Fe OXIDATION AND WEATHERING STUDIES

OF ANTARCTIC AND SNC METEORITES

by

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ABSTRACT

In recent years, there has been much debate over the origin of SNC meteorites, and many attempts have been made to prove or disprove the existence of preterrestrial weathering products. In order to address this problem, a Mossbauer study of the Nakhla meteorite and shergottites EETA79001 and ALHA77005 (from the Antarctic meteorite collection) was carried out to look for possible preterrestrial ferric phases occuring in these meteorites.

In order to understand these results, one must understand the processes that take place in the unique weathering environment of Antarctica. To this end, the first large scale study of Fe weathering products in Antarctica is presented here, encompassing H, L, and LL chondrites, eucrites, and diogenites, as well as the nakhlite and shergottites previously mentioned. Samples were obtained in all weathering categories, and control samples were obtained from falls of each type. All samples were studied by room temperature Mossbauer spectroscopy; the most weathered samples were studied by XRD and Mossbauer spectroscopy at 77K as well.

Results of this study show that weathering in Antarctica is much more extensive than previously believed. As much as 30% ferric Fe is found in some samples, and those samples classified as "unweathered" by thin section examination typically contain 2-5% ferric Fe. This weathering occurs all through the meteorite, as samples for Mossbauer analysis were taken as far away from the surface as possible. The Antarctic weathering classification scheme is shown to be inaccurate and should be used only as a rough guide to

weathering, because variations exist within the categories due to differences in mineralogy and Antarctic place of origin. It is shown, based on low temperature Mossbauer studies, that the ferric phase consists largely of microcrystalline FeOOH (<200A). It was also found that the control samples, classified as falls, had undergone Fe oxidation during museum storage, pointing out the need for better environmental controls and handling procedures than have previously been used.

None of the SNC meteorites was found to have >2% ferric Fe in any of their lithologies. This is particularly important with respect to the glass lithology C of 79001, as previously published microprobe studies assumed this glass to be ferric-rich, and will need to be revised. It is concluded that the SNC meteorites studied here are not surface rocks, but may have originated from deeper in the crust of Mars. It is clear, however, that the natural weathering processes these SNC meteorites have been subjected to in Antarctica are large enough to obscure any preterrestrial oxidation that may have taken place.

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Chapter 1. <u>Introduction</u>

Antarctic meteorite collecting has had an unusually exciting history--so much has happened in so little time. The first Antarctic meteorites were found in the early days of exploration, 1912-1964, but their significance was not realized until Japanese teams of researchers discovered over a thousand more specimens in only a few years--half as many as have been found in the whole history of the rest of the earth! Because of these discoveries, yearly expeditions to Antarctica began in 1976 for the sole purpose of collecting meteorites. Since then, U.S., Japanese, and German teams have found over 7000 fragments, probably comprising 1200 to 3500 separate events[1]. It is interesting to note that these meteorites have been found to have differences in trace element abundance from non-Antarctic meteorites, possibly indicating that the polar regions receive samples from different cosmic sources[2]. The reason meteorites collect in such numbers in Antarctica is still something of a mystery. It is thought that the meteorites are subducted deep within the ice sheets and carried along, only to be brought up to the surface when the ice runs into a barrier, such as a mountain range (see Figure 1). This explains why vast numbers of meteorites are found in certain areas of Antarctica. In addition, they are very easy to see against the blue ice.

These specimens have made possible a whole new wave of meteorite studies. Among the meteorites found are many which are unique or constitute groups previously unknown; for instance, the first lunar meteorites were found in 1979 and 1981 and represent a section of the moon not previously sampled. The most interesting,

Figure 1: Process of Antarctic meteorite accumulation

Meteorites fall onto the Antarctic ice sheet and are subducted along with it much as rocks are carried along by glaciers. When the ice sheet runs up against a barrier, such as a mountain range, the meteorites are forced to the surface, where they are easily seen against the blue ice.

Diagram from the Lunar and Planetary Institute, Houston

Snow accumulation

Equilibrium line

Ice ablation

Ice sheet

Transantarctic Mountains
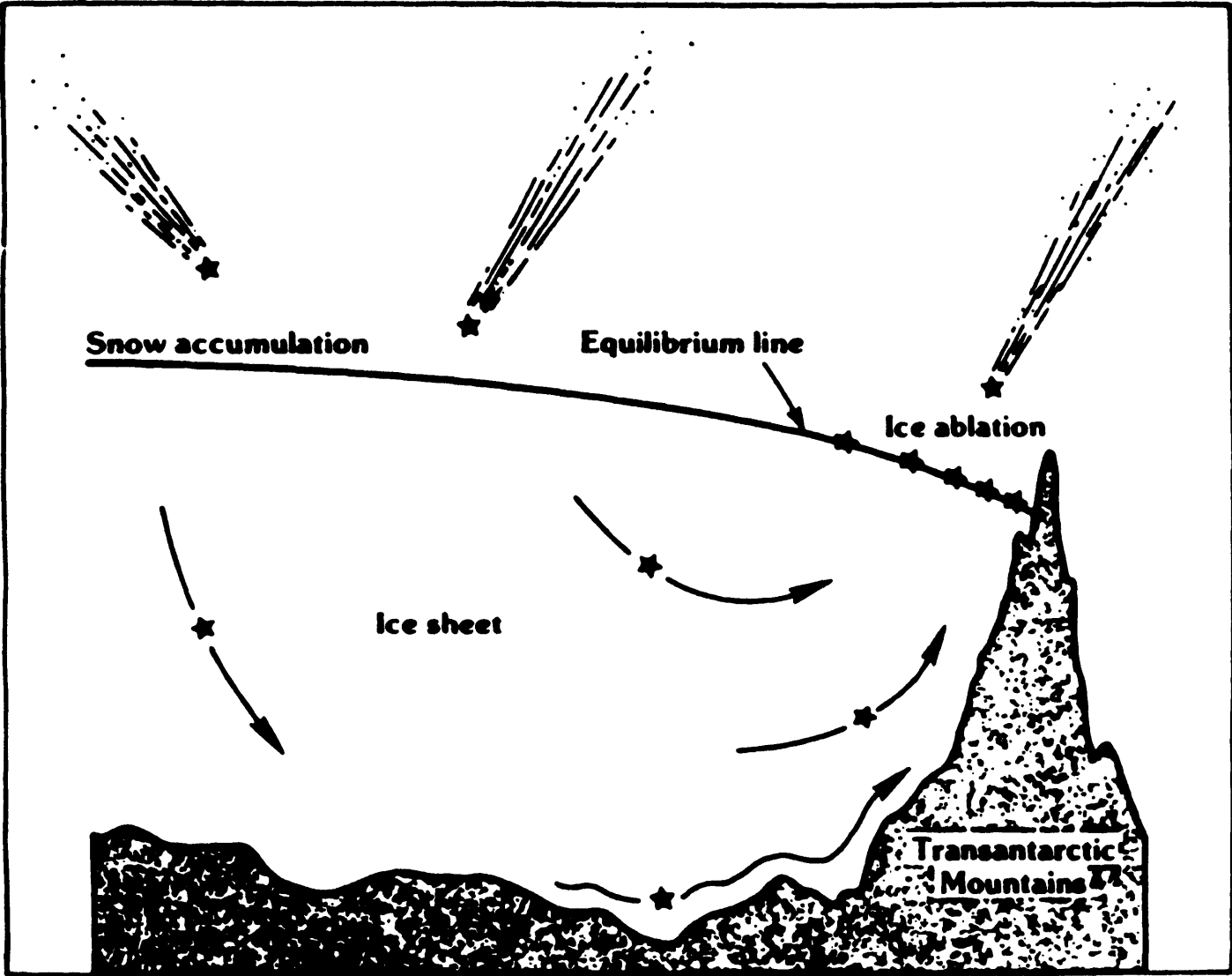
however, are the shergottites EETA79001 and ALHA77005, recent additions to the class of meteorites known as SNC's, and thought to have their origin on Mars. EETA79001 is particularly unusual, as it is the only meteorite known which includes a contact between two distinct igneous lithologies.

SNC's (Shergottite-Nakhlite-Chassignite) have been known for a long time to be unusual. They have a formation age of 1.3by, in contrast to all other meteorites, which formed between 4.4 and 4.6by ago[3]. This indicates that they are not of primordial nature. In addition, they are related by having an unusually high volatile content, a fact which fits well with possible Martian origin. They also contain higher-Ca pyroxenes, higher-alkali feldspar, and a higher oxidation state than other achondrites[4]. These meteorites contain igneous textures and rare earth element fractionation patterns which require a large parent body, roughly the size of Mars. The oxidation state of these meteorites has been shown to vary between the WM and QFM buffers, indicating an origin similar to the upper mantle-lower crust of earth[5,6]. The chemical composition of the SNC's is very similar to that deduced for the mantle of Mars, and Mars is believed to have experienced vulcanism at about the right time.

This evidence, though convincing, was not considered conclusive. However, one of the Antarctic specimens, EETA79001, contains a glass-rich fraction labeled lithology C in which trapped gases reside--gases which appear very similar to Martian atmosphere in their elemental and isotopic composition. Studies on noble gases, nitrogen and CO_2 abundances all come close to Martian values[7,8,9,10]. In addition, a major difficulty was removed when it

was demonstrated that an abundance of volatiles greatly decreases the strength of an impact needed to eject material from a planet such as Mars[11].

All of this evidence has greatly increased the credibility of Martian origin for the SNC meteorites, and has prompted several researchers to search for preterrestrial compounds in these meteorites which may give clues to the types of weathering processes occurring on Mars. Ostertag *et al*[12] noted that the brown color of olivine in ALHA77005 was due to ~5% Fe^{+3} in the olivine. However, the origin of this ferric Fe is not clear. They argued that because the color is spread evenly throughout the sample, it is of preterrestrial origin[12]. In addition, the original petrologic description of this sample states that there is "no sign of weathering"(see p. 23). However, other researchers found evidence for alteration of olivine and chromite grains throughout the sample and concluded that this was a result of Antarctic weathering[13].

Later, James Gooding began his search for preterrestrial minerals in EETA79001, particularly in lith C[7,14]. Using SEM/EDS and pyrolysis techniques, he found oxidized sulfur and chlorine-rich aluminosilicates in lith C which he believes to be of Martian origin. He cited lack of gypsum and other Antarctic weathering products shown to occur on the surface of this sample as evidence for the unweathered state of lith C[7]. However, in a later abstract, he reported the occurence of gypsum in lith C[14]. Although textural and petrologic arguments argue strongly for the origin of these minerals being Martian, Gooding's results illustrate some of the confusion on this subject.

During the last five years, weathering studies have begun on Antarctic meteorites, although none included more than six samples or measurements on the interiors of the samples--the part most likely to be used in a research project. One study used six Antarctic H6 and L6 chondrites which were classified as having moderate to extreme weathering and compared them to the Holbrook L6 meteorite which weathered in an Arizona desert[15]. Samples studied were taken from the outer 20mm of the specimens. Minerals identified were mainly hydrated Mg carbonates and sulfates, ferric sulfates, and occasional goethite. However, because XRD was used, presence of other possible Fe oxides such as hematite or magnetite could not be determined due to overlap of their peaks by olivine, hypersthene, and troilite. No relationship was found between terrestrial age and degree of weathering, suggesting that the meteorites do not weather uniformly upon reaching the surface of the earth. A later study added a group of "clay-mineraloids" resembling smectite, gypsum, and possibly zeolites to the list of observed weathering products[16]. Many of these products argue for liquid water somehow entering into the weathering process, in spite of the extremely cold, dry environment of Antarctica.

In these studies, the question of Fe oxidation and weathering was not treated extensively, partly due to the difficulty of distinguishing diagnostic XRD lines from those of the major constituents of the rocks. In addition, microprobe data are not very useful in identifying these products or their oxidation states. There is a lack of quantitative data which could be used as a guide to other researchers, or a way of updating the ABC system currently being

used by meteoriticists to identify degree of weathering. It should be determined how much weathering is present in the interior of the sample--the "best case" that researchers have to work with. Finally, a more extensive study needs to be done in order to give a more representative picture of Antarctic meteorites.

Mossbauer spectroscopy is an ideal tool for addressing these problems. Because it can distinguish easily between Fe^0, Fe^{+2}, and Fe^{+3}, it can provide a quantitative measure of the amount of oxidation in any given sample. In addition, Fe-oxides and sulfates are more readily identifiable in small amounts than with any other method utilizing bulk samples. Furthermore, it is a non-destructive and cost-efficient method of analysis.

The first paper on Mossbauer spectroscopy relating to meteorites appeared in 1964[17]. It pointed out that it is very difficult to obtain an analysis of iron partitioning between coexisting minerals using chemical methods--necessary assumptions and guesswork make the process inaccurate. On the other hand, the principal meteoritic iron phases (kamacite, taenite, troilite, olivine, and pyroxene) are easily identifiable using Mossbauer spectroscopy. Because the areas under the constituent peaks are directly related to the mole percentages of Fe-bearing minerals, this technique gives mineral proportions directly and thus provides a useful tool for meteorite classification[18].

The first mention of Mossbauer spectroscopy applied to terrestrial weathering products was in 1968[18], when a German team noted the weathering of metallic Fe and troilite to sheet silicates, such as iddingsite or nontronite, and subsequently to goethite and

magnetite. This weathering sequence was determined by looking for differences in mineralogy between groups of "finds" and groups of "falls". Later studies were used to further pin down the composition of the pyroxenes, identify minor Fe-compounds in NiFe meteorites, and identify other possible weathering products, such as maghemite, pyrrhotite, and other FeOOH polymorphs[19,20]. Unfortunately, there have been no Mossbauer studies done on weathering products of Antarctic meteorites until now.

This thesis encompasses a research project undertaken to address the problems of Antarctic meteorite weathering, with a view toward obtaining quantitative guidelines for amount and type of Fe oxidation products present, and applying these guidelines to the more specific problem of weathering in SNC meteorites-- preterrestrial or Antarctic. Antarctic meteorite samples were obtained from both the most and least weathered categories available in all of the following classes: H5&6, L3, L6, LL6, eucrites, diogenites, and shergottites. In addition, non-Antarctic samples were obtained as falls in each of the above categories to act as control samples in addition to the "unweathered" Antarctic samples. Magnetic and non-magnetic spectra were taken and fitted for each sample, and ferric/ferrous ratios were obtained. Liquid nitrogen Mossbauer and XRD analyses were made in an attempt to further clarify the mineralogy of the ferric phases.

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Chapter 2. Sample Preparation and Origin

Antarctic samples were obtained from the Antarctic meteorite collection at the Lunar and Planetary Institute. These samples were originally collected with teflon gloves and transported in separate bags, still frozen, to the Johnson Space Center, where they were documented and curated. The samples were handled with the same techniques as the moon rocks, and there is very little possibility of contamination. However, some of the earliest samples collected (in 1977), including the shergottite ALHA77005, were left in the sun and the ice melted. Because of this, these meteorites came into contact with water, but were otherwise uncontaminated[1].

Homogeneous powders were prepared by Eugene Jarosewich (Smithsonian Institution) in all but two cases, EETA79002 and ALHA77257, which were obtained as chips and pulverized by the author. The powders had been separated into metal and metal-depleted fractions using a 100-mesh. Only the latter fractions were acquired and used in this study. Powders were prepared using only meteorite interiors, where possible.

The origins of the Antarctic meteorites are as follows (see map in Figure 2). All of these localities are encompassed by Victoria Land:

ALHA: Allan Hills

EET, EETA: Elephant Moraine

PCA: Pecora Escarpment (near Thiel Mtns.)

TIL: Thiel Mountains

Figure 2: Map of Antartica and meteorite collection sites
from Lunar and Planetary Science Institute, Houston

A list of the Antarctic meteorites obtained appears in Table 1.

Reference meteorites were obtained from the Harvard Mineralogical Museum. The Harvard samples are classified as falls and were collected at various times ranging from 1825 to present. Their histories are, unfortunately, not well-documented. They are stored under normal room conditions in plastic bags. These samples were obtained whole, and powders were made from fresh interior chips by pulverizing with an agate mortar and pestle. Magnetic and non-magnetic fractions were separated with a small hand magnet.

For Mossbauer analysis, powders were pulverized and mixed under acetone with sugar to add bulk and reduce orientation effects. 50 to 100 mg of powder were used in each mount. Separate mounts were made of magnetic and non-magnetic fractions. Powders were used without further treatment for XRD analysis.

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Table 1

Specimen	Weathering Index	Meteorite Type
ALHA 77271	C	H6 chondrite
ALHA 77294	A	H5 chondrite
ALHA 77214	C	L3 chondrite
EET 83213	B	L3 chondrite
ALHA 77216	A/B	L3 chondrite
ALHA 81027	C	L6 chondrite
ALHA 77155	A/B	L6 chondrite
ALHA 77297	A	L6 chondrite
TIL 82402	A/B	LL6 chondrite
PCA 82507	A	LL6 chondrite
EET 83232	B	eucrite
ALHA 80102	A	eucrite
EETA 79004	B	eucrite
EETA 79005	B	eucrite
ALHA 77256	A/B	diogenite
EETA 79002	A	diogenite
EETA 79001 lith A	unspecified	shergottite
EETA 79001 lith C	unspecified	shergottite
ALHA 77005	unspecified	shergottite

Chapter 3. Sample Descriptions

Antarctic Meteorite Collection

Guide to weathering classification[1b]:

> A=none or minor rust halos around metal flecks, minor oxide staining along cracks
> B=large rust halos around metal flecks, extensive oxide staining along cracks
> C=uniformly stained brown, no evidence of metal

ALHA77271 H6 C

Surface covered with 25% fusion crust, rest of surface is weathered dark brown. Chondrules sparsely distributed in a granular matrix. Interior weathered along fissures. Small areas and veins of "limonite". Ol 32%, opx 32%, NiFe 20%, plag 5%, troil 5%[1b,2].

ALHA77294 H5 A

Surface completely covered with fusion crust. Polygonal fractures filled with white (evaporite?) material on one surface. Whitish-grey matrix with some oxide staining visible, chondrules and inclusions throughout up to 2mm diameter. 15-20% metal. Mostly ol, opx, some NiFe, minor troilite. $Ol=Fa_{17}$, $pyx=Fs_{15}$[1c,2].

ALHA77214 L3 C

30% fusion crust. Surface fractured and fissured. Material around fissures very weathered. Rest of surface weathered to a brownish-black. Oxide stains visible near fracture, fissures. Fe weathered to "limonite". Fluid-drop chondrules, easily visible, containing glass, olivine, pyx. Abundant troilite. $Ol=Fa_1-Fa_{49}$, $opx=Wo_1Fs_{13}En_{86}$. Possible hematite[1a,2].

EET83213 L3 B

Mostly covered with fractured fusion crust. Rest of surface weathered to reddish-brown 5mm thick. Grey interior with some oxidation. Abundant metal with staining. Chondrules up to 3.5 mm. Abundant $plag=An_{11}Ab_{84}Or_5$. Abundant troilite. Two metal phases, and chromite. $Ol=Fa_{24.5}$, $pyx=Fs_{23}$[1j].

ALHA77216 L3 A/B
50% fusion crust. Greenish-grey with white-dark grey inclusions. Heterogeneous, fractured, various degrees of weathering. No visible metal. Chondrules .3-1.2mm. Mostly ol, pyx, minor troilite, limonite. Ol=Fa$_{23-26}$, pyx=Fs$_{10-19}$[1c,2].

ALHA81027 L6 C
Mostly covered with fusion crust. Reddish-brown surface. Interior is very weathered. Plag is shocked to maskelynite, composition low-Na An$_{10}$. Mostly ol, pyx, minor mask, NiFe, troil, lim. Ol=Fa$_{25}$, opx=Fs$_{21}$[1h,4].

ALHA77155 L6 A/B
Partial fusion crust. Weathering slight to moderate-limonite staining on surface and around metal grains. Sparse, poorly defined chondrules. Orange-brown surface, light grey matrix, unfractured. Mostly olivine, opx, minor plag, NiFe, troil, diop, chrom, whitlockite. Ol=Fa$_{24}$, opx=Fs$_{21}$, plag=An$_{11}$[1c,2].

ALHA77297 L6 A
As above, but less weathered. 5% metal with oxide halos. Ol=Fa$_{24}$, opx=Fs$_{20}$, plag An$_{11}$[1c,2].

TIL82402 LL6 A/B
Covered by fusion crust. Light grey matrix with light and dark chondrules. Mostly ol, opx, and minor plag, troil. Oxide halos around metal. Ol=Fa$_{29}$, pyx=Fs$_{24}$, plag=An$_{10}$[1i].

