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CONVERSION ELECTRON MOSSBAUER SPECTROSCOPY STUDY
OF r.f. SPUTTERED $\text{Cd}_{0.95}\text{Fe}_{0.05}\text{Ie}$ THIN FILMS*

by

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Abstract

Conversion electron Mössbauer Spectroscopy (CEMS) studies have been performed on $\text{Cd}_{0.95}\text{Fe}_{0.05}\text{Te}$ thin films grown by r.f. sputtering on quartz and silicon substrates. The CEMS spectra show the presence of Fe^{2+} and Fe^{3+} in the films. It was studied the dependence of the population of both ions on substrate temperature, annealing temperature and substrate type.

Key-words: Conversion Electron Mössbauer Spectroscopy (CEMS); Thin films; CdTe.

Classification numbers: 7360F, 7680, 6855.

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I - INTRODUCTION

Cadmium Telluride is a direct gap semiconductor with a room temperature energy gap of 1.5 eV. It has a broad range of technological applications¹. However, the built of electronic devices using this semiconductor is limited due to the lack of deep understanding of the role of impurities in the doping process. The knowledge about atom vacancies in the lattice host and its interaction with the atom impurities, is also limited. Several experimental techniques have been used in the study of doping and defects structure of this semiconductor²⁻⁴, but it is still necessary to increase the number of these techniques in order to pursue the solution of the problem. Mössbauer Spectroscopy is an experimental technique that can help a lot in the above mentioned problem⁵. In the present work we report, for the first time, the application of conversion electron Mössbauer Spectroscopy (CEMS) in the study of iron diluted in CdTe films grown by radio frequency sputtering.

II - EXPERIMENTAL PROCEDURE

The films were grown in a diode r.f. sputtering system. A target of 1 cm-diameter, mounted on an air-cooled cathode, was made by vacuum pressing 99.999% pure CdTe powder from Cerac Inc. (TM*) together with an 7 x 2mm² Fe enriched foil. The films were grown on quartz or silicon single crystal substrates. Several samples were prepared in each run, one of them was in a central position and the others in the periphery of the anode. The target

to substrate distance was 3cm. Prior to film growth the chamber was evacuated at a pressure of 3×10^{-6} Torr; 99.999% pure Argon was used in the sputtering process. Just before deposition, the target was usually presputtered for 15 minutes under growth conditions. The samples were grown under the following conditions: background pressure = 3×10^{-6} Torr; Ar pressure = 3×10^{-3} Torr; r.f. power = 100 Watts; deposition time = 120 minutes; and substrate temperatures = 55C and 200C. A deposition rate of 6.4 Å/sec was estimated by measuring the film thickness with a Dektak Sloan profile analyser. Film compositional analysis was made using a SAM-ESCA system. The SAM measurements show that the distribution of Fe in the film is homogeneous. The concentration of Fe in the films was 5 at.% and is independent of the deposition time. From Transmission Electron Microscopy (TEM) measurements the films grown at 55C show an amorphous like pattern while those for $T_s = 200C$ are well crystallized.

Mössbauer spectra were taken in the constant acceleration mode using a $^{57}\text{Co/Rh}$ source. All measurements were made with source and absorber at room temperature. Calibration was made from $\alpha\text{-Fe}$ spectrum and in the present work all the isomer shifts are given relative to metallic iron. The quartz or silicon substrates containing the films were mounted in a conversion electron counter⁶ operating with a continuous flow of He-6.4% CH_4 . Our homemade counter has three central anode wires and was made in order to have a small gas chamber⁷.

III - EXPERIMENTAL RESULTS AND DISCUSSION

In Fig. 1, it is shown the Mössbauer spectra of three films of CdTe grown at 550 on quartz substrates. Letter C indicates the sample that was grown at the central position of the anode; R and L indicate the samples that were on the right and left position respectively to the central one, during growth.

