS matrix is used. The maximum proportion of Fe^{1+} has been observed in the source 3, where the crystallization state of the matrix is the worst (finest particles and probably largest sulphur vacancy level). However further preparation tests which have been made in order to show a possible influence of the sulphur vacancies on the Fe^{1+} proportion have not been conclusive, and the exact mechanism which governs this proportion has not yet been established.

6. CONCLUSION

We have observed in the Mössbauer spectra emitted by ^{57}Co diluted in ZnS (blende) the presence of a monovalent charge state Fe^{1+} whose contribution is superimposed on the Fe^{2+} main line. This Fe^{1+} contribution presents an unusual thermal dependence, as its intensity drops to zero at about 255 K, in a way which is incompatible with a regularly decreasing Debye-Waller factor. We conclude therefore that the actual proportion of Fe^{1+} decreases to zero at 255 K, probably because Fe^{1+} is converted into Fe^{2+} in a time which becomes shorter than the characteristic time τ required for the Mössbauer observation. A delayed coincidence Mössbauer experiment should be useful to check this time dependence, as the apparent proportion of Fe^{1+} should be modified in the transition region, around 240 K, where the life time of the transient state Fe^{1+} is supposed to be comparable with τ. If positive, such an experiment would also support the model of electronic vacancy that we propose in section 3.4 to account for the various observed phenomena.

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FIGURE CAPTIONS

Fig. 1. Some Mössbauer spectra and fitted curves of $ZnS : {}^{57}Co$ (source n°2).

N.B. Increasing positive velocities correspond to increasing transition energies in the source.

Fig. 2. Thermal variation of the Fe^{1+} intensity (source n°2)

2a. relative area $P(Fe^{1+})$ versus T.

2b. unsuccesful attempts to fit $y(T) = \dfrac{P(Fe^{1+})}{1-P(Fe^{1+})} \times f(Fe^{2+})$

(full line curve) to various Debye-Waller factors $f(T)$ (dashed curves, with indication of the Debye temperatures).

Fig. 3. Source n°2. Isomer shifts versus temperature (ref. $K_4Fe(CN)_6,3H_2O$)

a. Fe^{2+} contribution

b. Fe^{1+} contribution.

Fig. 4. Splitting QS of the Fe^{1+} line versus temperature (source n°2).

Fig. 5. Decomposition of the spectrum at 1.35 K (source n°2)

a. Fe^{2+} central line ; b. Fe^{2+} internal doublet ;

c. Fe^{2+} external doublet ; d. Fe^{1+} doublet.

T(K)	Contribution	IS(mm.s^{-1}) ± 0.02	G(mm.s^{-1})	QS(mm.s^{-1}) ± 0.05	P(%)
295	Fe^{2+}	0.69	0.26		100
255	Fe^{2+}	0.72	0.34		100
230	$\{Fe^{2+}$	0.73	0.31		91.4
	Fe^{1+}	1.07	0.27		8.6 ± 2
100	$\{Fe^{2+}$	0.80	0.30		84.3
	Fe^{1+}	1.15	0.31		15.7 ± 2
20	$\{Fe^{2+}$	0.82	0.42		88
	Fe^{1+}(doublet)	1.20	1.10	1.8	12 ± 5
1.35	Fe^{2+}(central line)	0.85	0.58		50
	Fe^{2+}(int. doublet)	0.77	0.29	1.33	22
	Fe^{2+}(ext. doublet)	0.86	0.35	2.99	9
	Fe^{1+}(doublet)	1.18	0.90	1.72	19 ± 5

Source ZnS : ^{57}Co n°2. Fitted parameters of some spectra

T. : Temperature

IS : isomer shift (reference : $K_4Fe(CN)_6,3H_2O$)

G : line width   (natural : 0.20 mm.s^{-1} ; instrumental : 0.24 mm.s^{-1})