PCA82507 LL6 A
Mostly covered with fusion crust. Rest of surface brownish. Blue-grey matrix with white and dark grey chondrules up to 5mm. Ol and pyx with minor plag, troil, 1% NiFe. No trace of weathering. Ol=Fa$_{30}$, pyx=Fs$_{25}$, plag An$_{11}$[1i].

EETA79004 euc B
Thin fusion crust on most of surface. Medium-dark grey with light and dark clasts and vugs up to 1cm deep. Interior light grey. Spots of severe oxidation. Monomict breccia of pyx, feldspar in fine matrix, possibly recrystallized. Pyx=Wo$_2$En$_{45}$Fs$_{53}$-Wo$_{40}$En$_{36}$Fs$_{24}$, Fspr=Or$_1$Ab$_6$An$_{93}$-Or$_1$Ab$_{14}$An$_{85}$[3].

ALHA80102 euc A

Covered with fusion crust. Many large vugs, grey, white, yellow, and black clasts. Polymict breccia of pig, plag, minor ilmenite. No sign of weathering. $Pig=Wo_6Fs_{34}En_{60}-Wo_{12}Fs_{52}En_{36}$, $ferroaugite=Wo_{33}Fs_{30}En_{37}$, $plag=An_{76}-An_{94}$[1f,4].

ALHA77256 dio A/B

15% fusion crust, rest of surface weathered to yellow-brown. Patches of oxide staining. 97% opx $clasts=Wo_2Fs_{23}En_{75}$, minor cpx, 1% plag, 1% troil, $NiFe$[2].

EETA79002 dio A

Covered with fusion crust. Medium grey matrix with light clasts. Some oxidized areas- red-brown, many fractures, no metal. Angular breccia mostly opx, minor ol, possible ilm or chrom. $Pyx=Wo_2En_{76}Fs_{22}$, $ol=Fo_{75}$[1d,3].

PCA82506 ure A/B

75% fusion crust. Greenish-brown surface with grey-green interior. Aggregate of ol, pyx, rimmed by C material, troilite, trace NiFe weathered to oxides. $Ol=Fa_{21}$, $pig=Wo_6Fs_{18}En_{76}$[1i].

ALHA77257 ure A

50% fusion crust. Surfaces are brownish-black with areas of oxide stain. Hydromagnesite vein across surface. Interior fine black matrix with grains. 80% olivine, 15% pyx. C rims at grain boundaries, trace troilite, and NiFe partially altered to oxide. $Ol=Fa_{9-23}$, $pyx=Wo_7En_{81}Fs_{12}$[2].

EETA79001 sherg lith A (see diagram of this specimen, Figure 3)

Mostly covered with fusion crust. Surface white-grey and porous. Pig-mask groundmass with zoned pyx inclusions. Shocked; plag altered to mask. Interior weathered, possible uptake of H_2O, CO_2. Mostly pyx, some mask, trace chromite, troil, ilm. $Pig=Wo_5En_{70}Fs_{25}-Wo_{12}En_{50}Fs_{38}$, $mask=Or_1Ab_{42}An_{57}$, $ol=Fo_{75}$[1d,3].

EETA79001 sherg lith C

Surrounded by lith A. Glass with olivine, pyx, mask inclusions. Dark brown-black, with both glassy and microcrystalline textures.

Figure 3:   Sawcut of EETA79001
            from Antarctic Meteorite Newsletter Vol. 9, no.1

Lithology A

Lithology B

Lithology C

glass veins

white druse

X marks area from which our
lithology C sample was taken

EETA 79001

1 cm.
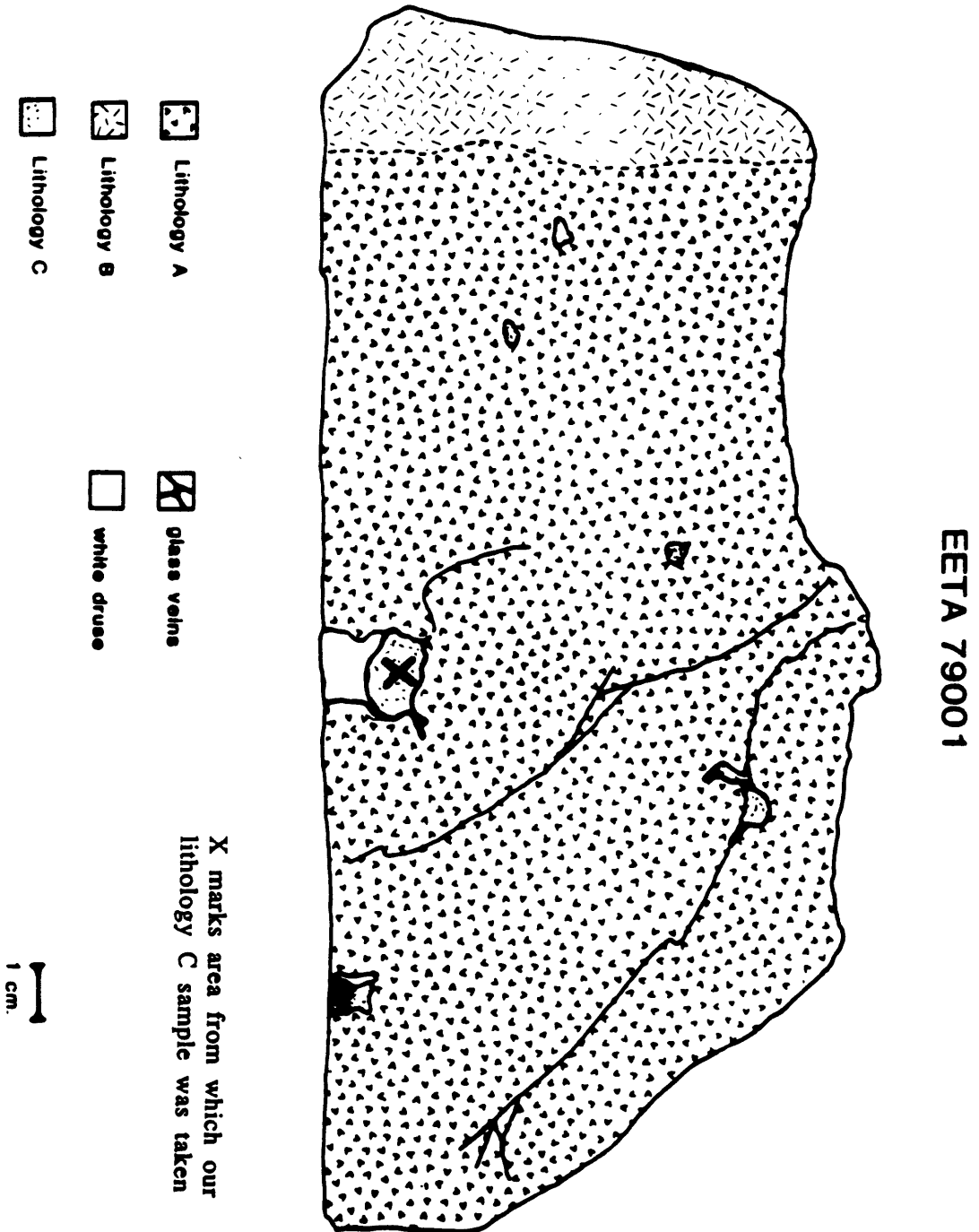
Large vugs and small vesicles with light colored phases. Aluminosilicates rich in S, Cl not of terrestrial composition. No weathering or volatiles present. High concentration of S-species[1d,k].

ALHA77005   sherg

5% fusion crust. Little evidence of weathering. Heterogeneous, some cumulate olivines and chromite enclosed by low and high-Ca Mg pyx. Other ol with interstitial mask, chrom, ilm, troil, whit, pyx. Plag shocked to mask. Olivine brown-colored, containing up to 5% Fe^{+3}. Chromite and olivine altered slightly to orange material. Weak preferred orientation of olivine grains. 55% ol, 35% pyx, 8% mask; chrom, NiFe, ilm and troil 2%. $Ol=Fa_{28}$, $pyx=Wo_5Fs_{23}En_{72}$, mask=labradorite An_{53}[1a,2,5,6].

Harvard Mineralogical Museum Collection

Nanjemoy   H

Unfortunately, no documentation exists for this meteorite; Harvard has it classified as an H-group meteorite.

Ehole   H

Olivine-bronzite chondrite. $Ol=Fa_{19}$[7].

Forest City   H

Olivine-bronzite chondrite, with minor clinobronzite. Well developed chondrules. $Ol=Fa_{19}$, $Pyx=Fs_{16}$, $Plag=An_{10}$[8].

Mezo-Madaras   L3

Highly brecciated olivine-hypersthene chondrite. Ol 50%, pyx 25%, plag or mask 10%, FeNi 8%, troil 5%, chrom, diop, whit, goethite. $Ol=Fa_{16-30}$[9].

Holbrook   L6

Olivine, opx, troilite, FeNi, goethite[8].

Dhurmsala   LL6

Similar to Holbrook.

Juvinas   euc

Fine-medium grained matrix.   56% pig, 40% plag, 1% silica. Plag=An_{80}[10].

Tatahouine   dio

Hypersthene achondrite.   Highly shocked.   Pyx=$En_{75}Wo_{1.5}$[11].

Goalpara   ure

Highly shocked, brecciated.   Ol 63.5%, pyx 31.7%, kama 1.6%, troil 1.1%.   Ol=$Fo_{78.6}$, pig=$En_{76}Fs_{19}Wo_{4.4}$[12].

Nakhli   nakhlite

Clear glass fusion crust.   Mostly augite, some ol, plag, K-spar, Fe-Ti oxides, FeS, pyrite, chalcopyrite, iddingsite, magnetite (?). Cumulate texture.   Fe-rich ol, pyx=$Wo_{39}En_{38}Fs_{23}$, plag=$Or_5Ab_{63}An_{32}$, K-spar=$Or_{75}Ab_{22}An_3$[13].

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Chapter 4. Mossbauer Spectroscopy

The technique of Mossbauer spectroscopy uses gamma rays emitted from a ^{57}Co source to excite nuclear transitions in ^{57}Fe located in the sample of interest. All the gamma rays are transmitted, except those matching the nuclear spin state (I=3/2) 14.4KeV above the ground state (I=1/2). These gamma rays are re-emitted over all angles and the spectrum is measured in terms of absorbance. The nuclear energy levels of Fe have slightly different energies due to differences in coordination environment; in order to detect this, energy coming from the source is doppler-shifted by means of an oscillator, $\pm 10mm/sec$. Thus, different coordination environments appear at different energies and are separable into discrete peaks. This technique can detect differences in Fe oxidation state, coordination number, and size and shape of the coordination site.

The source used for this study was ^{57}Co in rhodium. The spectrometer is an Austin Science Associates model S3K3 with a 1024-channel multi-channel analyzer. The spectra use only 512 channels each, and are half of the mirror-image spectra normally obtained. Thus, two spectra may be run simultaneously, utilizing two sources set up on the same oscillator. The powder containing the sample is mounted with tape onto a plexiglass holder and shielded with lead. It is placed about 15cm from the source and 1-2cm from the detector. The samples are calibrated against Fe foil, and frequent calibration runs are made (once a month, or every time the system is set up differently) to guard against drift.

Liquid nitrogen runs are made by mounting the sample on a copper rod, shielding as usual, and inserting the rod into a 25-liter tank of liquid nitrogen. The sample and rod are insulated with styrofoam. Spectra can be run for a maximum of four days without changing samples, on one tank of liquid nitrogen. This configuration requires that the sample be moved 3-5cm farther away from the source than usual.

Chapter 5. <u>Mossbauer Data and Fitting Procedure</u>

The spectra were fit using the programs READ and STONE, which use a least squares fitting procedure, written by A.J. Stone, *et al* (1969), modified by F.E. Huggins (1974)[1]. All peak shapes were assumed to be Lorentzian. When using this program, the operator enters "guesses" for the baseline parameters, peak positions, halfwidths, and areas. A number of constraints can be entered relating the center, halfwidth, or area of one peak to another; in addition, parameters can be fixed to a particular value. The program then proceeds through a series of iterations to the best fit for the initial parameters. The result is converted to mm/sec scale by comparison with a fitted Fe foil calibration.

In all fits, halfwidths of component quadrupole doublets were constrained to be equal among all peaks, except for the largest ferrous peak at high velocity (~2.5mm/sec), which consistently gave a better fit if allowed to vary (however, the areas of the pair were required to be the same). The halfwidth of this high velocity peak never deviated more than 3 channels from its mate, as it is very well-defined in the spectra. Areas of pairs of peaks were always constrained to be equal. Pairs of peaks which formed part of a magnetic sextet were constrained to have the area ratio 3:2:1. This was necessary, as these peaks were not usually large, and the innermost two peaks were usually overlapped by other doublets. The outer two peaks are not visible in the velocity range we were using, however, the middle pair was sufficiently well-defined to give a good area assessment for the inner pair.

Because many of the inner peaks overlapped, especially in the ferric region, it was sometimes necessary to constrain peak positions. In this case, the first peaks to be constrained were always the ones with well-known parameters; i.e. ilmenite, metallic Fe, and troilite (in the case of the magnetic sextets, the positions of the inner peaks could be determined by their outer counterparts, and in the case of Fe, by the foil calibration). However, it was usually the case that the low velocity ferric peak almost directly coincided with the low velocity Fe^{+2} pyroxene peak, so that the positions of these two peaks had to be constrained. When this was necessary, the position of the pyroxene peak was determined from the least oxidized spectrum, and the ferric peak subsequently adjusted to give the best fit. Examples of fitted spectra and constraints are provided in Figures 4-6.

Particular difficulties were encountered when it was necessary to fit two ferric doublets; it was determined that the second one was invariably overlapped by the low velocity olivine peak. Nevertheless, successful fits were obtained for these spectra. In addition, a minor amount of Fe metal occasionally remained in the sample, and it proved to be difficult to fit the two innermost peaks, in addition to the fitted troilite sextet, so that in most cases only the outer Fe peaks were fit. In no case did these missing peaks exceed 1% of the area.

Goodness of fit was determined by the chi-squared value, and by the appropriateness of the final parameters to the minerals known to be present. For the SNC's, spectra were fitted to three Fe^{+2} doublets, one Fe^{+3} doublet, and ilmenite. The ferrous doublets are

Figure 4: 4 peaks, 11 constraints

baseline constraints	2
% gaussian = 0	4
areas of pairs =	2
wdths of 1,2,3 =	2
position of 1	1
	11

ALHA77256 DIO A/B
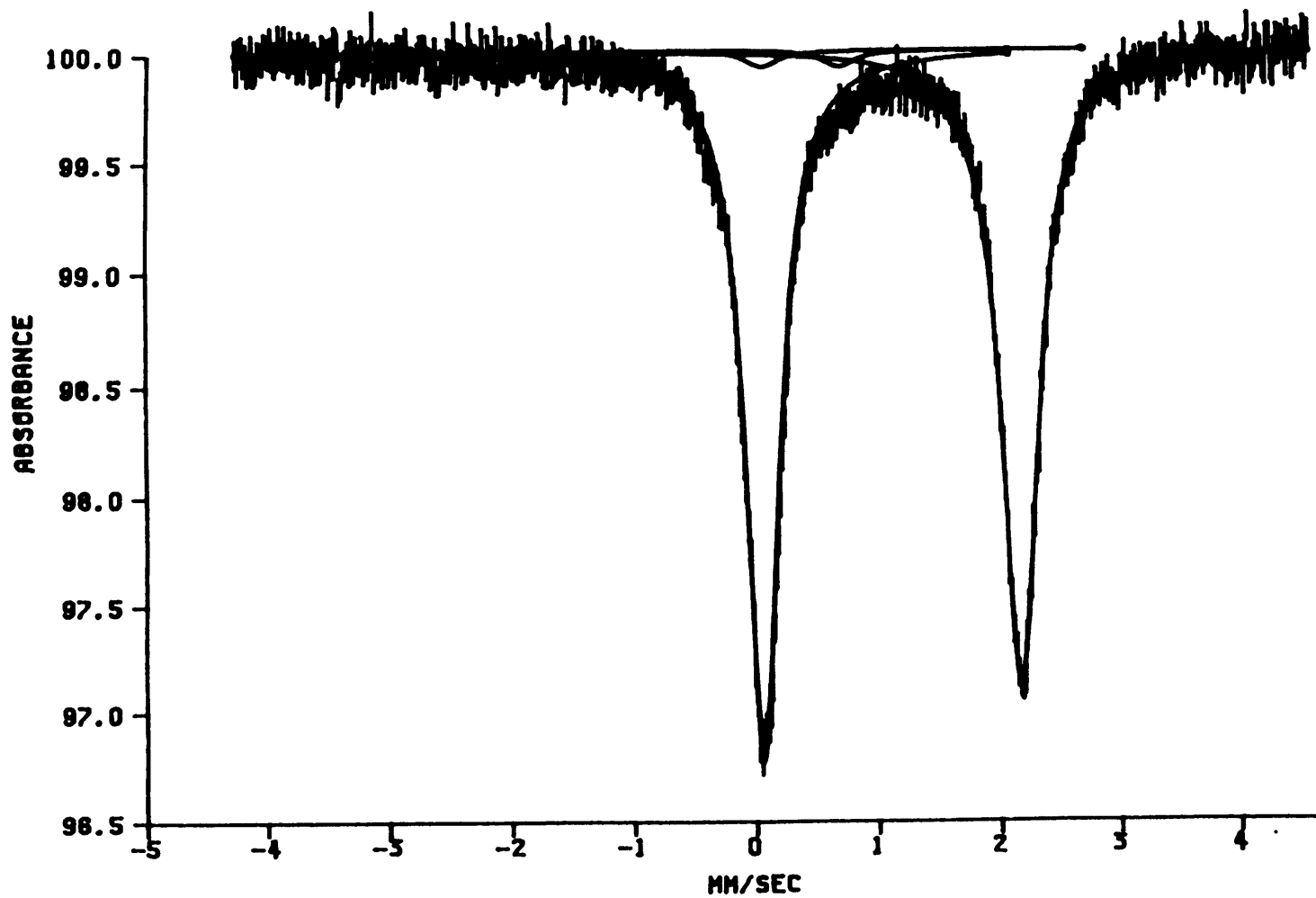
Figure 5: 10 peaks, 29 constraints

baseline constraints	2
% gaussian = 0	10
areas of pairs =	5
wdths =	9
positions of 3,6,7	3
	29

SHERGOTTITE 79001 LITH A

33
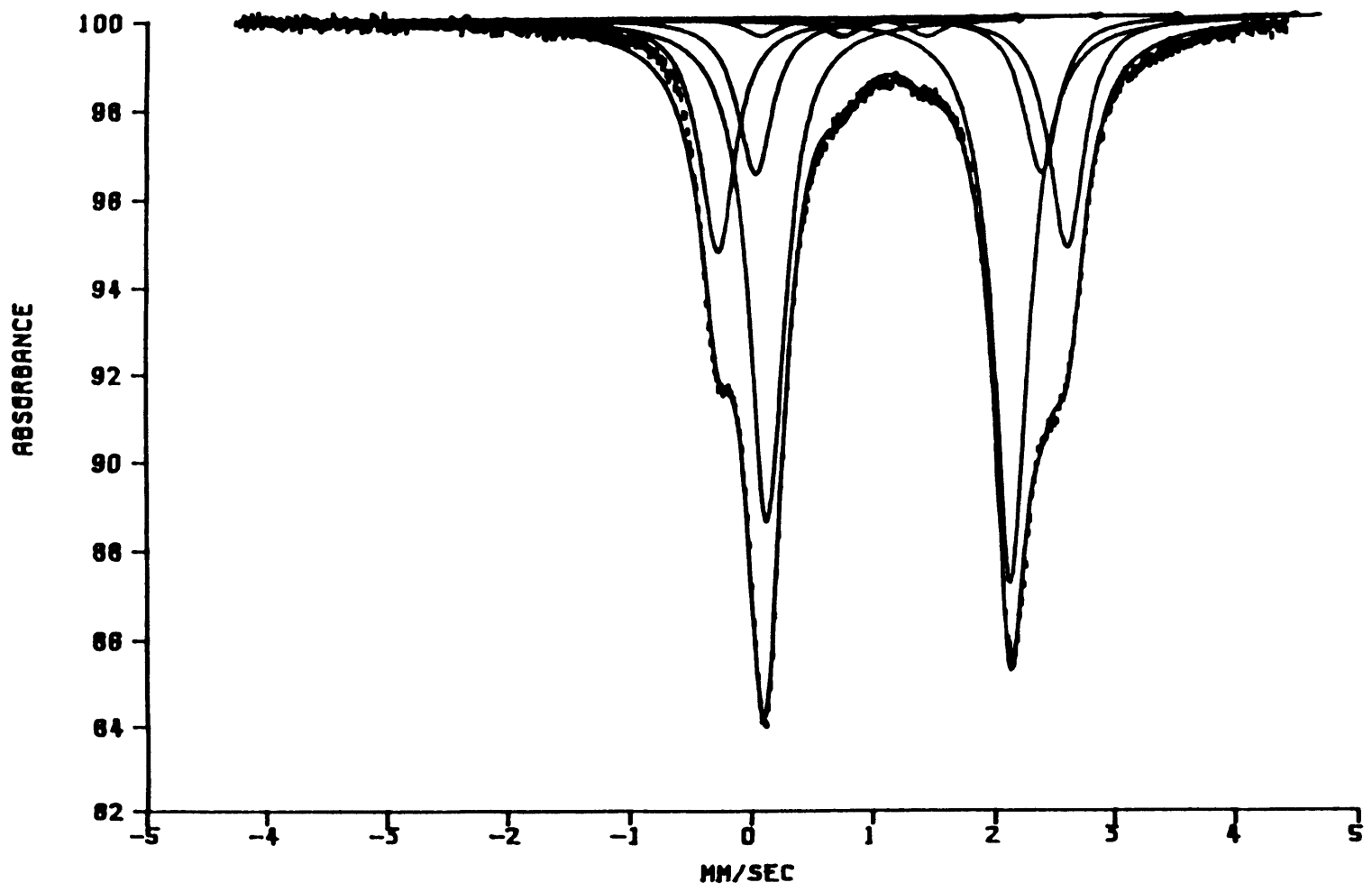
Figure 6: 12 peaks, 36 constraints

baseline constraints	2
% gaussian = 0	12
areas of pairs =	6
area ratio of mag. sextet	1
wdths =	11
positions of 2,3,4,5	<u>4</u>
	36