From the Mössbauer spectra of films grown on the quartz substrates at 550 we can identify Fe^{3+} with nearly broad lines, whose proportion decreases from the center to the periphery, and large quadrupole splittings (QS). A second doublet is obtained from the fitting which can be ascribed to Fe^{2+} with very broad lines. The Mössbauer parameters (Table I) are nearly the same for sample C and R, but a significant difference in the quadrupole splitting is observed for sample L. We do not have any explanation for such difference. In opposition to the Fe^{3+} , the Fe^{2+} proportion increases from the center to the periphery, as well as we observe much higher amount of Fe^{2+} (72% - 82%).

In Fig. 2, we show the Mössbauer spectra of films grown on quartz substrates at 2000. As before we observe Fe^{2+} and Fe^{3+} , however with much larger proportion of Fe^{3+} , which can be well understood as due to the higher temperature of the substrates. The observed Fe^{2+} has almost the same Mössbauer parameters compared to the former ones; also we found a larger QS for sample L, however smaller than the one observed for the sample grown at 550. In addition, we found two non equivalent Fe^{3+} sites. One of them has parameters similar to the one observed for the films on substrates at 550 and the other shows thinner linewidth and

smaller quadrupole splitting, with approximately the same hyperfine parameters (see Table I) for all three samples. In addition, this second Fe^{3+} site is present in lower proportion compared to the first one, whose amount in each sample increases from the left to the right position. We should also mention that the broadening of the spectra observed for Fe^{2+} as well as for Fe^{3+} in both substrates temperatures, may be an indication of inhomogeneous environments. Also we should expect that the Fe^{2+} occupy the Cd^{2+} site while the Fe^{3+} could either be isolated occupying a Cd^{2+} site near to a Cd^{2+} vacancy, which is possible due to charge compensation effect, or occupy a Cd^{2+} site near to a Fe^{2+} placed in a Cd^{2+} site, which can led to a $\text{Fe}^{2+}/\text{Fe}^{3+}$ donor site. Also a much higher amount of Fe^{3+} together with a higher proportion of vacancies should be expected in the films grown on quartz substrates at 200C. The presence of the second Fe^{3+} doublet in the spectra is probably associated to a more complex atomic arrangement around the Fe^{3+} site. The difference in proportion of $\text{Fe}^{2+}/\text{Fe}^{3+}$ as we go from the central position to the periphery of the anode, may be associated to variation in the growth rate due to thermal and geometrical effects.

In Fig. 3, it is shown the Mössbauer spectra for films samples L, C and R grown on single crystal silicon substrates at 55C. As in the films grown on quartz we found Fe^{2+} and Fe^{3+} with similar hyperfine parameters (Table II) compared to the same in quartz, but we observed an additional single line of small intensity (9% to 15%) with an isomer shift close to -0.1 mm/sec. Here in opposition to the result observed for quartz substrates, the Fe^{3+} proportion shows a much higher amount and a less remarkable

dependence on the position of the sample relative to the anode.

The Mössbauer spectra of the films grown on silicon substrates at 200C are shown in Fig. 4, in which we have the spectrum of the sample at the central position and respectively two samples on the left and right positions. There is small differences in the hyperfine parameters (see Table II) between the left and right samples, with a small amount of Fe^{2+} in the former one, but almost only Fe^{3+} is observed in all cases. The single line observed for the substrate at 55C is not present in any of the samples which means that this phase may not form at 200C. Also, in a similar way to quartz substrates, a second doublet ascribed to Fe^{3+} was observed for sample R_1 , indicating Fe^{3+} in a different environment. Although this second Fe^{3+} doublet occurs only in one sample of the series prepared on the silicon substrates at 200C, this is very similar to the result obtained for quartz substrates at the same temperature. We are inclined to interpret the presence of that doublet by following the same ideas outlined for the quartz substrates, that is, it is due to a more complex Fe^{3+} site. All those differences observed above, either in the spectra or on the hyperfine parameters shown in Table II, may be attributed to a variation in the growth conditions, as for example small differences in the temperature between the center position and the periphery of the anode.