QS : Quadrupole splitting

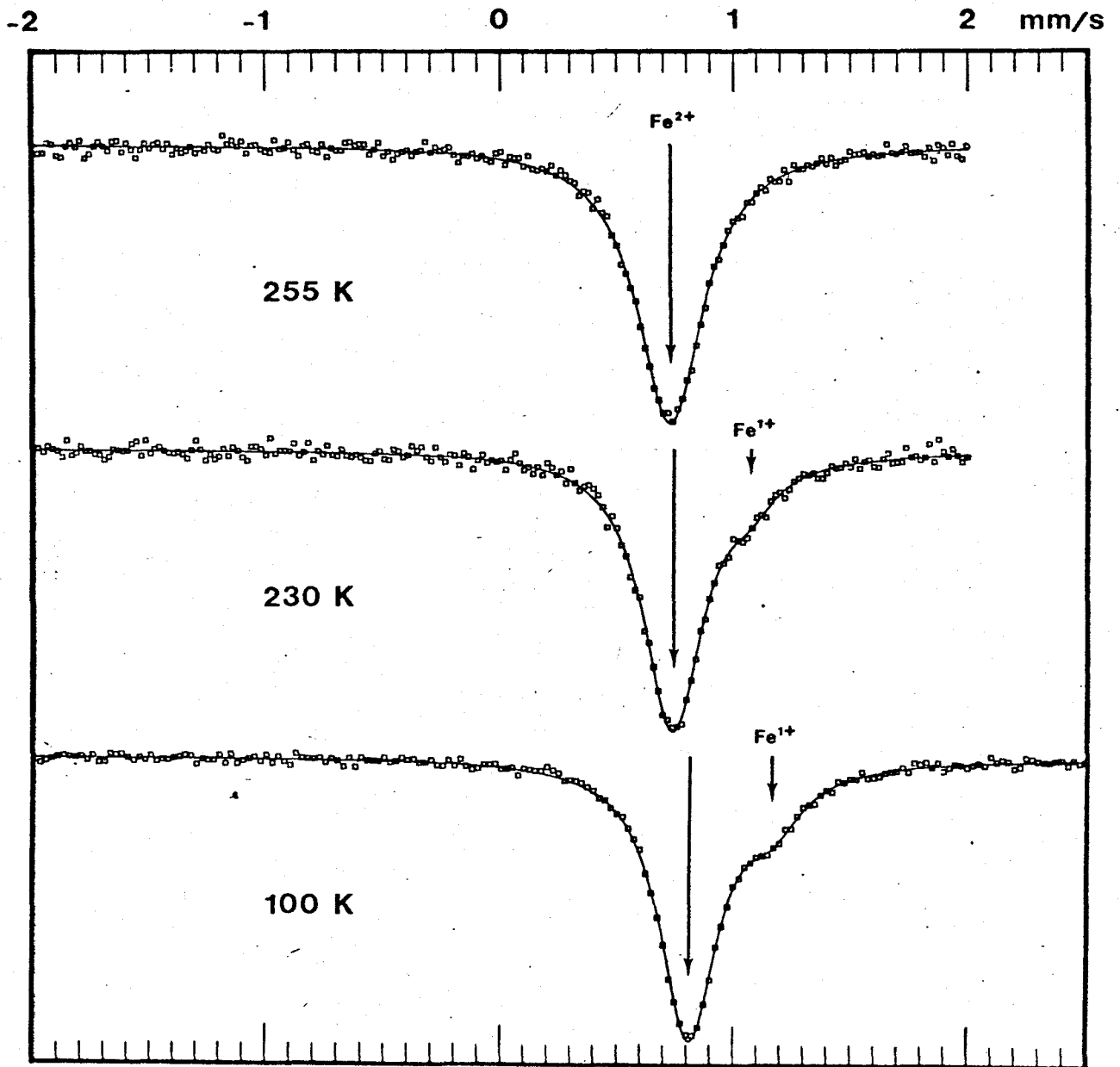