ALHA77214.18 L3 C

ABSORBANCE

MM/SEC
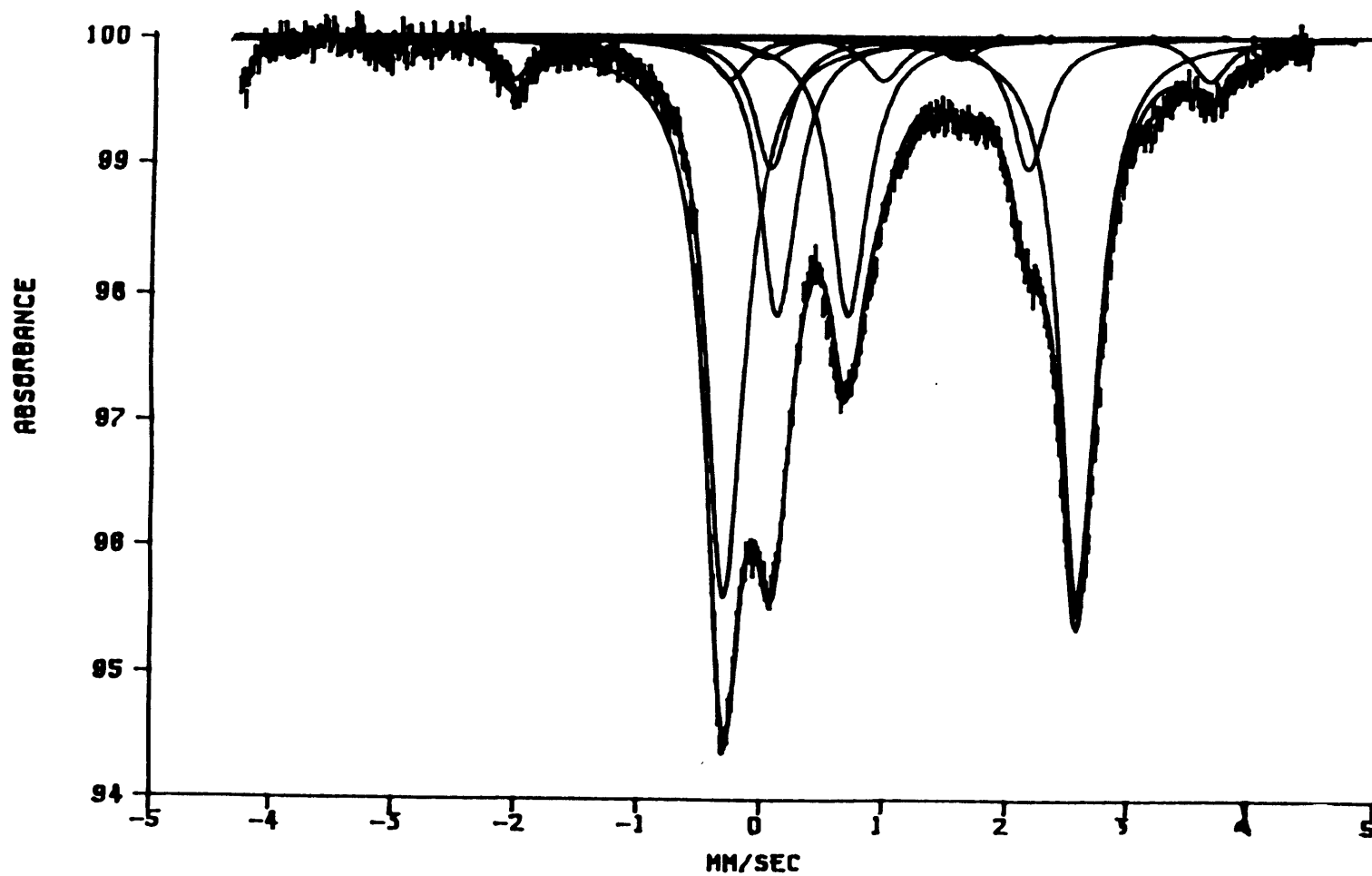
assigned as follows: The outermost is attributed to olivine with a small contribution from the M1 sites of augite and orthopyroxene. The innermost doublet is attributed to the M2 sites of augite, pigeonite and hypersthene. Occasionally, a middle doublet was resolved arising from the pigeonite M1 site. Lith C of EETA79001 contained an additional ferrous peak, assigned to Fe^{+2} in the glass phase. The chondrites were fitted to the same three Fe^{+2} doublets, troilite, occasional Fe metal, and one or two ferric phases. All peak parameters are in agreement with previous literature values; due to variations in composition (of the pyroxenes, in particular) the parameters occasionally vary beyond experimental error. However, it is not really necessary to pin down the exact pyroxene parameters for this work. All of the other ferrous parameters are very well-constrained and do not vary considerably. Unfortunately, the only set of peaks whose parameters could not be independently worked out were the ferric peaks, due to the nature of the overlap between their positions and other interior peaks. It was determined, by a series of successive fits, that this uncertainty in peak position did not unduly affect the areas involved. However, it became necessary to use other techniques to determine the mineralogy of the ferric phases.

The fitted Mossbauer spectra of all meteorites examined here are presented in Figures 7-30, grouped by meteorite class. The fall specimen appears first in each group, followed by the Antarctic specimens in order of increasing degree of weathering. Table 2 summarizes the isomer shift and quadrupole splitting parameters

obtained, and Table 3 summarizes the areas under constituent doublets.

References:

1. Stone, Parkin, and Dyar (1984) <u>STONE: A program for resolving Mossbauer spectra</u> DEC User's Society Program Library, **#11-270**, Marlboro MA