In order to investigate the effect of the temperature on the oxidation process of Fe^{2+} to Fe^{3+} , we have annealed, at 200C and 300C for one hour in H_2 atmosphere, three different samples grown on silicon substrate. As it is shown on Table II their

hyperfine parameters are almost the same for all three samples, independent of the preparation procedure, as compared to the result before annealing. This may be correlated with a better crystallinity observed by TEM measurements, as it is shown in Fig. 5, of the films grown on silicon substrates at 200C as compared with those grown at 55C, which means that the iron atoms are in a more homogeneous environment. For sample C prepared at 55C we observe a reduction in the intensity of the single line after annealing and, as before, a similar decreasing occurs in the linewidth. For sample L grown with the substrate at 55C and annealed at 300C in H₂ atmosphere we found the same result as in the sample C, except for a small decrease in the Fe²⁺ proportion, in opposition to the one observed on sample C. These are very important results because they show that the iron atoms are in stable environments in the crystal lattice of CdTe.

Concerning the presence of the single line, although we can not give a direct proof, it seems that it is due to γ -Fe stabilized in the crystal lattice of CdTe. Its isomer shift shows the same value observed for γ -Fe precipitates in cooper^{8,9}. Because it is a metastable phase we should expect a reduction on its proportion due to the annealing as it has been observed (see Table II). Probably longer annealing may cause its complete destruction.

CONCLUSIONS

From our study we can outline the following conclusions: Both Fe^{2+} and Fe^{3+} were detected in the films. When the films are grown at 200C the iron atoms are preferentially in the Fe^{3+} form, independently of the nature of the substrate. When they are grown at 55C the Fe^{3+} population is around 50% in the films grown on silicon substrates and around 20% in the films grown on quartz substrates. Also for both substrates the Fe^{2+} and Fe^{3+} have very broad lines in both substrate temperatures, indicating inhomogeneous iron environments. The $\text{Fe}^{3+} / \text{Fe}^{2+}$ ratio decreases from the center to the periphery of the anode during the sputtering process. Both Fe^{2+} and Fe^{3+} are probably in substitutional sites in the lattice host. We can propose, based on charge compensation effect, that the Fe^{3+} forms a pair $\text{Fe}^{3+}\text{-Cd}^{2+}$ vacancy or even in some films grown at 200C it is possible the formation of a more complex Fe^{3+} site. The annealed films show similar hyperfine parameters independent of the preparation procedure which imply that the iron atoms are in stable environment in the crystal lattice of CdTe. Finally we have observed a single line in the spectra of films grown on silicon substrates at 55C, which seems to arise from $\gamma\text{-Fe}$ precipitates. Iron-oxygen compounds were not detected in any of the films.

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Table captions

Table I - Mössbauer parameters for all films, samples sputtered on quartz substrates at temperatures of 55C and 200C. The letters indicate the position of the sample in the anode: L - left sample, R - right sample and C - central sample. IS (mm/sec) - isomer shift relative to metallic iron; QS (mm/sec) - quadrupole splitting; Γ (mm/sec) - linewidth at half maximum and A% - relative spectral area. Average errors in mm/sec: IS (0.03), QS (0.02) and Γ (0.03).

Table II - Mössbauer parameters for all films samples sputtered on silicon substrates at temperatures of 55C and 200C and for the samples annealed in H₂ atmosphere. As before, L, R and C indicate left, right and center position relative to the anode; L was annealed at 300C, C at 200C and C* was grown at 200C and annealed at 200C, all for one hour. IS, QS and Γ are given in mm/sec. Average errors in mm/sec: IS (0.02), QS (0.03) and Γ (0.03).

Table I

Quartz substrate at 55C								
sample	Fe ²⁺				Fe ³⁺			
	IS	QS	Γ	A%	IS	QS	Γ	A%
L	1.13	2.78	0.96	81.0	0.40	1.08	0.73	18.2
C	0.87	2.08	0.68	72.0	0.31	0.75	0.60	28.0
R	0.90	2.07	0.88	81.9	0.30	0.76	0.58	18.1
Quartz substrate at 200C								
L	0.74	2.38	0.57	20.0	0.41	0.58	0.28	10.2
					0.33	1.13	0.60	69.8
C	0.87	2.05	0.77	33.4	0.43	0.54	0.28	14.9
					0.30	1.15	0.59	51.2
R	0.81	2.17	0.96	26.4	0.39	0.61	0.35	19.6
					0.29	1.22	0.51	54.0