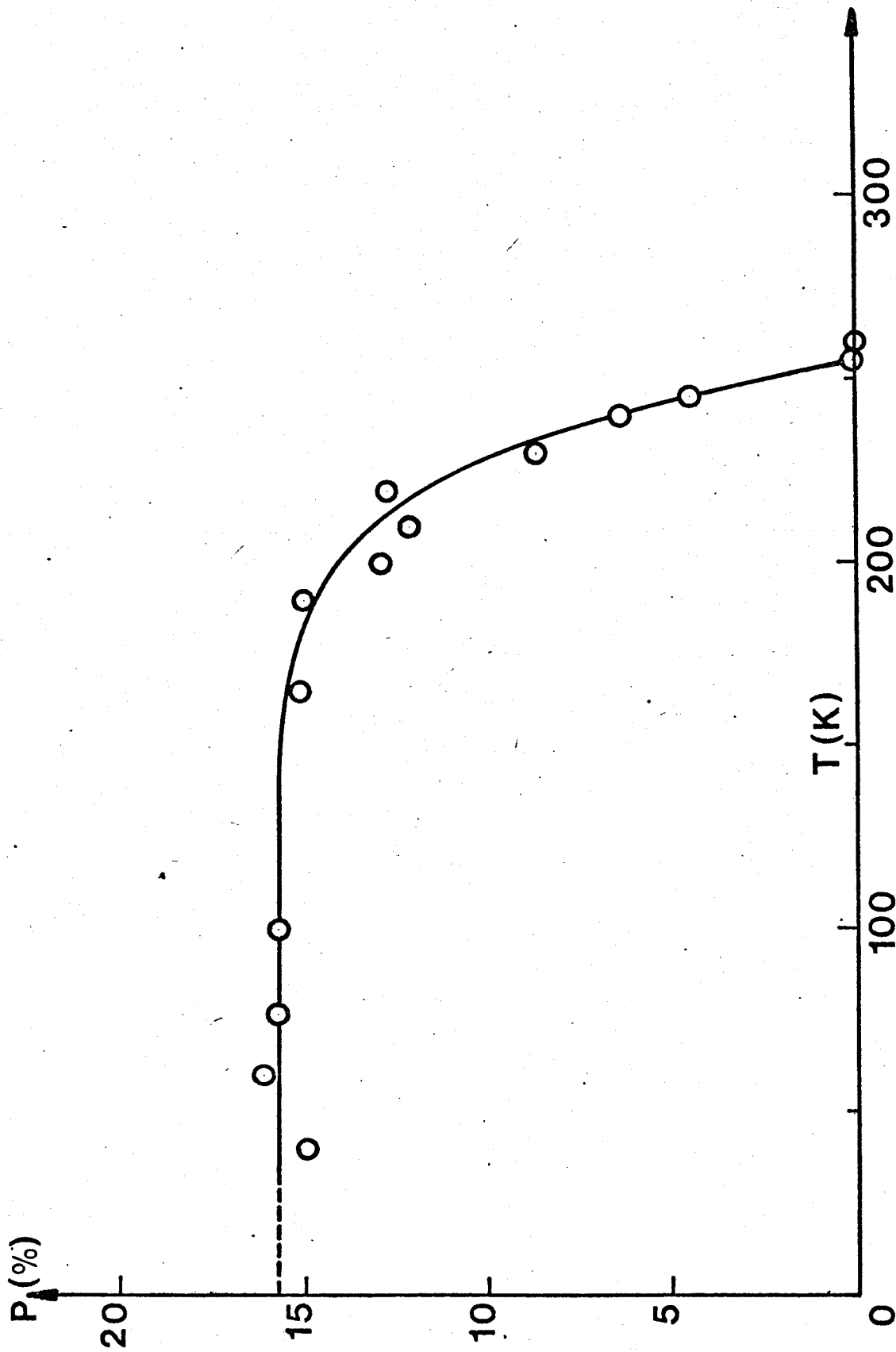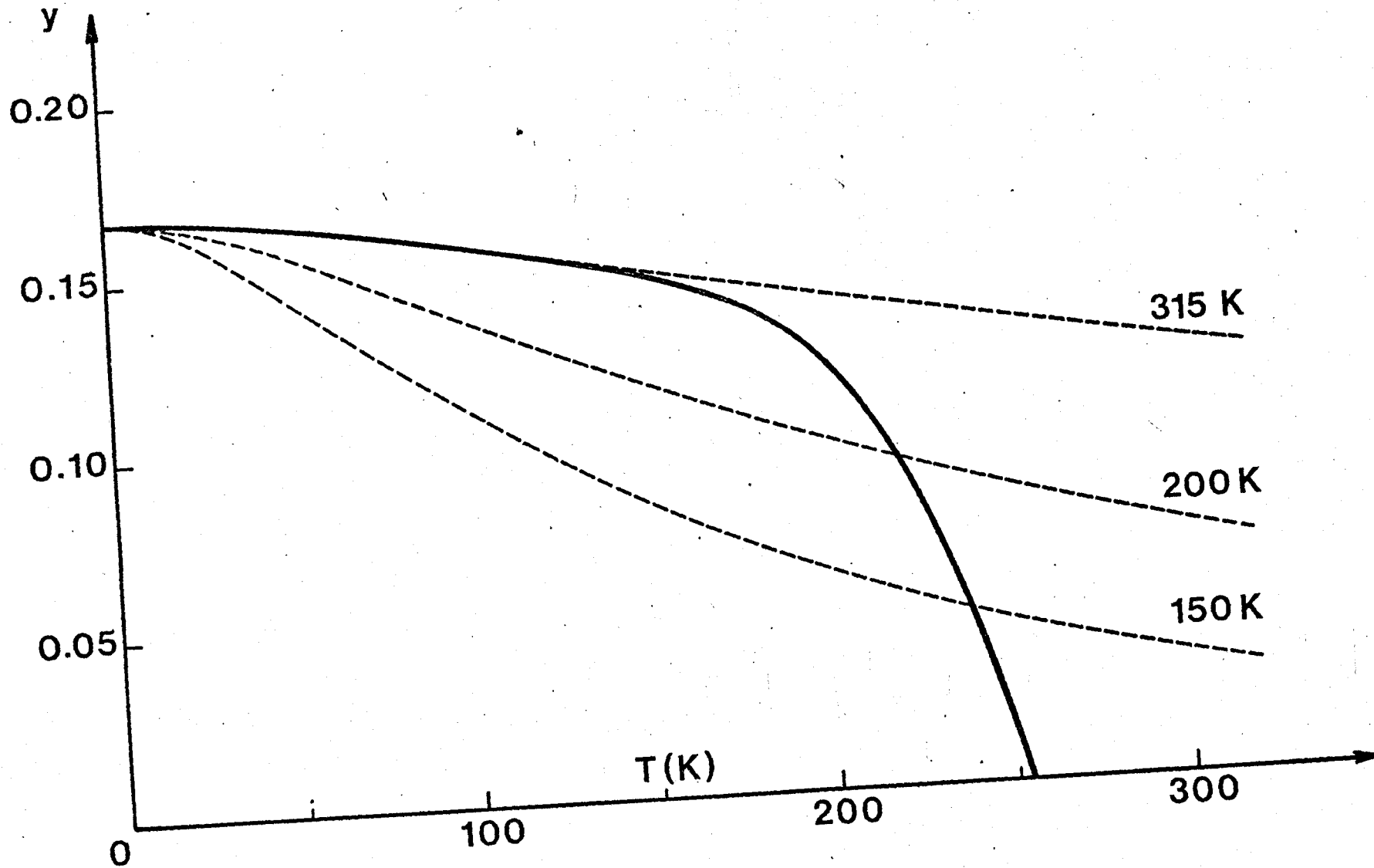