Fitted Mossbauer Spectra

Figures 7-10: L3 chondrites. Fall, A/B, B, C

Figures 11-14: L6 chondrites. Fall, A, A/B, C

Figures 15-17: LL6 chondrites. Fall, A, A/B

Figures 18-20: H chondrites. Fall, A, C

Figures 21-23: eucrites. Fall, A, B

Figures 24-26: diogenites. Fall, A, A/B

Figures 27-30: SNC's. Nakhla, ALHA77005, EETA79001 liths A & C

MEZO-MADARAS   L3 FALL
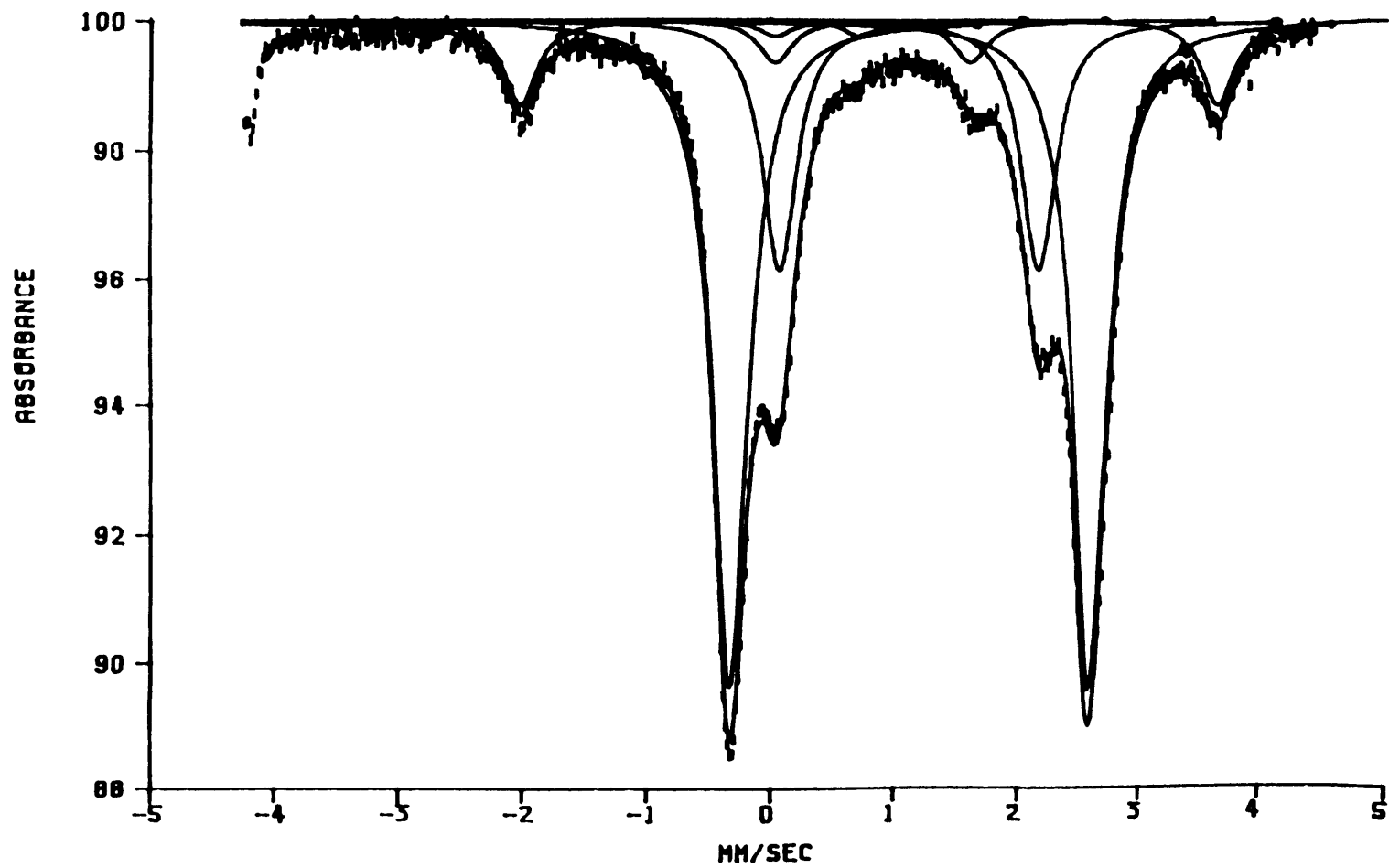
ALHA77216 L3 A/B

EET83213.38 L3 B

41

ALHA77214.18 L3 C

HOLBROOK L6

ABSORBANCE

MM/SEC
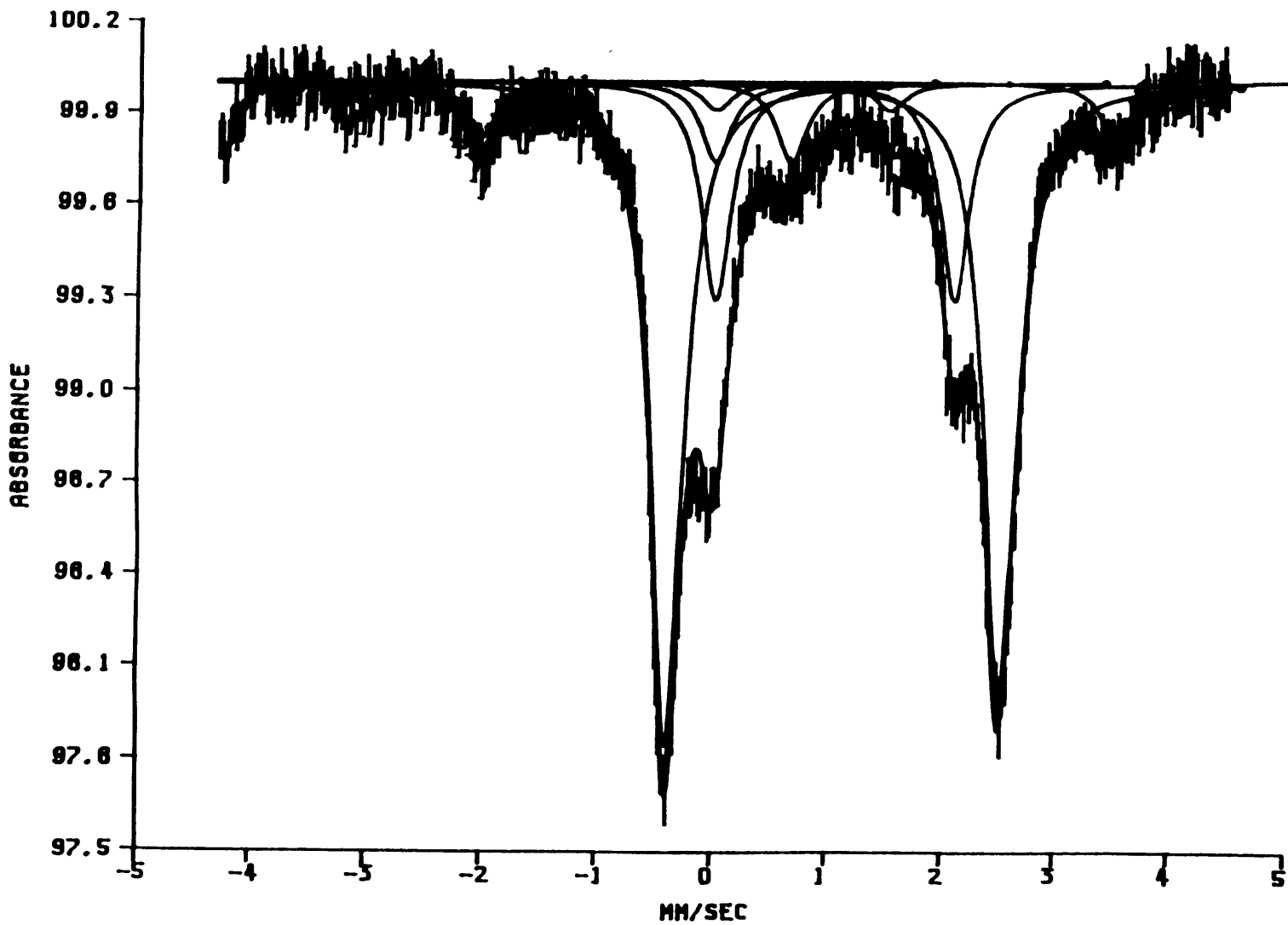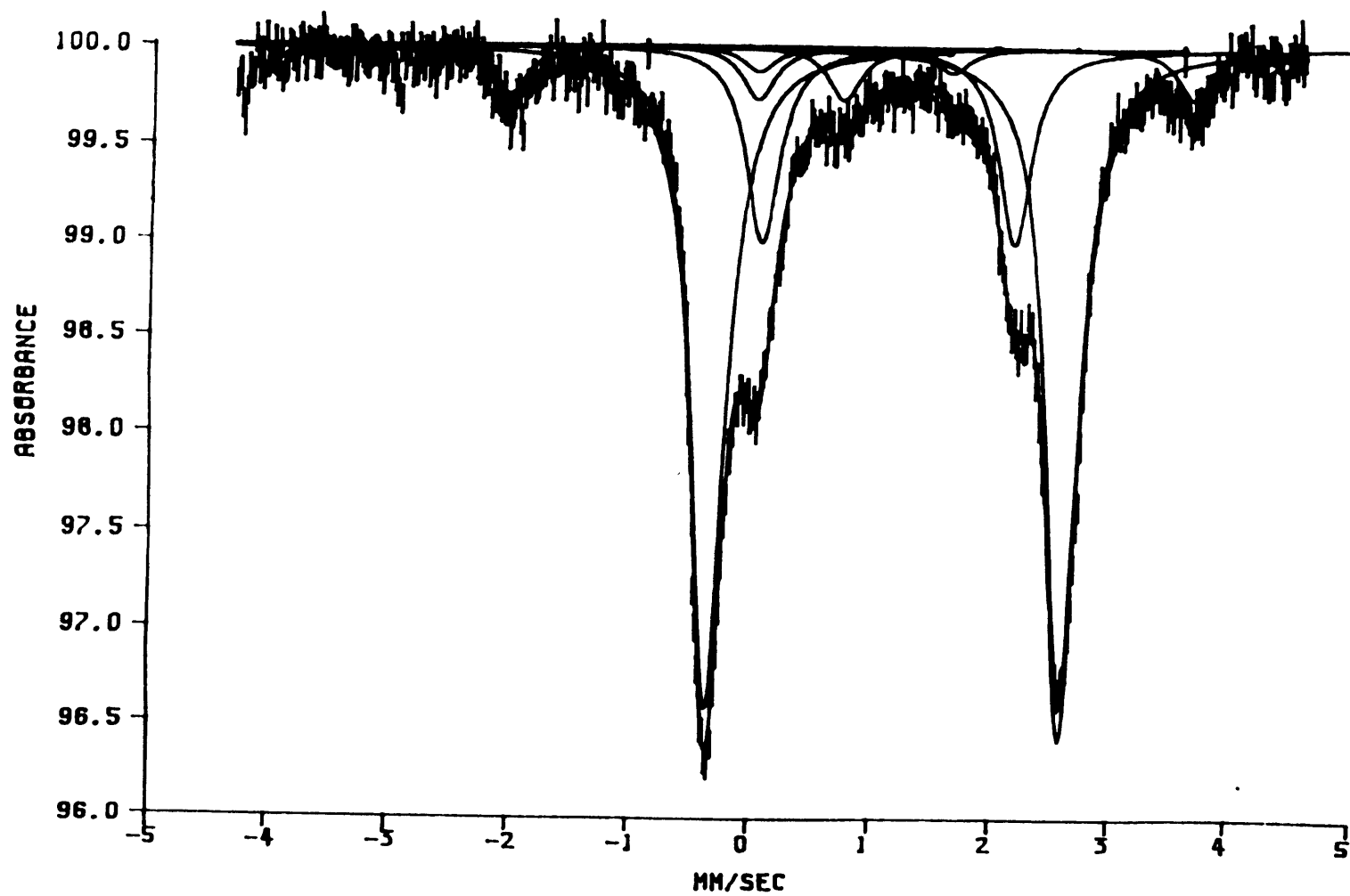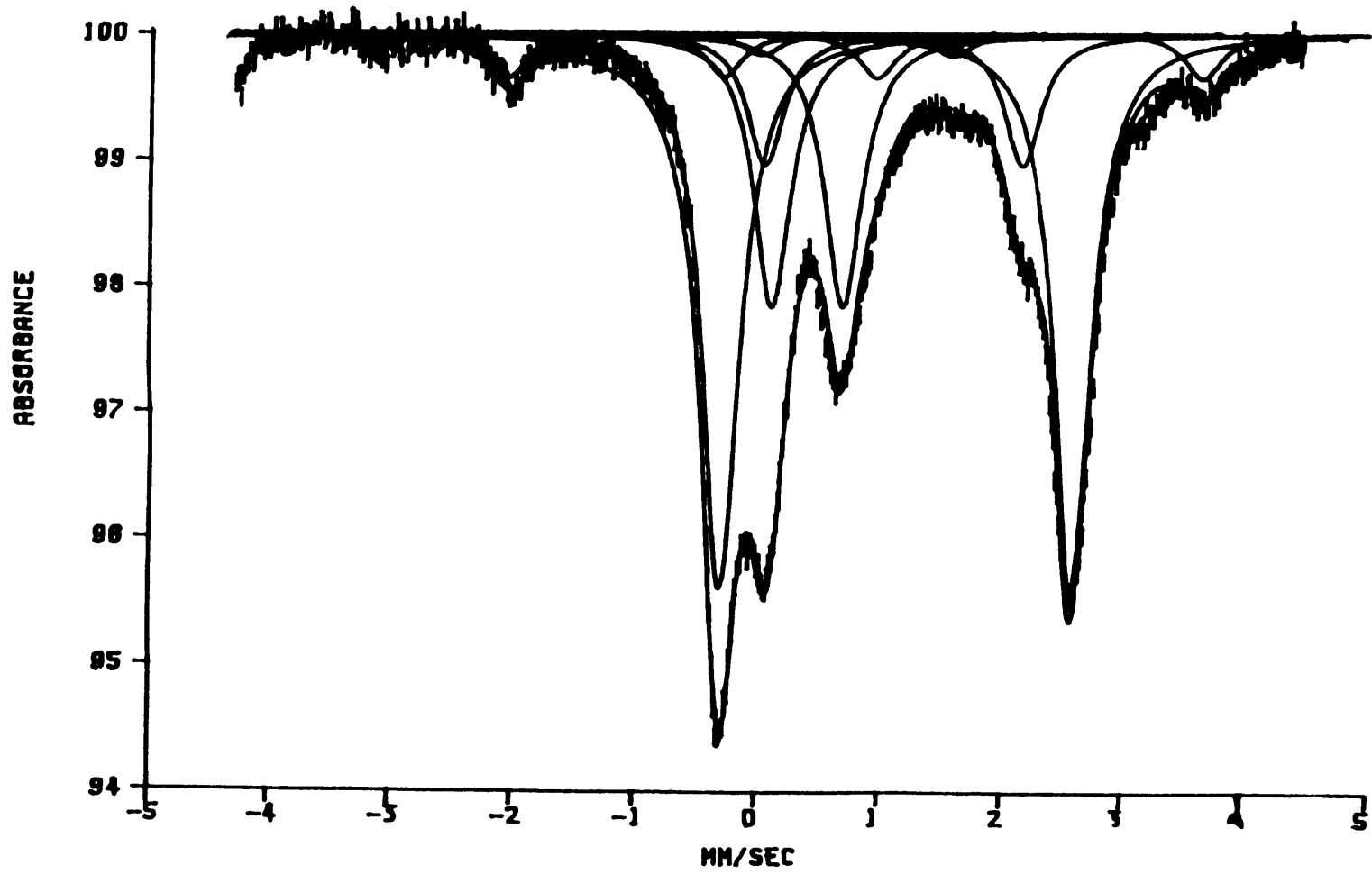
43
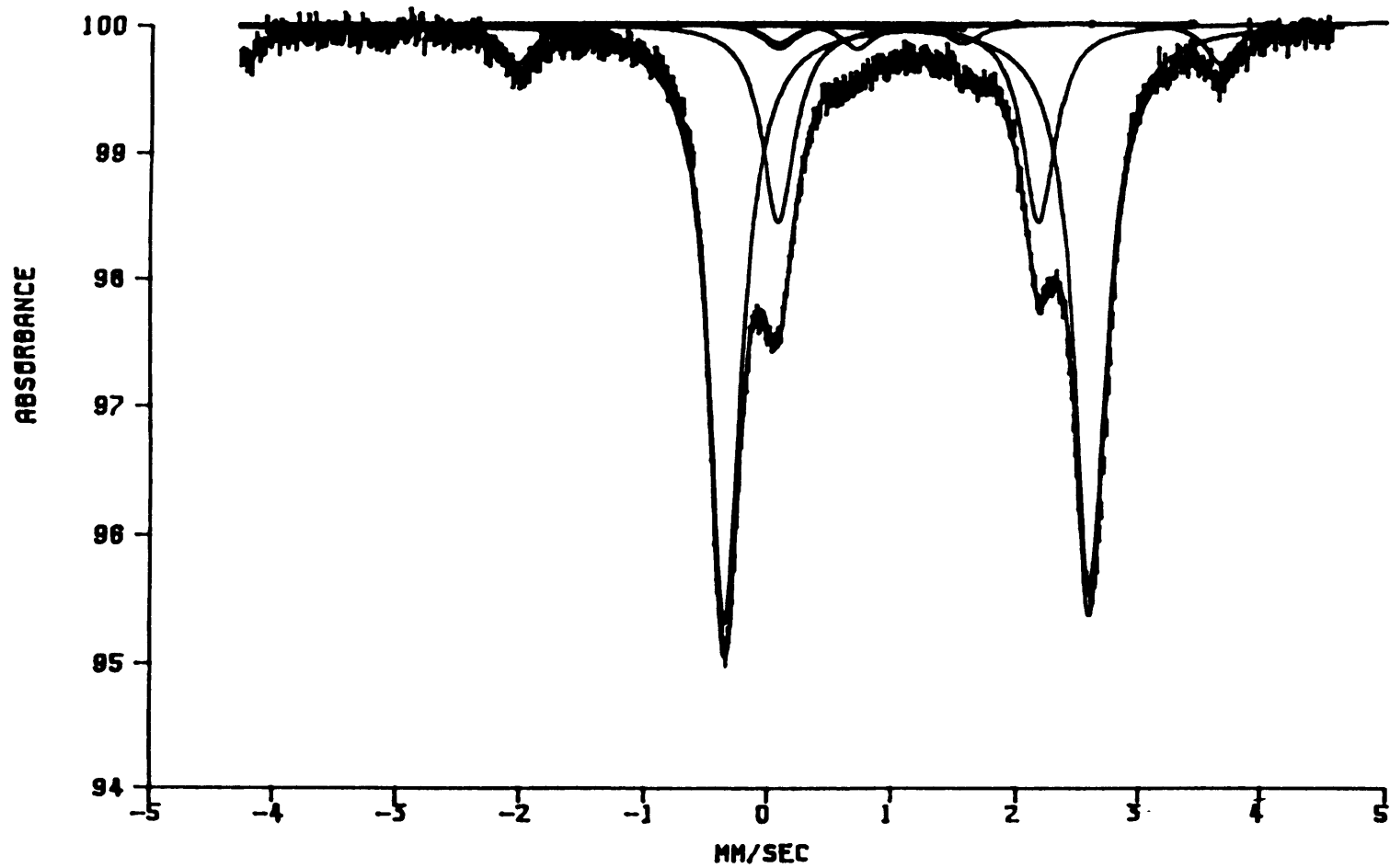
ALHA77297.23 A L6
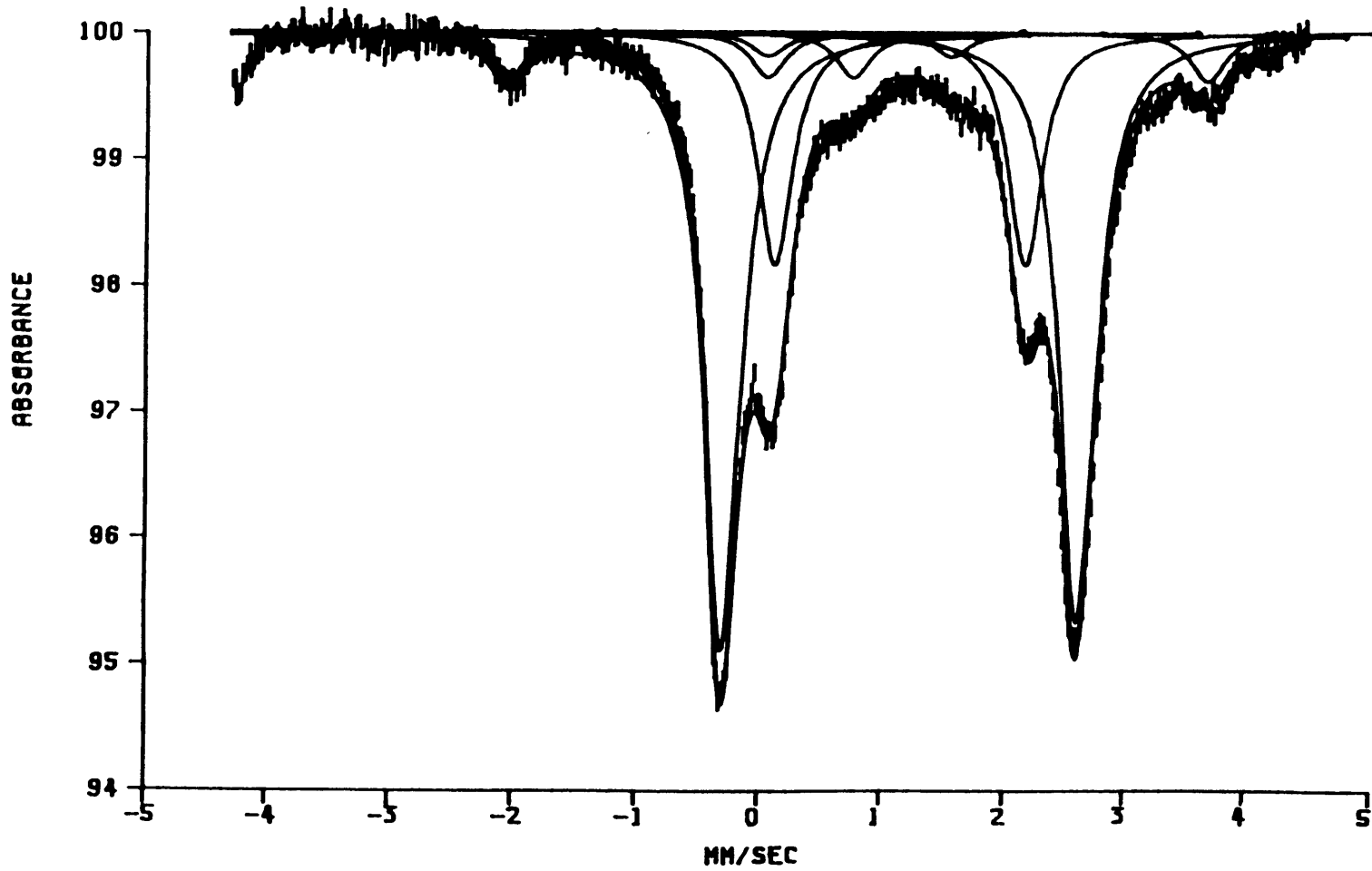
ALHA77155.12 L6 A/B

45
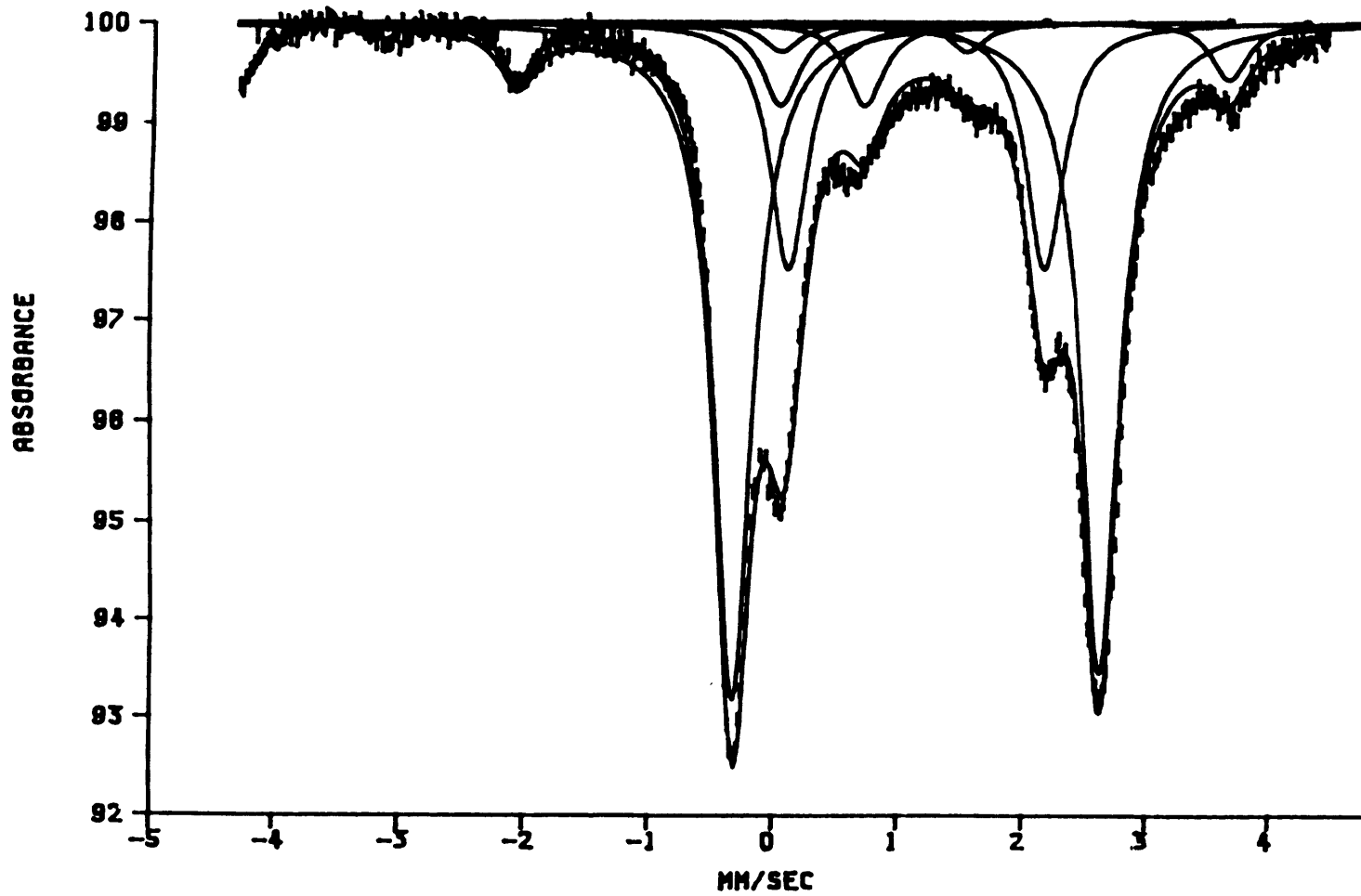
ALHA81027 L6 C
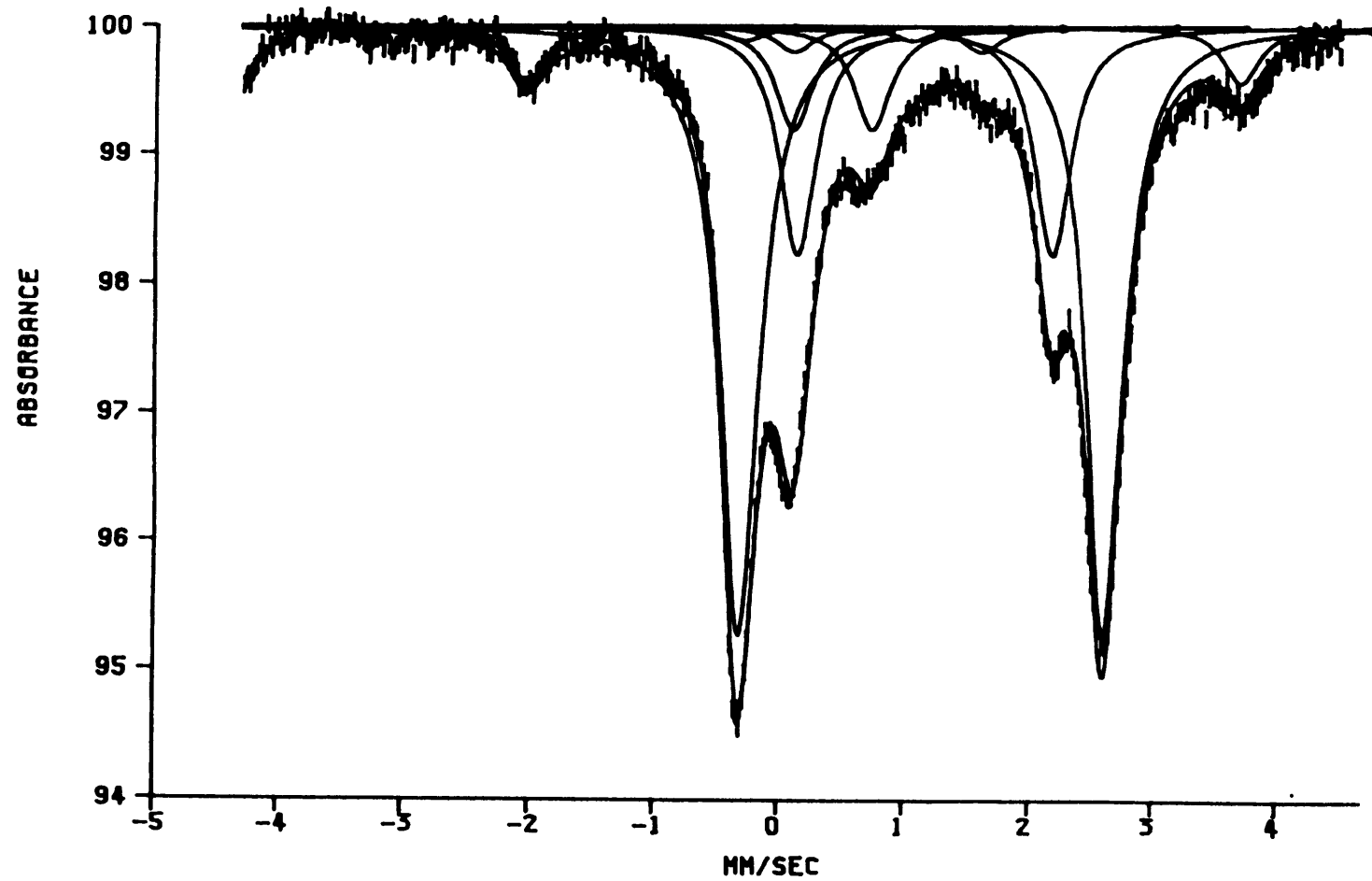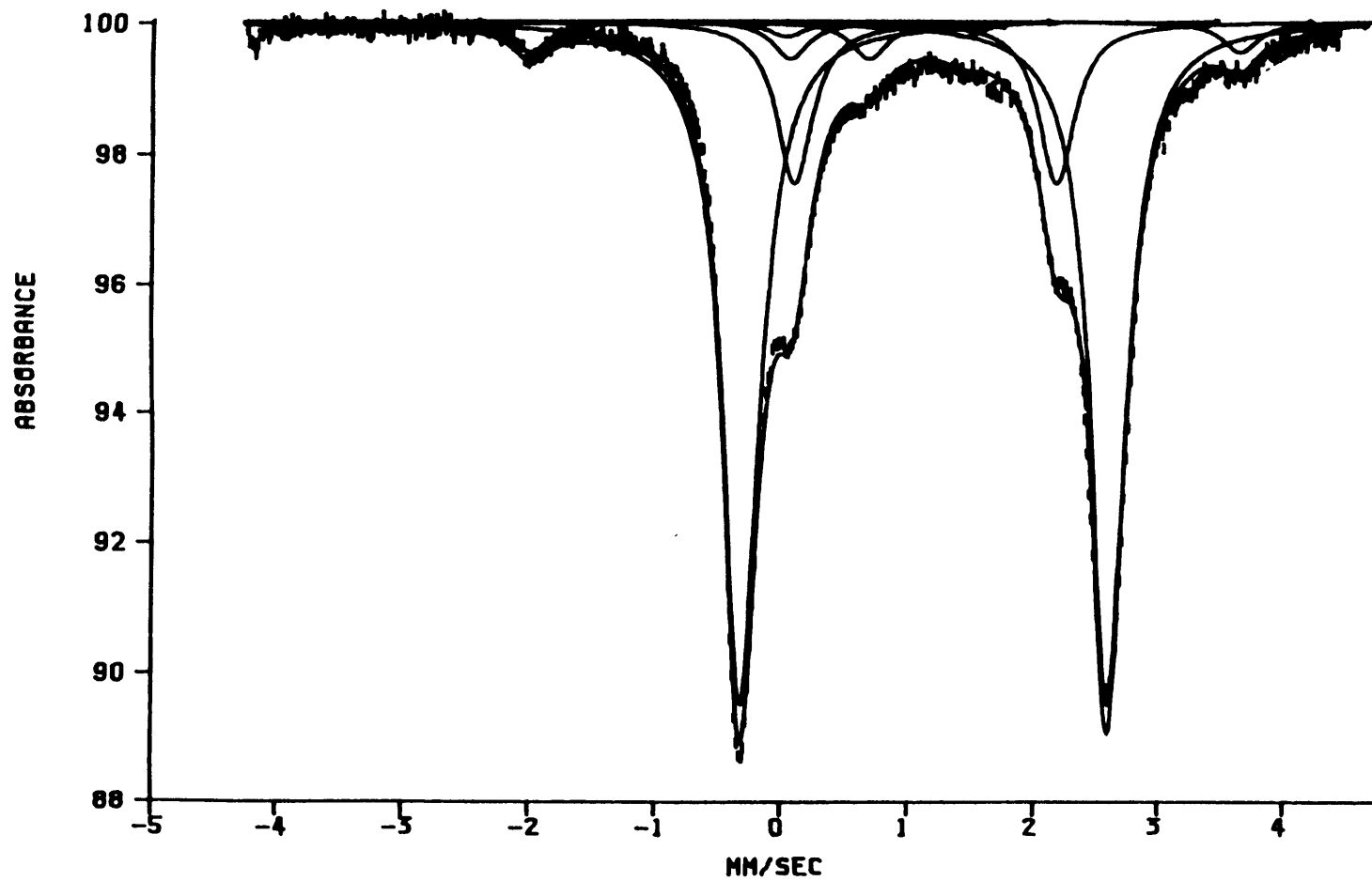
46