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Table II

Silicon substrate at 55C									
sample	Fe^{2+}					Fe^{3+} + singlet			
	IS	QS	Γ	A%		IS	QS	Γ	A%
L_1	0.92	1.96	0.84	55.8		0.30	0.71	0.61	35.0
						-0.10	-	0.58	9.2
C	0.90	2.00	0.85	48.1		0.33	0.65	0.65	37.9
						-0.09	-	0.66	14.0
R_1	0.91	1.94	0.90	49.4		0.34	0.65	0.67	35.7
						-0.08	-	0.64	14.9
Silicon substrate at 200C									
L_2	0.76	1.76	1.20	31.6		0.20	0.61	0.47	68.4
L_1	1.05	1.92	0.72	20.6		0.23	0.61	0.45	79.4
C						0.24	0.56	0.44	100.0
R_1						0.23	0.49	0.37	78.8
						0.23	0.85	0.34	21.2
R_2						0.23	0.59	0.49	100.0
Annealed in H_2 atmosphere									
L_1	1.00	1.82	0.86	53.2		0.25	0.63	0.54	42.6
						-0.06	-	0.36	4.2
C	0.91	1.95	0.77	52.9		0.26	0.61	0.52	42.1
						-0.09	-	0.46	5.0
C*						0.26	0.56	0.44	100.0

Figure captions:

Fig. 1 - Conversion electron Mössbauer spectra of films grown at 550 on quartz substrates; L, C and R refer to the position of the samples. See text.

Fig. 2 - Conversion electron Mössbauer spectra of films grown at 2000 on quartz substrates; L, C and R refer to the position of the samples. See text.

Fig. 3 - Conversion electron Mössbauer spectra of films grown at 550 on silicon substrates; L, C and R refer to the position of the samples. See text.

Fig. 4 - Conversion electron Mössbauer spectra of films grown at 2000 on silicon substrates; L_2 , L_1 , C, R_1 and R_2 refer to the position of the samples. See text.

Fig. 5 - Transmission Electron Microscopy results of films grown on silicon substrate: a) film grown at 550 showing an amorphous like structure; b) film grown at 2000 showing a well crystallized structure.

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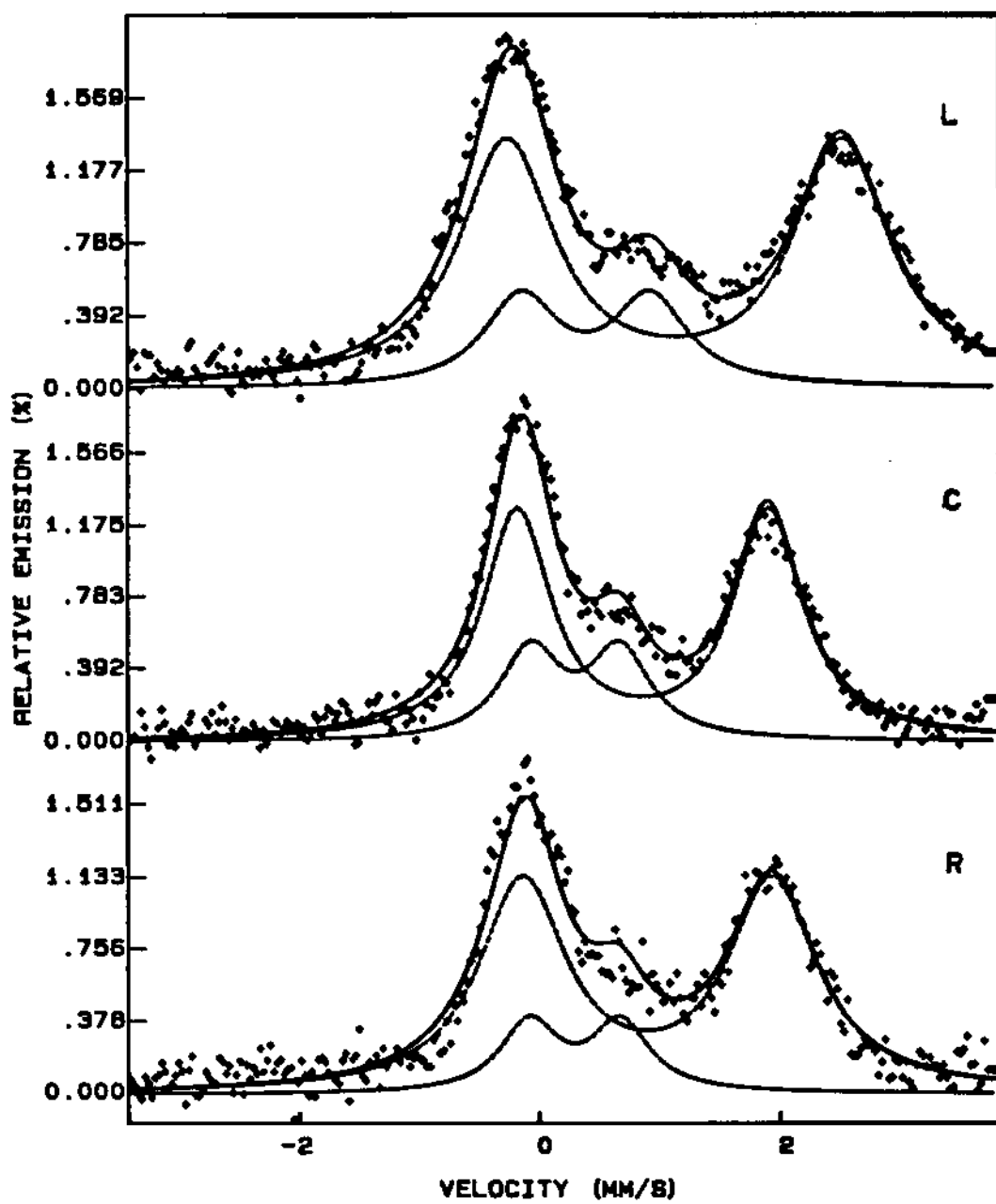