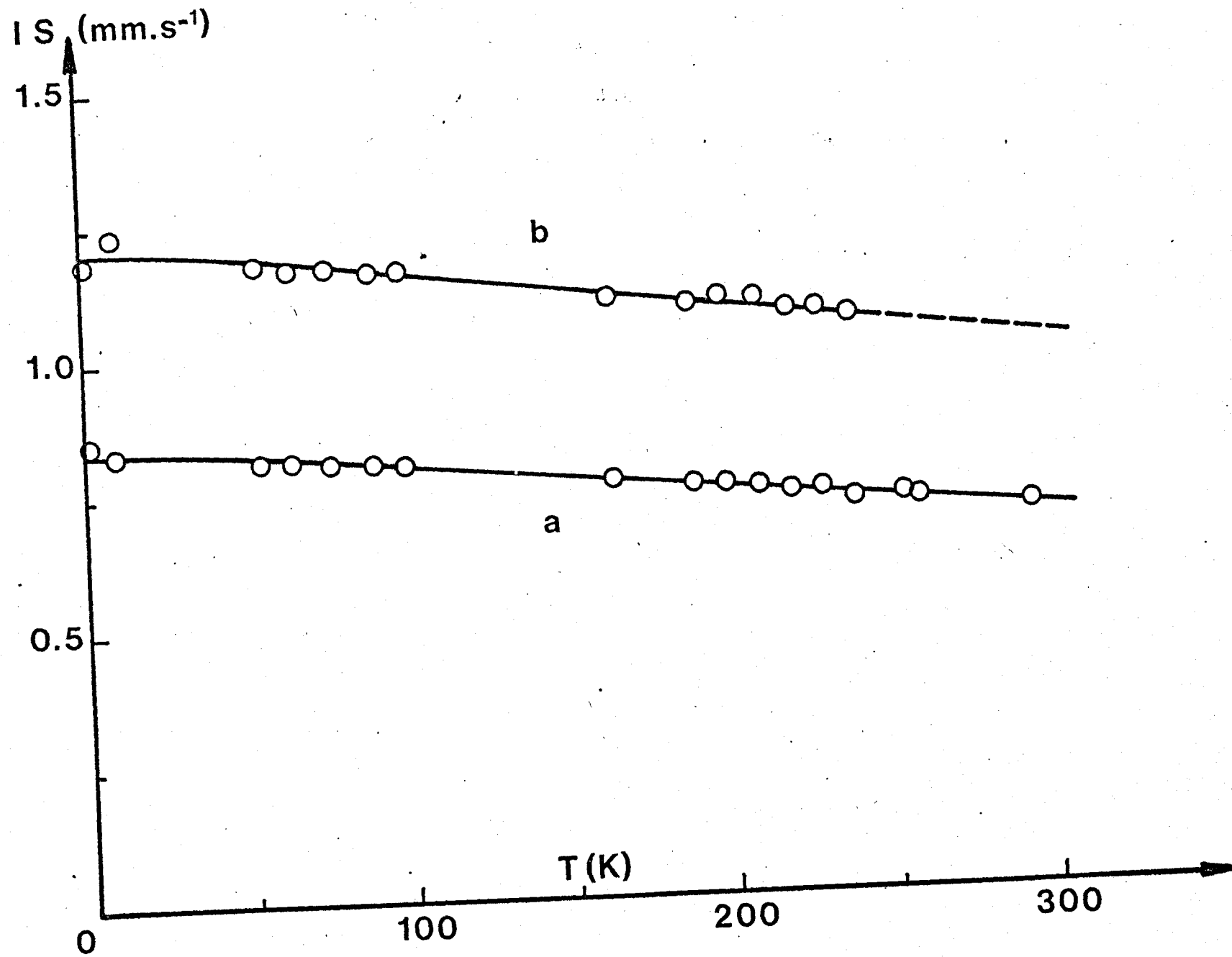P : relative area of each contribution.

fig. 1

fig.2a

fig. 2ₗ

fig.4

fig. 5