DHURMSALA LL6

47

PCA82507 LL6 A

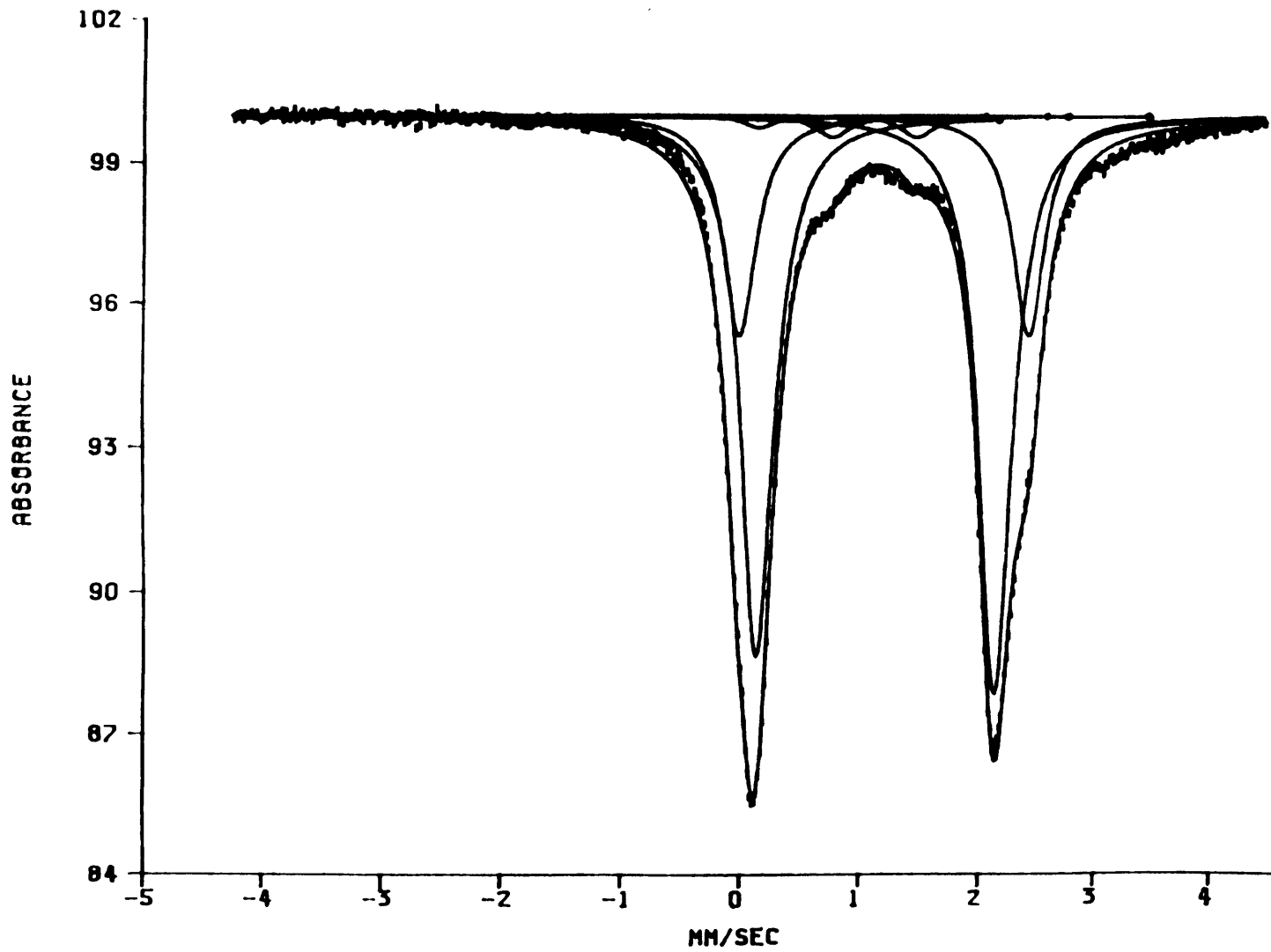TIL82402 LL6 A/B

49

NANJEMOY H6

50

ALHA77294 H5 A

51
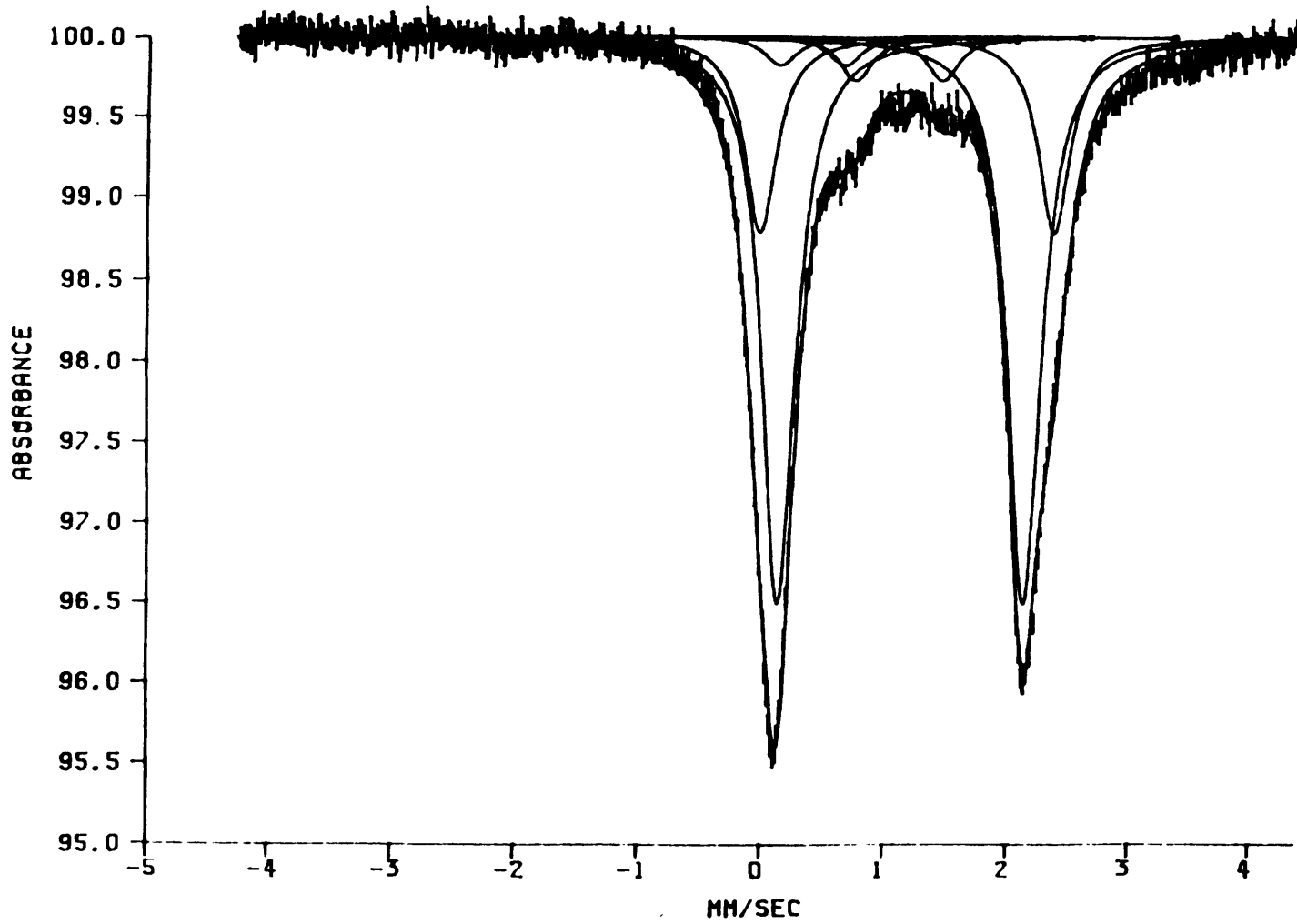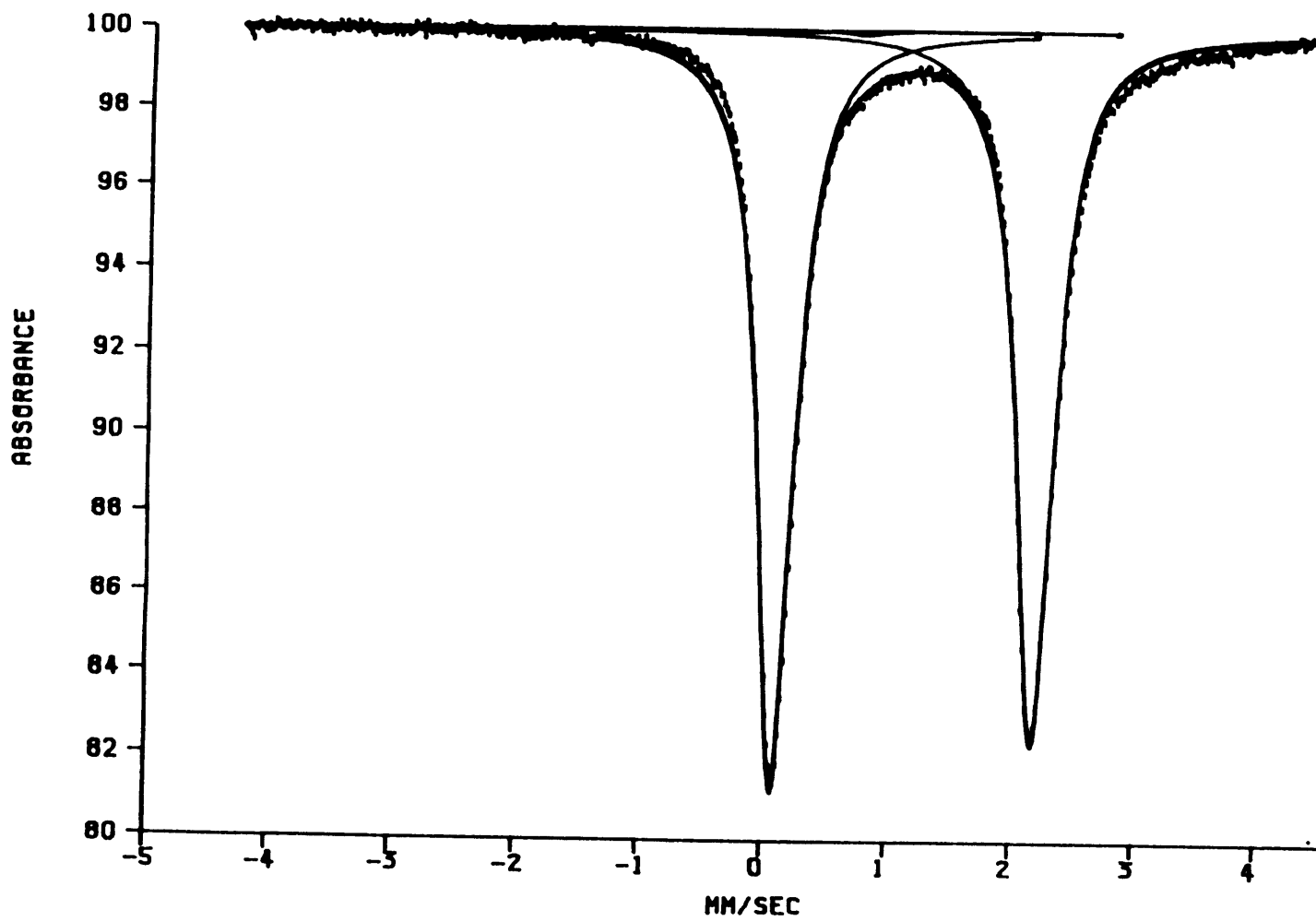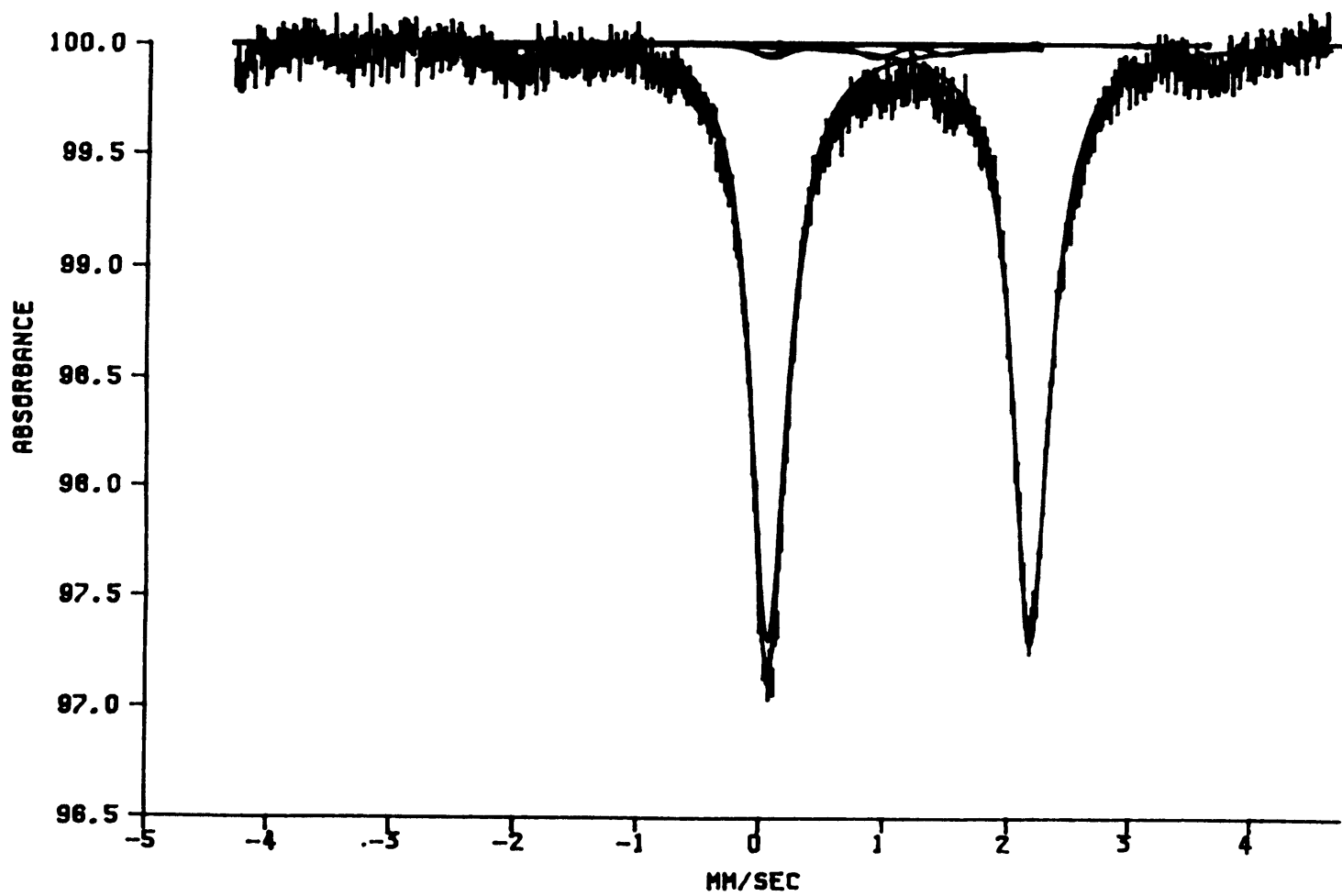
H6 C   ALHA 77271