FIG. 1

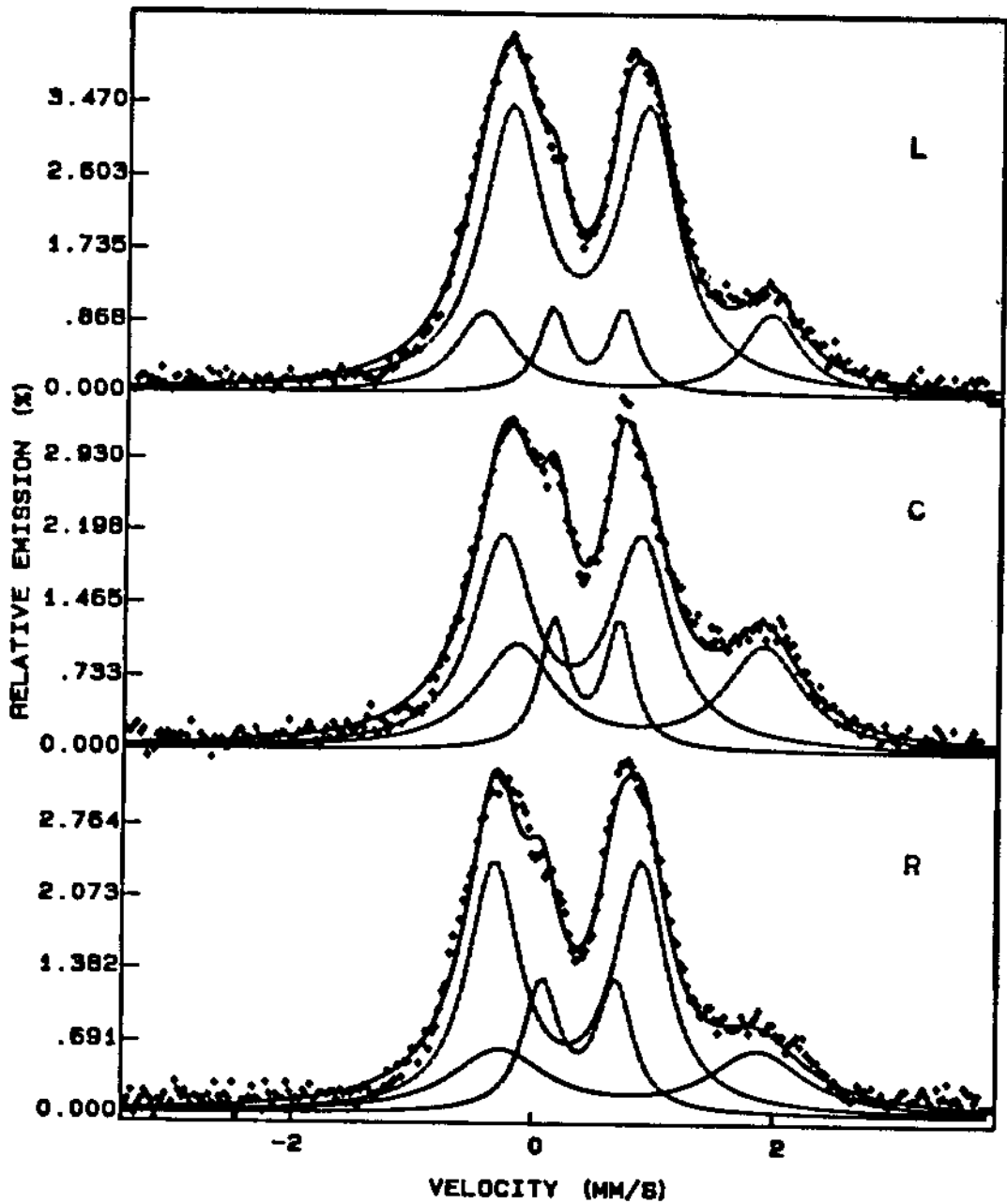


FIG. 2