52
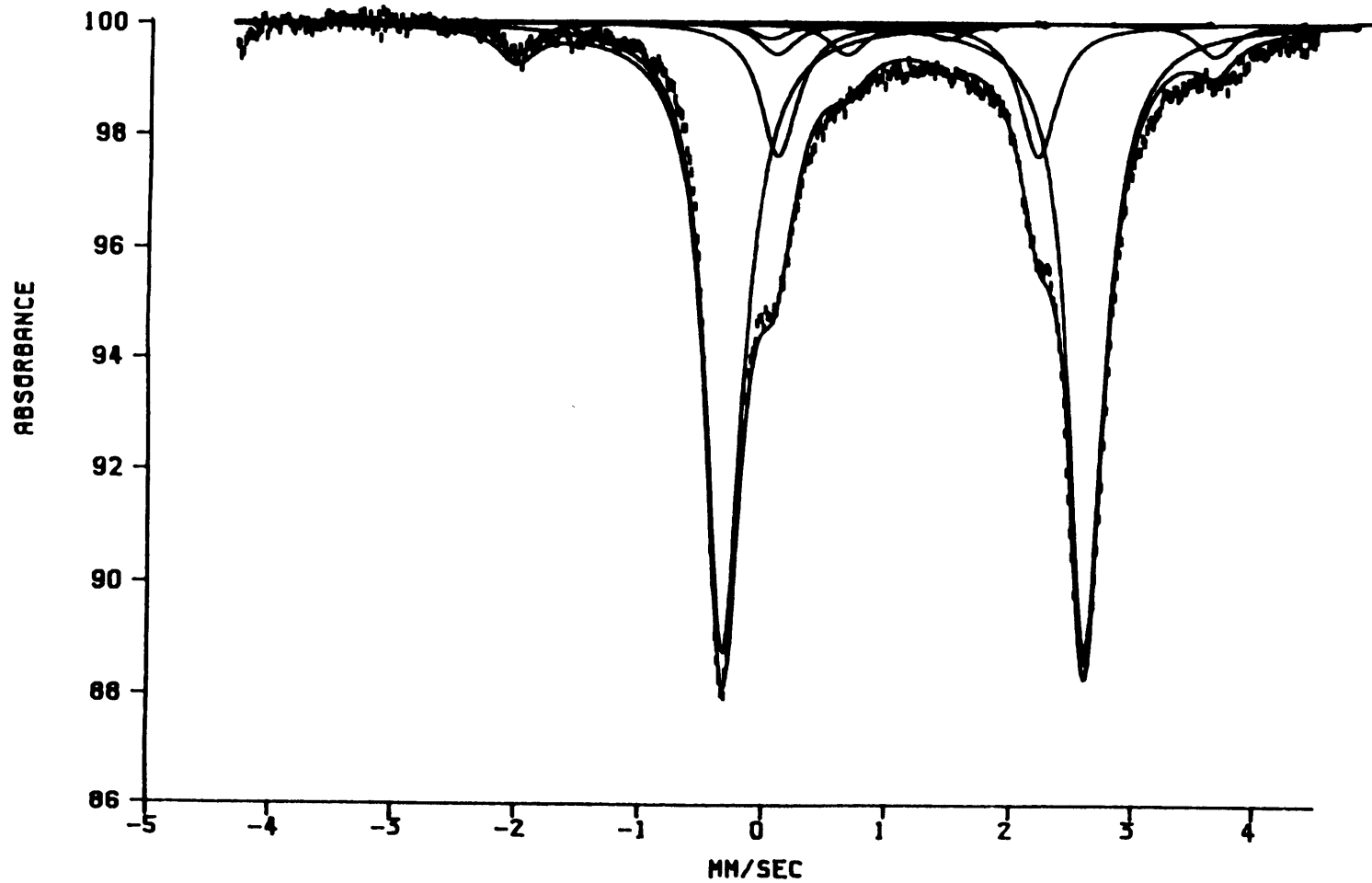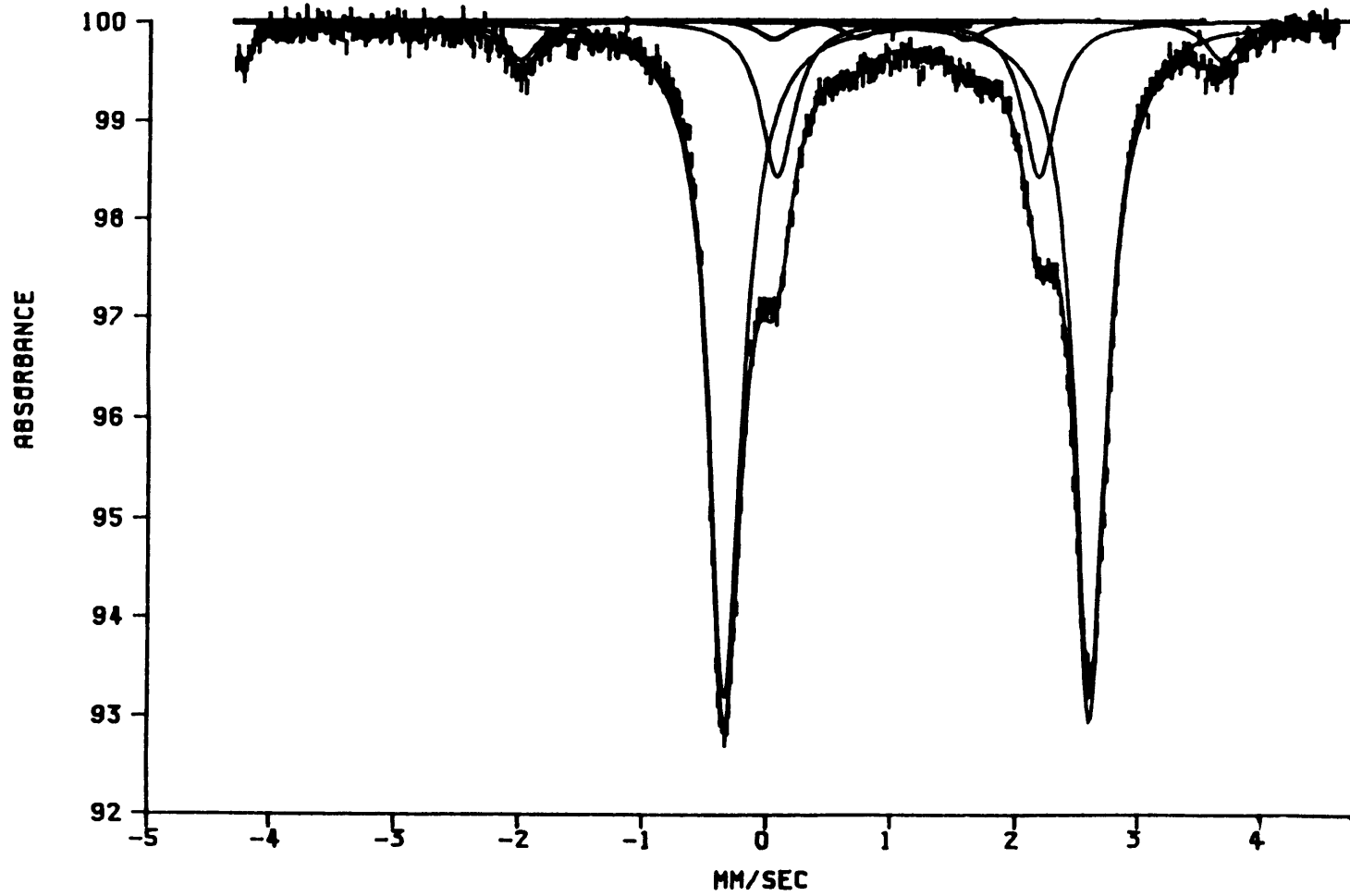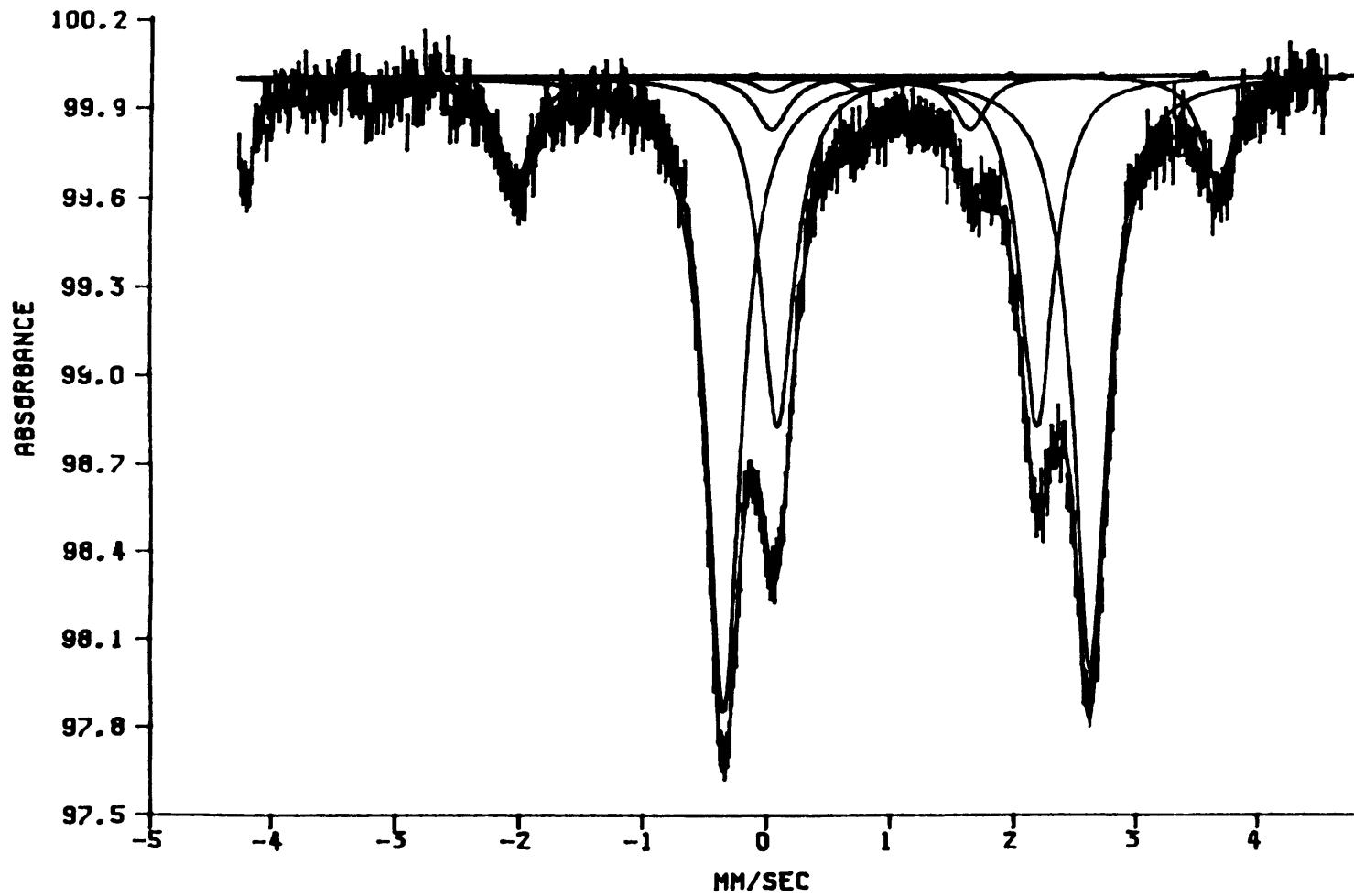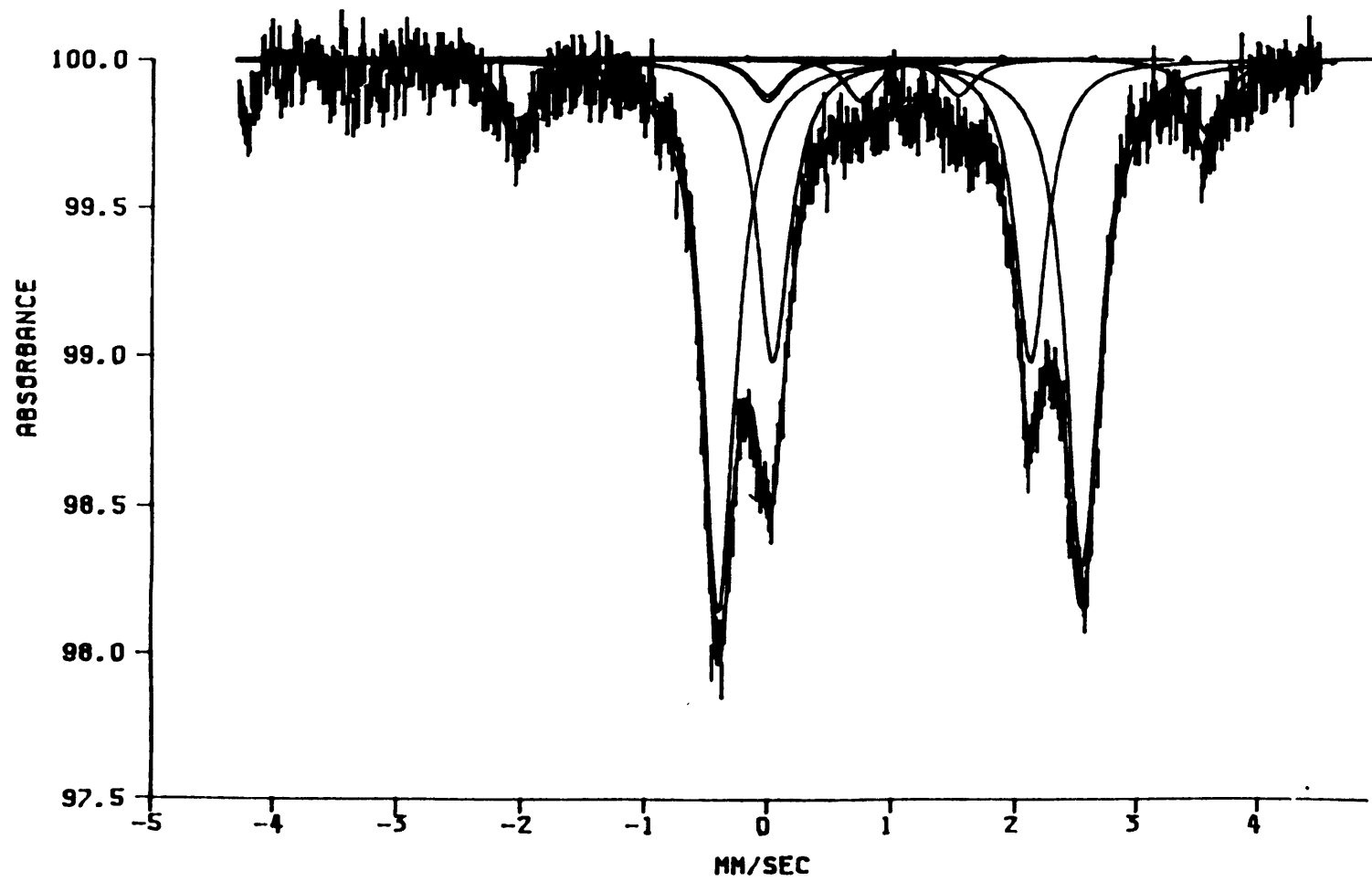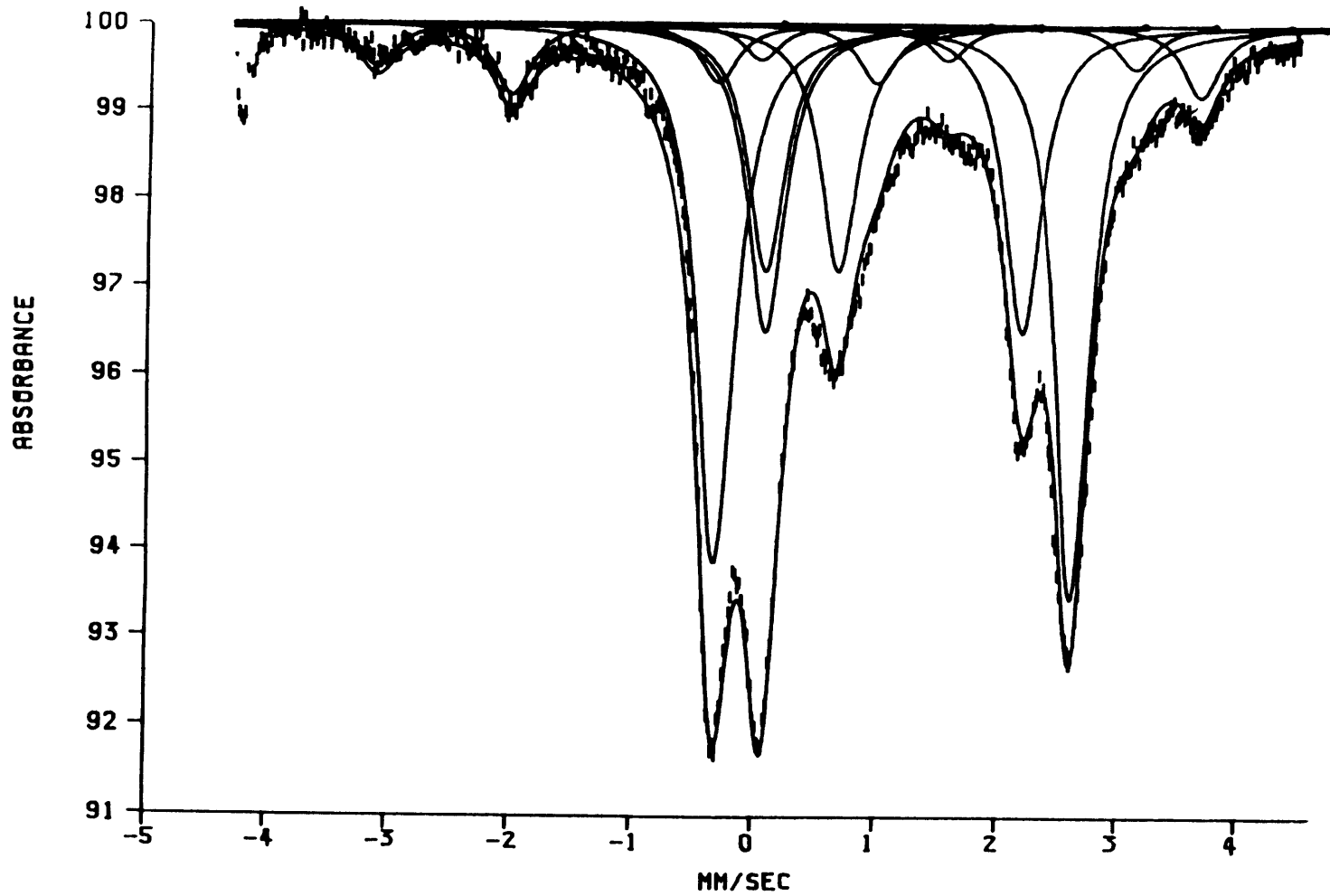
EUCRITE JUVINAS

ALHA80102 EUC A
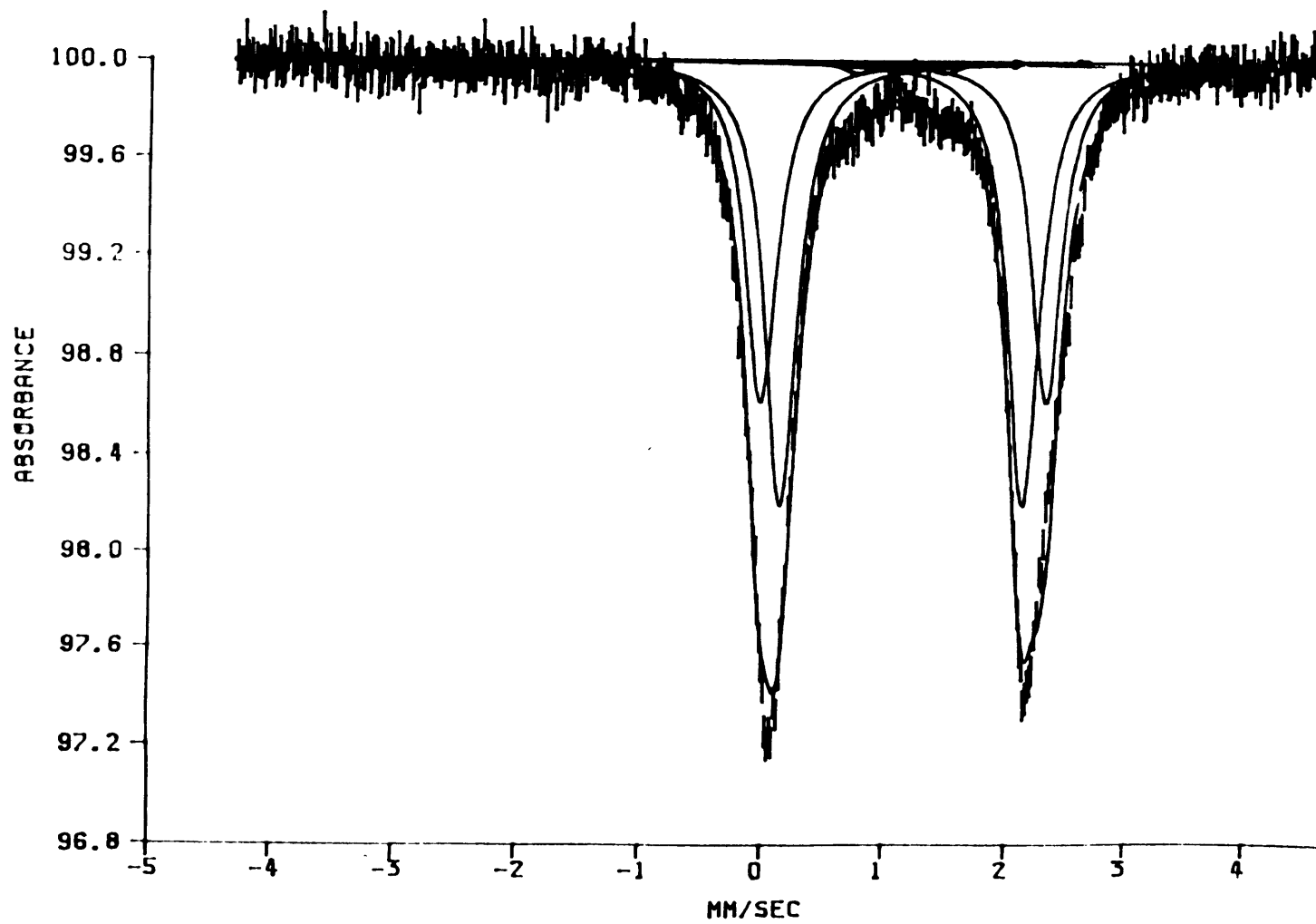
MM/SEC

ABSORBANCE

54

EET83232 EUC B

TATAHOUINE DIO

ABSORBANCE

MM/SEC

EETA79002 DIO A

57

ALMA77256 DIO A/B

58

NAKHLA

59

SHERGOTTITE 77005

ABSORBANCE

MM/SEC

60

SHERGOTTITE 79001 LITH A

ABSORBANCE

100

98

96

94

92

90

88

86

84

82

-5 -4 -3 -2 -1 0 1 2 3 4 5
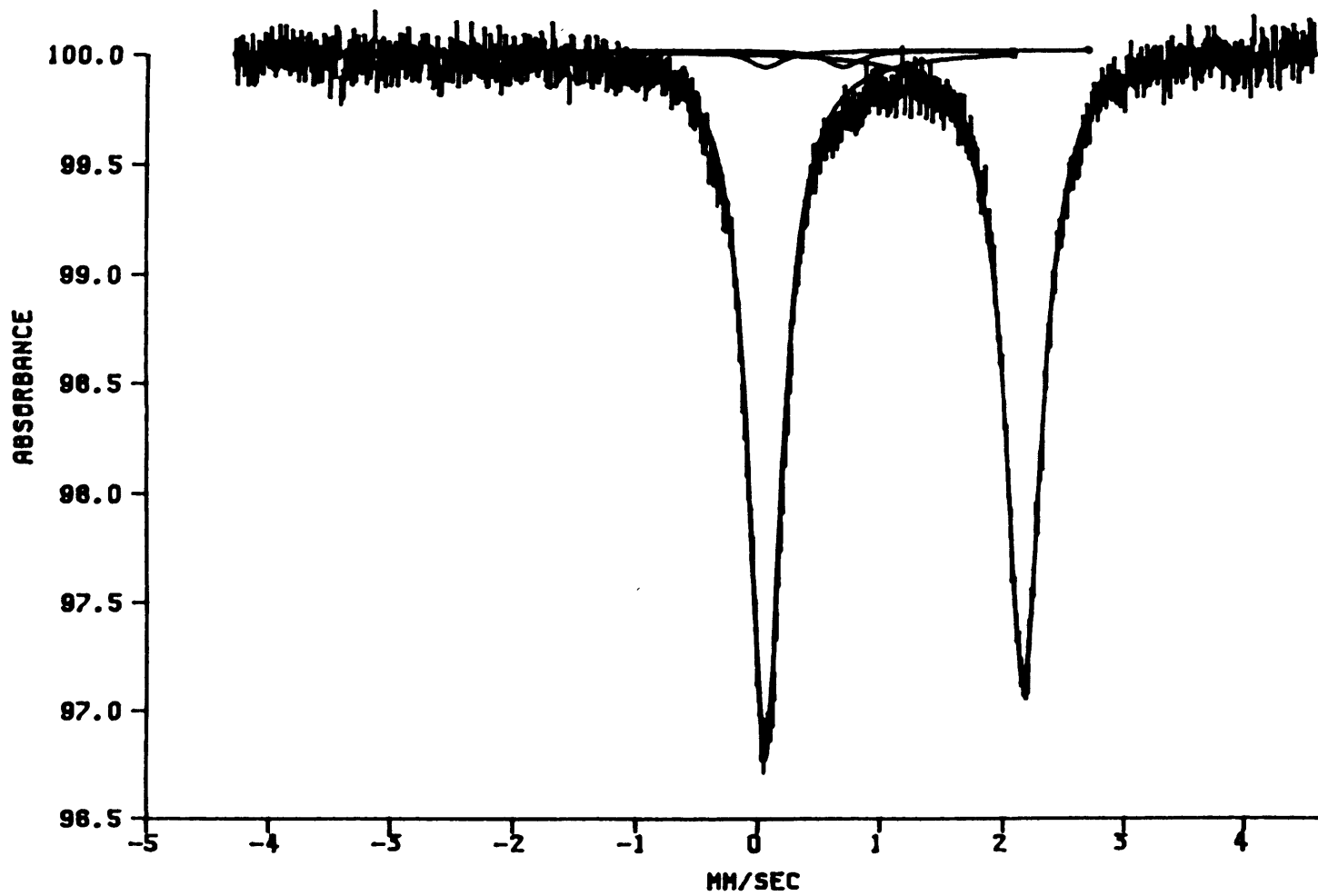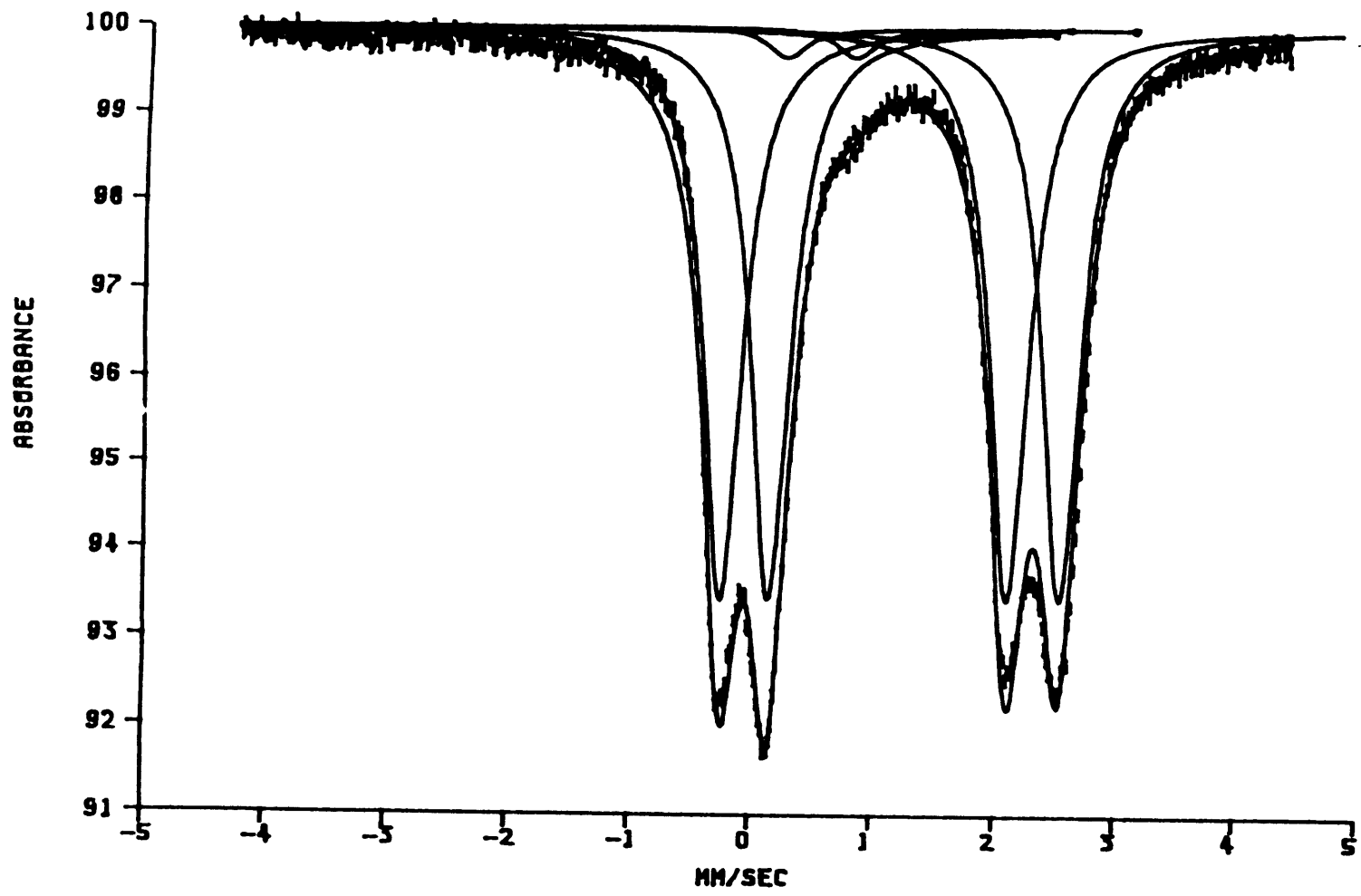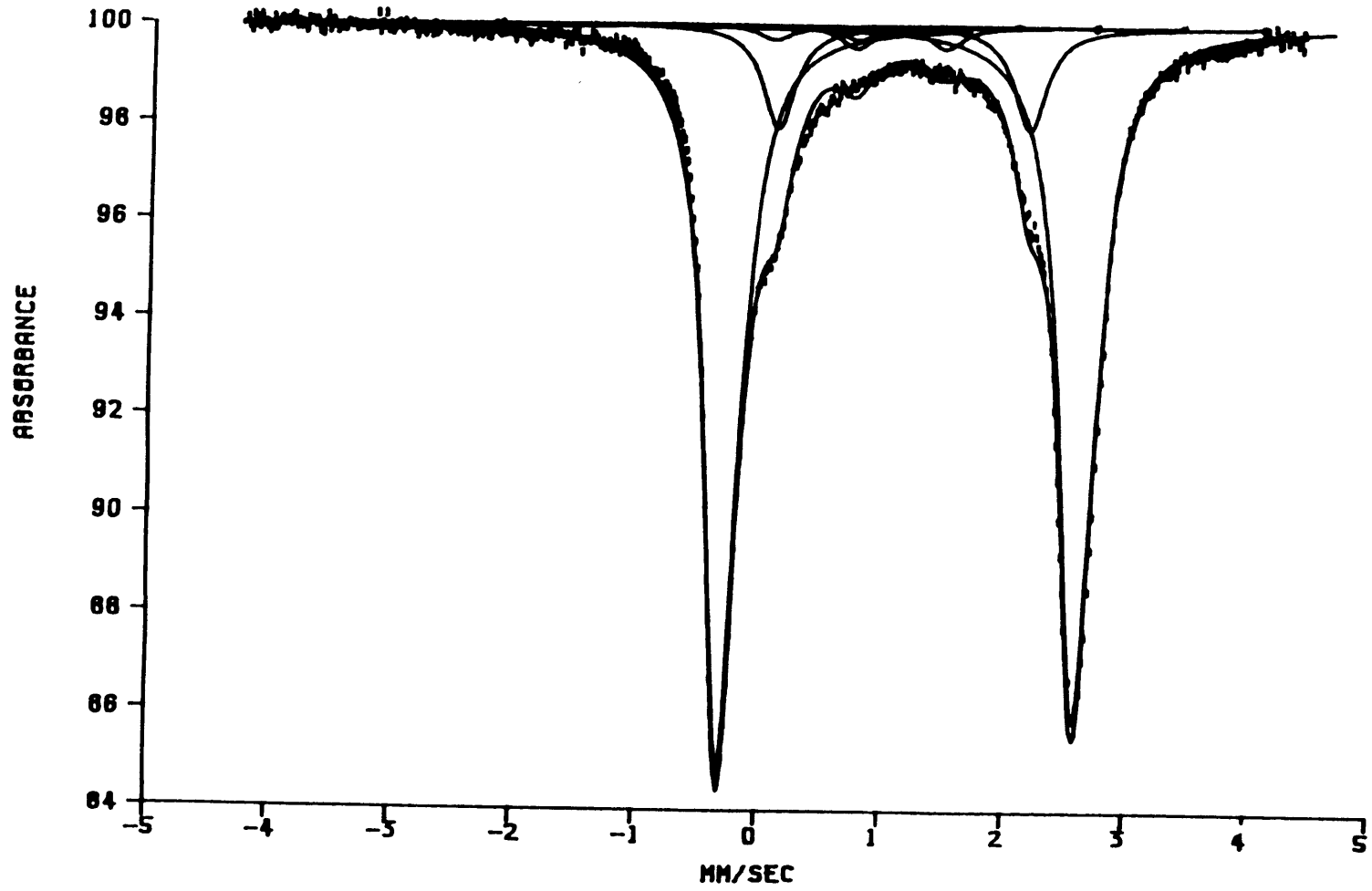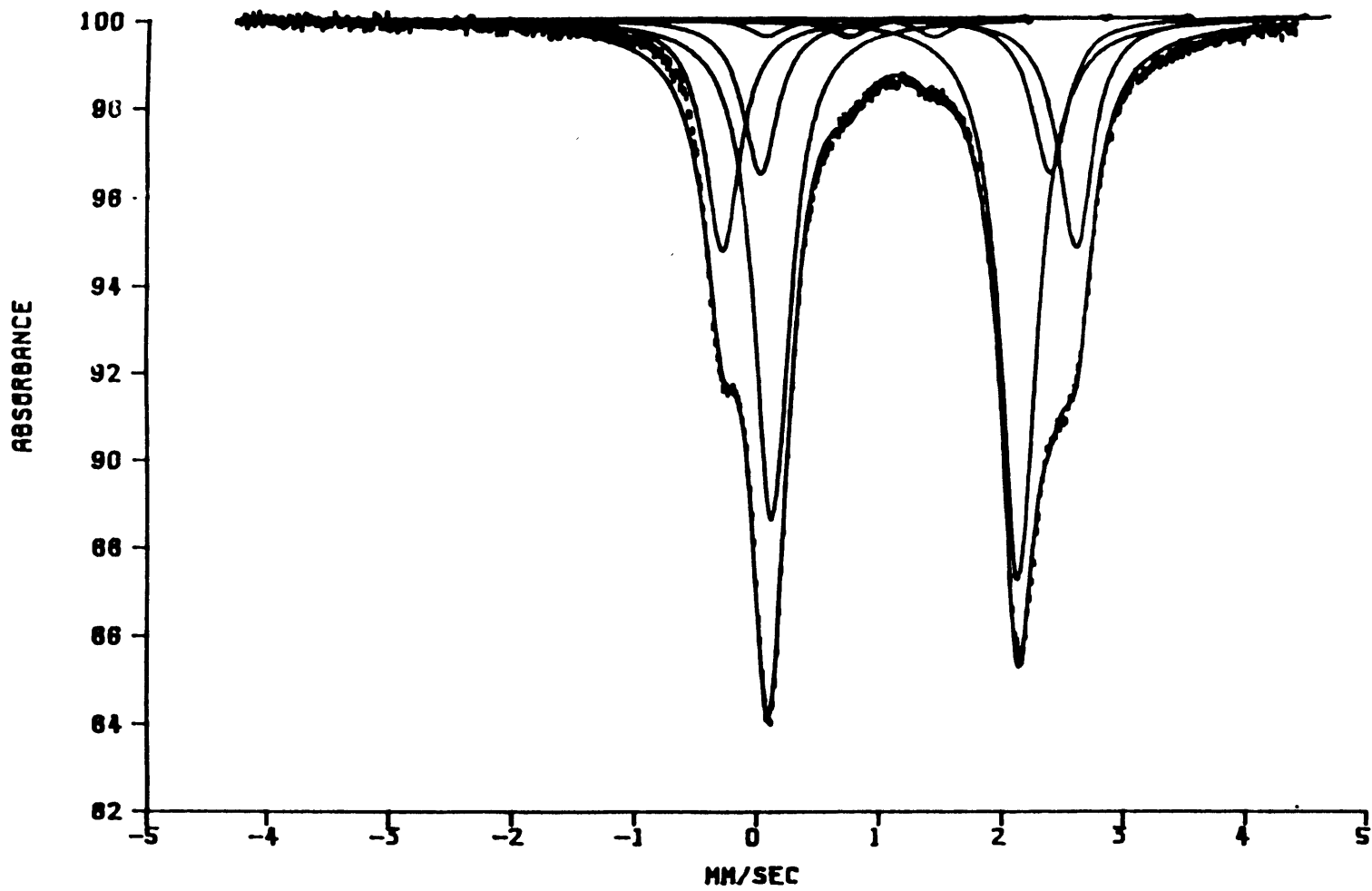
MM/SEC

SHERGOTTITE LITH C 79001

62
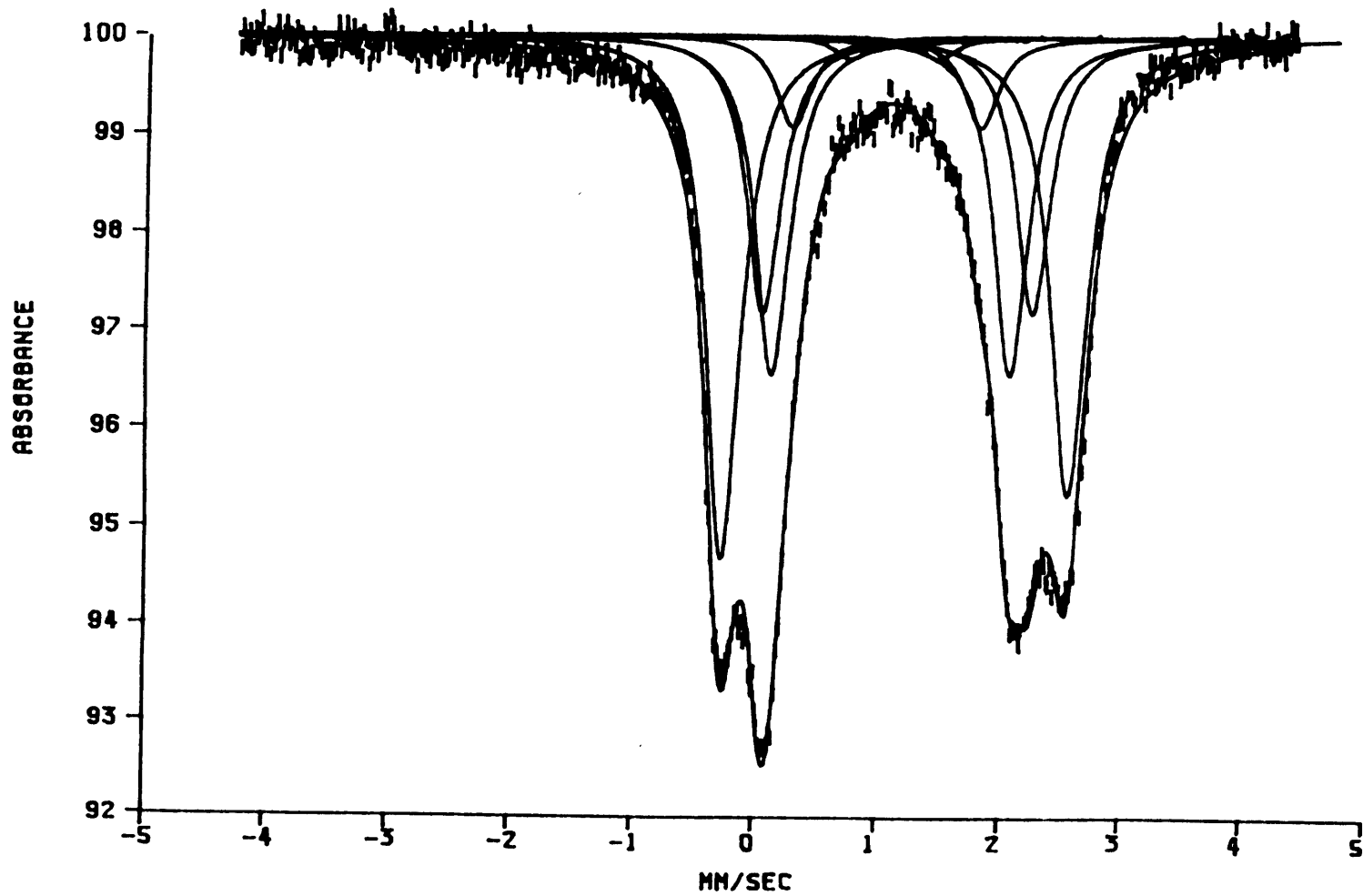
Table 2: Mossbauer parameters (in mm/sec)

Specimen	ol + py M1	py M2	pig M1	Fe^{+3} 1	Fe^{+3} 2	ilm	troil
L3 fall	1.14*	1.12*		.39*			.83*
	2.91**	2.09**		.69**			5.67#
L3 A/B	1.14	1.14		.39			.83
	2.90	2.07		.67			5.72
L3 B	1.13	1.13		.39			.84
	2.93	2.09		.71			5.70
L3 C	1.16	1.12		.42	.35		.82
	2.88	2.10		.58	1.25		5.70
L6 fall	1.14	1.14		.40			.84
	2.94	2.09		.63			5.70
L6 A	1.16	1.15		.42			.82
	2.90	2.04		.70			5.73
L6 A/B	1.17	1.16		.41			.82
	2.94	2.05		.68			5.73
L6 C	1.15	1.15		.41	.37		.83
	2.91	2.03		.62	1.32		5.72
LL6 fall	1.14	1.14		.38			.81
	2.90	2.07		.62			5.67
LL6 A	1.15	1.16		.37			.81
	2.93	2.10		.60			5.68
LL6 A/B	1.14	1.13		.38			.83
	2.93	2.10		.69			5.67
H fall	1.14	1.14		.42			.83
	2.95	2.09		.76			5.71
H A	1.14	1.14		.39			.82
	2.93	2.07		.75			5.72
H C	1.15	1.14		.39	.33		.83
	2.93	2.10		.60	1.30		5.68
euc fall		1.13	1.19	.40		1.11	
		1.98	2.42	.53		.70	
euc A		1.13	1.14	.41		1.10	
		1.98	2.33	.54		.70	
euc B		1,13	1.18	.41		1.11	
		1.99	2.38	.52		.70	
dio fall		1.14		.42			
		2.08		.67			
dio A		1.13		.49			.82
		2.11		.83			5.69

dio A/B		1.12		.39	
		2.10		.62	
nakhla	1.16	1.14		.55	
	2.78	1.95		.56	
sherg	1.15	1.15		.43	1.12
77005	2.89	2.04		.68	.73
sherg	1.17	1.13	1.22	.43	1.11
79001 A	2.88	2.00	2.35	.69	.70
sherg	1.15	1.10	1.15		1.10
79001 C	2.82	1.94	2.19		.70

* isomer shift values listed first (above) in each pair

** quadrupole splitting listed second (underneath) in each pair, except:

values for troilite = splitting (in mm/sec) between the 2nd and 5th peaks in the sextet; included as a consistency check.