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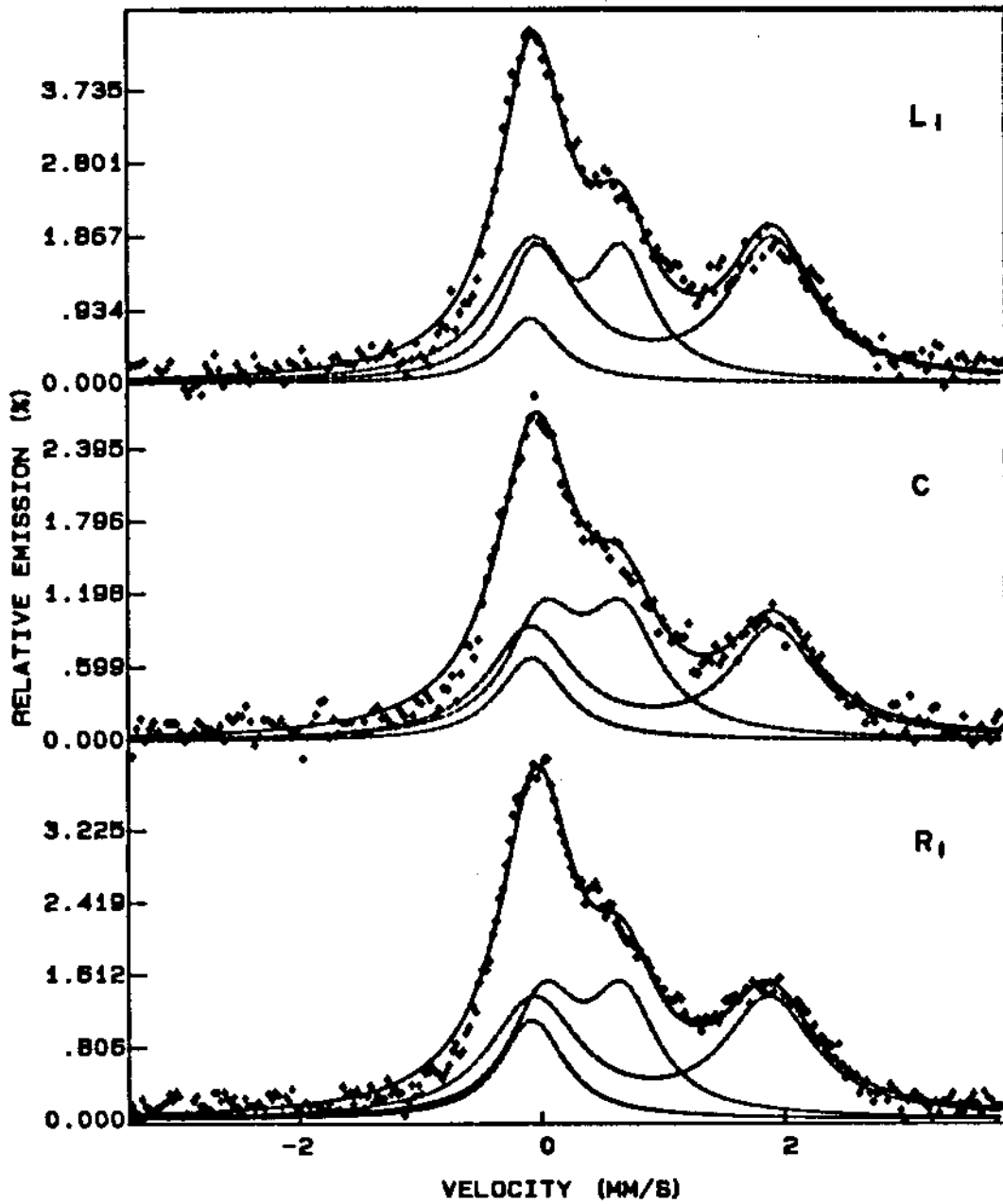


FIG. 3

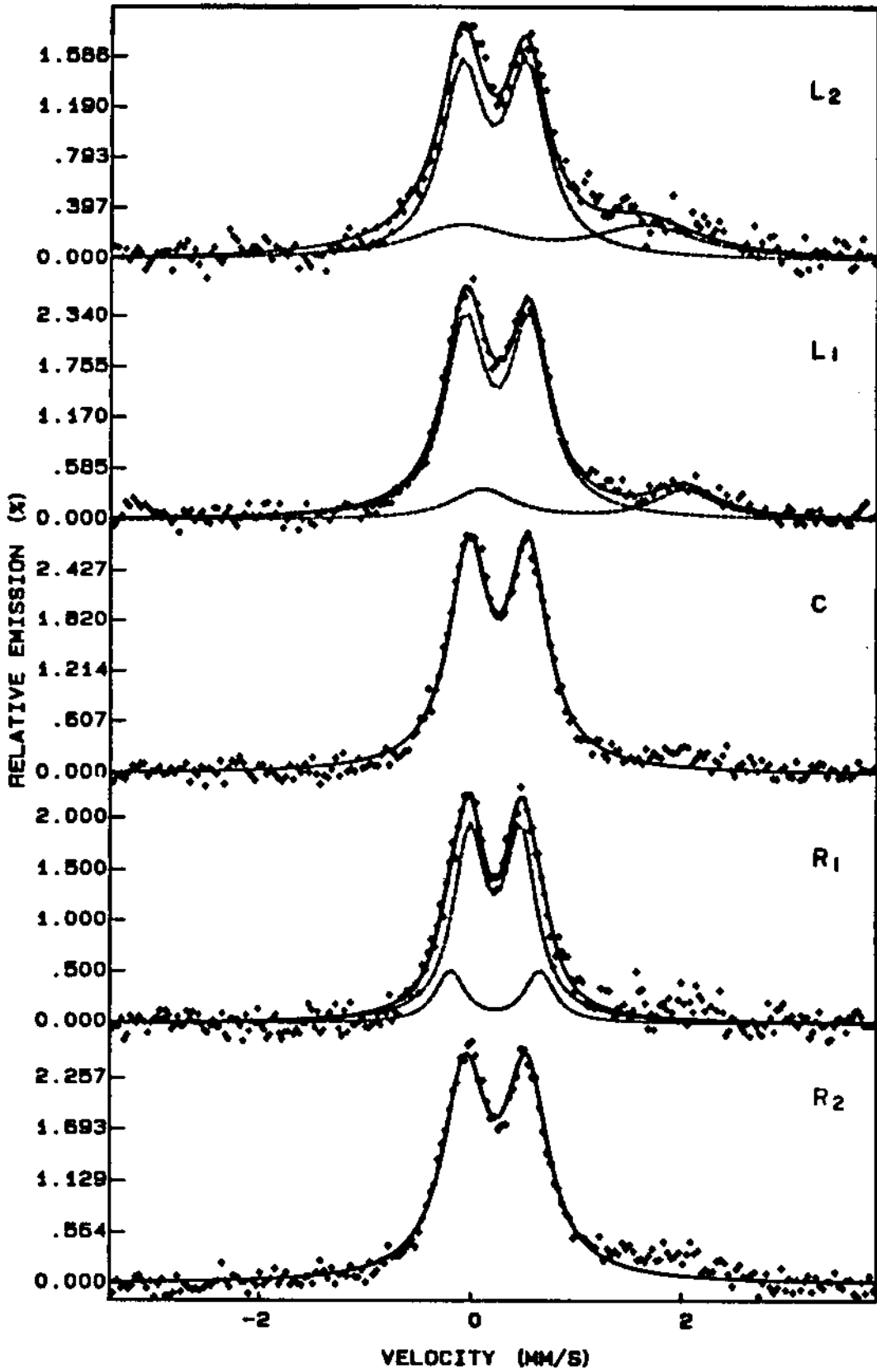


FIG. 4

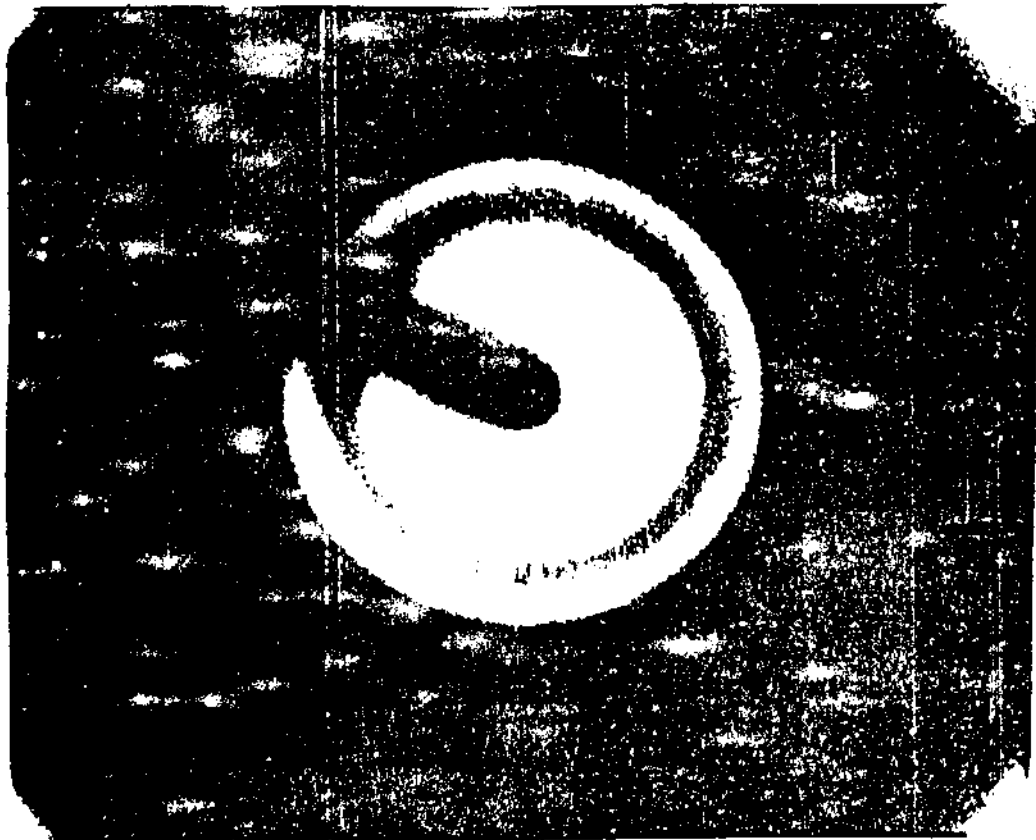


FIG. 5(a)



FIG. 5(b)

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