65

Table 3: % Areas Under Peaks

Specimen	ol + py M1	py M2	pig M1	Fe^{+3} 1	Fe^{+3} 2	ilm	troil
L3 fall	62.98	23.52		1.54			11.98
L3 A/B	63.15	20.74		7.81			8.31
L3 B	67.24	19.86		5.32			7.56
L3 C	51.68	12.31		25.59	4.12		6.27
L6 fall	67.78	22.60		2.84			6.78
L6 A	63.78	23.92		4.74			7.55
L6 A/B	62.04	22.52		7.58			7.83
L6 C	58.42	22.00		10.08	1.42		8.31
LL6 fall	73.70	17.32		4.04			4.95
LL6 A	74.54	15.76		3.76			5.91
LL6 A/B	74.17	17.34		1.99			6.51
H fall	54.65	30.01		1.41			13.92
H A	54.56	30.01		4.28			11.13
H C	41.18	23.51		18.94	4.56		8.37
euc fall		69.00	27.23	.66		3.10	
euc A		55.56	42.67	.23		1.54	
euc B		67.58	23.44	3.54		5.43	
dio fall		99.40		.60			
dio A		92.32		2.32			5.34
dio A/B		97.64		2.36			
nakhla	48.76	49.64		1.58			
sh 77005	83.94	11.70		1.71		2.64	
sh 79001 A	24.03	55.78	16.18	1.93		2.08	
sh 79001 C	41.40	26.24	23.20			1.80	7.36*

*Fe^{+2}
glass

Chapter 6. <u>Interpretation of the Mossbauer Data</u>

In table 4, the data are summarized in the form of $\%Fe^{+3}$ for each class of meteorite and weathering type included in the study. Many useful and interesting conclusions can be reached from this table. First, one notices that the "control" samples, non-Antarctic meteorites classified as falls, have undergone some oxidation of their own. This was at first glance surprising, as these samples should not have undergone any terrestrial weathering if they were, in fact, picked up right away (with the possible exception of the Holbrook sample, this is a pretty good assumption). Because each sample was extracted from the interior of the meteorite, oxidation products from the fusion crust can be ruled out. Except for Nakhla, these are all standard classes of meteorites which would not be expected to have any preterrestrial ferric phases whatsoever.

This, then, leaves only one alternative: the weathering occurred during museum storage (!). The possibility of museum weathering of specimens is corroborated in part by the discovery of a museum curator that meteorites "breathe"; that is, that they take up moisture from the air, causing measurable differences in weight from day to day[1]. This has interesting implications for past and future studies of meteorites. The data in Table 4 show a range of ~0.5-4% Fe^{+3}; these numbers are significant, especially if one is looking for small amounts of preterrestrial ferric phases. A possible error is introduced of up to 4% in any study of museum specimens. For instance, all ferric Fe reported in one large study (giving 0.3-1.2% ferric Fe for ordinary chondrites) falls well within this range[2].

Table 4: %Ferric Fe by class

Class	Fall	A	A/B	B	C
L3	1.5		7.8	5.3	29.7
L6	2.8	4.7	7.6		11.5
H	1.4	4.3			21.2
LL6	4.0	3.8	2.0		
eucrite	1.5	0.2		3.6	
diogenite	0.6	2.3	2.4		
nakhla	1.6				
77005		1.7			
79001 A		1.9			
79001 C		0.0			

However, the problem of museum weathering should not exist in Antarctic samples, whose atmospheres have been quite carefully controlled during all stages of curation (with the possible exception of samples collected prior to 1978, see pg 16).

One of the main objectives of this study was to provide quantitative data which would clarify the Antarctic weathering classification scheme currently in use (ABC). The study was successful in setting upper and lower bounds for these categories, although unfortunately the variation within each field is substantial. Another problem is that although the ABC categories are usually self-consistent, this is not always the case. For instance, the L3 specimen labeled B was less weathered than the L3 specimen categorized as A/B (A should be least weathered, C most).

In order to arrive at numbers for classes of weathering, it can be seen from Table 4 that all meteorites cannot be treated alike; a division needs to be made between chondrites and achondrites, the achondrites being as a rule less weathered in a given category than chondrites. For instance, the eucrite labeled B is less weathered than any of the H or L meteorites labeled A. This principle is further illustrated by the fact that there are very few, if any, achondrite specimens available in the C class, while class C chondrites abound. This is partially because the weathering scheme is based on the amount of rust surrounding metal grains, a system which simply does not apply to many achondrites which do not contain significant metal. It is not clear why these meteorites were not all classified as A, other than the possibility that this type of weathering may appear to be more in thin section than it really is. Researchers should take

note of this discrepancy, and possibly the classification system should be changed to take it into account.

The reason for this difference can be easily explained by differences in mineralogy. Eucrites and diogenites contain only trace amounts of FeNi and troilite, the phases which one would expect to be the most easily weathered. On the other hand, most ordinary chondrites contain significant amounts of these minerals, sometimes up to ~20-25%. The SNC meteorites have a mineralogy which falls between these two extremes; they contain various oxides and sulfides such as pyrite, chalcopyrite, and magnetite not found in the other achondrites, but in general these minerals constitute only 2-3%, less than the chondritic Fe metal and troilite percentages.

It is possible that there are two different types of weathering going on, accounting in part for these differences. This is corroborated by that fact that all samples exceeding 8% Fe^{+3} show spectral evidence for a second set of ferric peaks (spectra shown in Figures 31-33). The first ferric doublet to appear is due to oxidation of the metallic Fe, a fact clearly shown by the thin section descriptions; most describe a weathering halo around FeNi grains. This probably makes up the bulk of the ferric phase in chondrites. The second type of weathering is either due to oxidation of troilite or of the silicates present, olivine and pyroxene. This may be the predominant type of oxidation in the achondrites, and explains why weathering is so slow to appear in these specimens. These two types of rust were reported by Gooding, classified as "metallic" and "sialic" respectively, based on microprobe compositional analysis[3].

Figures 31-33

These figures show the presence of two ferric doublets in all three spectra of meteorites classified as C. The first doublet to appear is the largest, and can be found in the region between 0 and 1 mm/sec. The second doublet has its high velocity peak just to the right of the high velocity peak of the first doublet, ~0.8mm/sec. The low velocity peak is offset more to the left, and can be found at ~-0.3mm/sec.
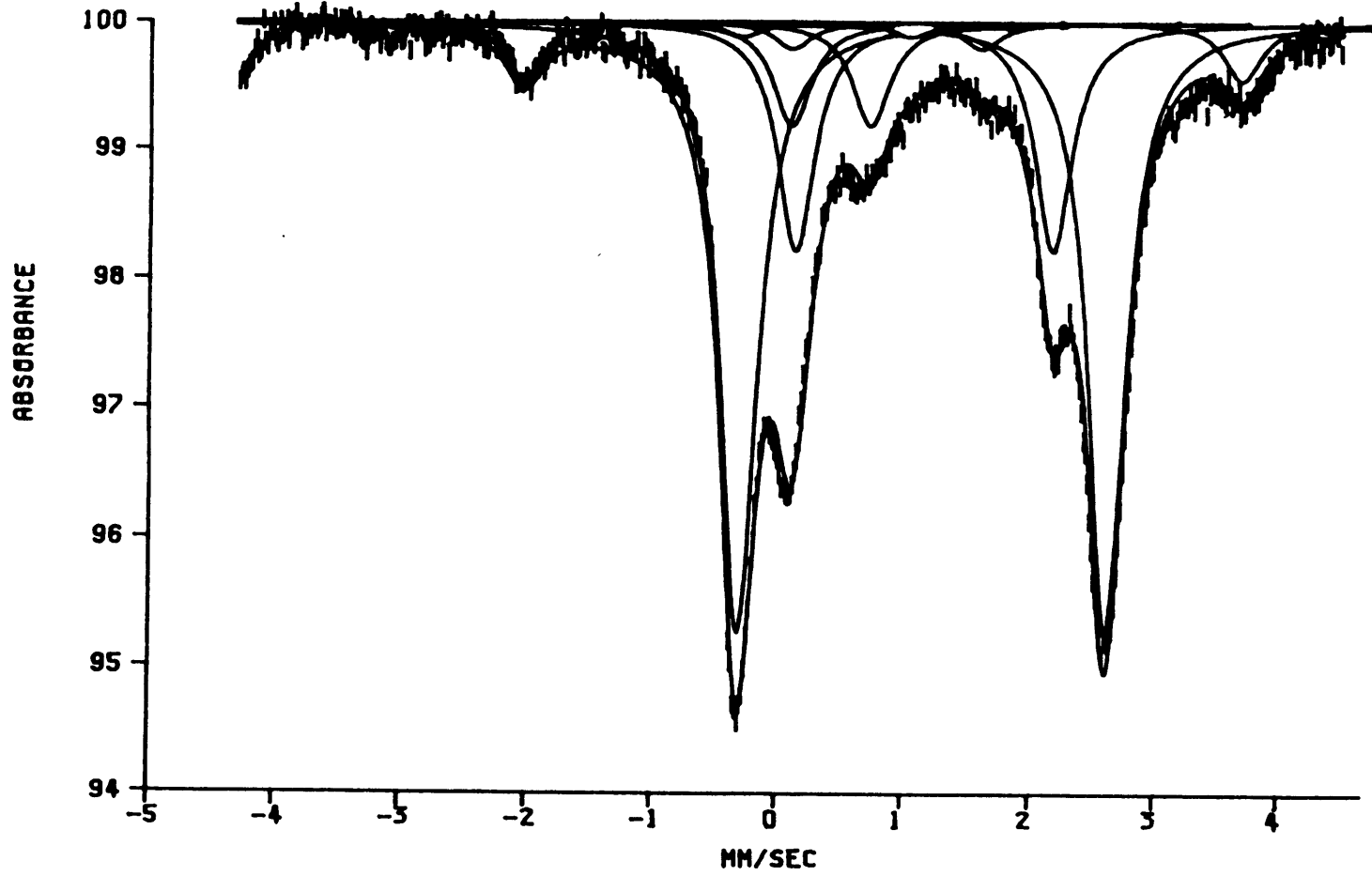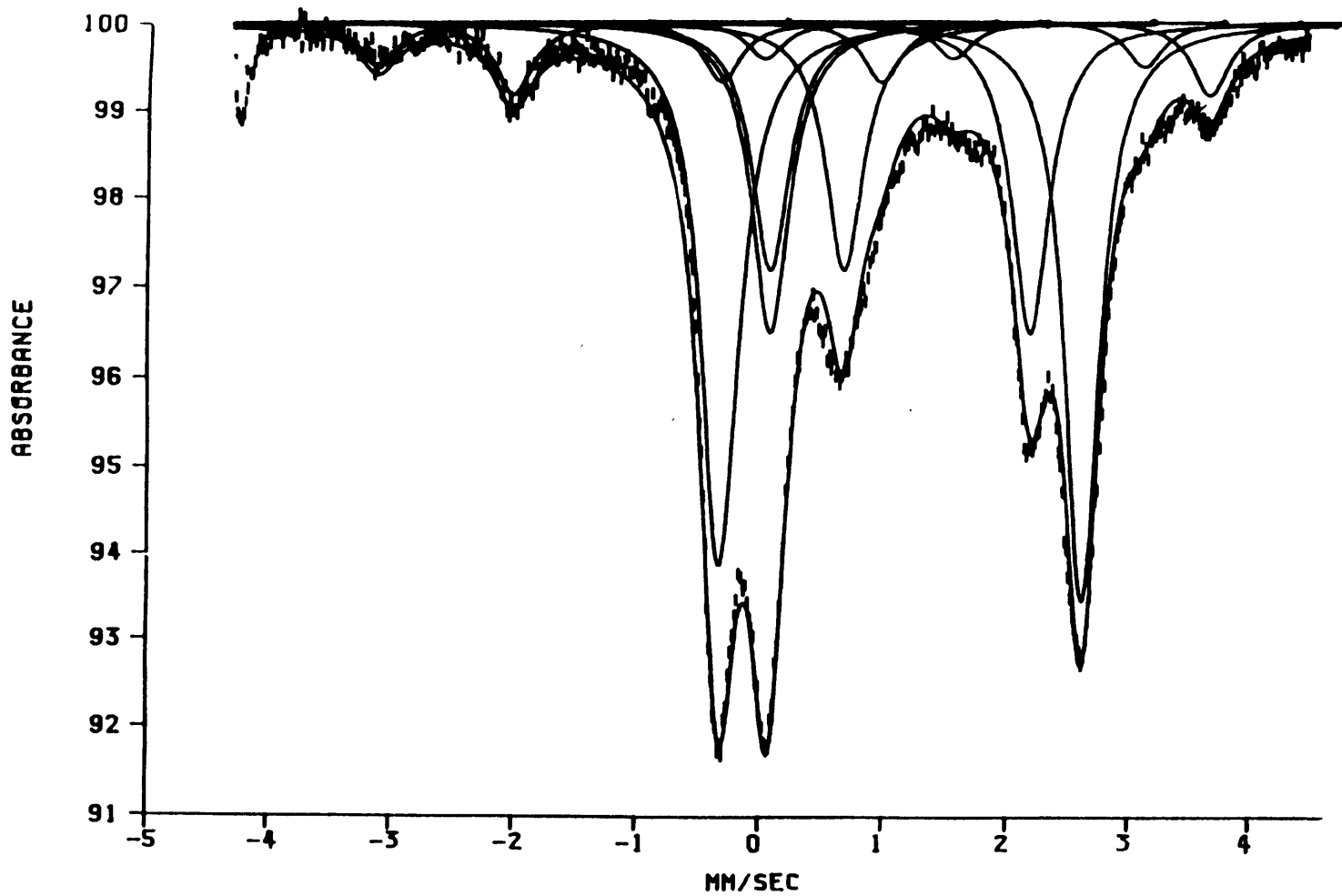
ALHA77214.18 L3 C

71
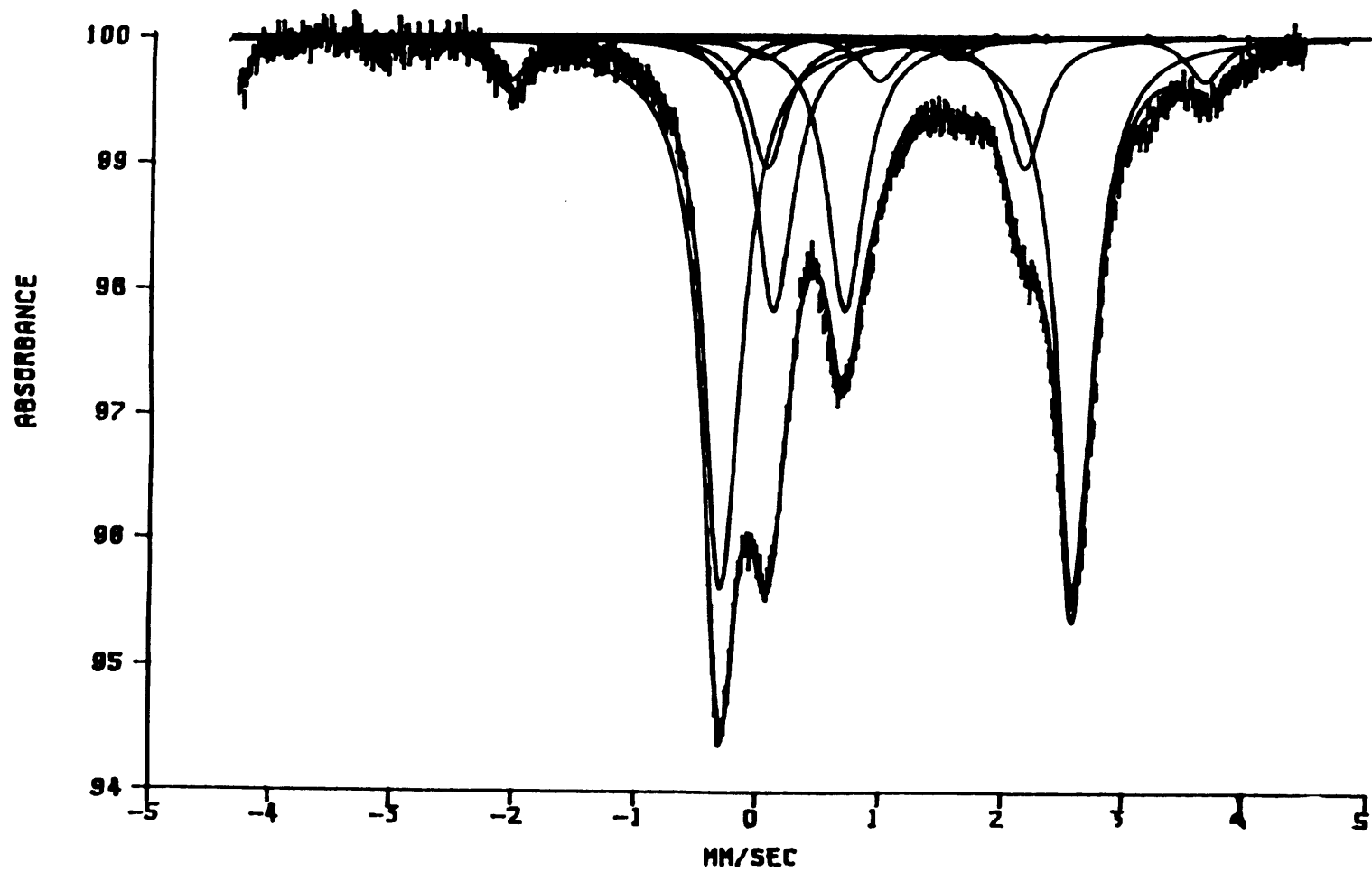
ALHA81027 L6 C

72

H6 C ALHA 77271

73

In addition to the above effect, there also seems to be a clear difference in the amount of weathering undergone in the different localities of Antarctica. Those chondrites which are less weathered than most, both LL6 samples and the previously mentioned anomalous L3 B sample, are all from localities outside the Allan Hills area, whereas the remaining chondrites originated from the Allan Hills. In addition, the two LL6 specimens originated from separate regions. It is also true that most, though not all, of the achondrites were collected outside of the Allan Hills area. This is very interesting, as it hints at differences in the ice field flows, surface exposure times, or terrestrial ages. Differences in terrestrial age have been reported between Victoria Land specimens and the other Antarctic localities[4]. Unfortunately, not enough data exist to compare ages of various localities within Victoria Land. However, specimens from the Allan Hills and Elephant Moraine are found in geographically close proximity (see Figure 2), but still exhibit quite large weathering variations. This evidence seems to argue strongly in favor of weathering taking place during burial; the greatest difference between sample histories is presumably not the amount of time they have spent at the surface, but the amount of time they spend buried in the ice sheet, this variable being controlled by the ice-flow kinetics at that site. More work needs to be done to solve the question of whether such burial weathering is possible, and to determine what makes the Allan Hills different from all other collection sites. Meanwhile, researchers should take note that Allan Hills specimens are likely to be more weathered than other specimens.

It is clear that the present classification scheme is inadequate; inaccuracies exist because of differences in mineralogy and origin. However, some useful guidelines can be put forward. The vast majority of samples now available for research are chondrites from the Allan Hills. For these specimens, the following categories can be set forth: "A" samples contain at least 4-5% ferric phases, "B" samples from 7% to ~8-10%, "C" samples from 10% to 30% (the highest in this study). Specimens from other locations, as well as achondrites in general, will show lesser degrees of weathering.

Now that the groundwork has been laid, the other important objective of this study can be pursued--how do the SNC's fit into this scheme, and what can be learned about them using Mossbauer analysis? The nakhlites and shergottites in this study (except EETA79001 lith C, which will be dealt with later) all fall between the chondrites and achondrites with respect to their ferric content. If preterrestrial weathering is ignored for the moment, this is just what would have been predicted based on their mineralogy. (All three samples fall within a narrow range: 1.5-2% Fe^{+3}, so the differences in their origin are probably unimportant.) From this, one must conclude that any Martian weathering products present are present in relatively small quantities, at most, 1%. Unfortunately, it seems that Antarctic weathering processes are of sufficient magnitude, even in the most unweathered specimens, to make this level of detection impossible by Mossbauer spectroscopy, and difficult for other techniques as well. SEM petrologic evidence seems to hold out the only hope for such work, and is currently being pursued with interesting results by James Gooding, et al[5]. However, it can

definitely be said that SNC meteorites found so far are not rocks from the *surface* of Mars, where one might expect to see much higher degrees of weathering, but probably have their origins in the crust or upper mantle.

One place where a larger amount of Fe^{+3} might have been expected was in the glass-rich lith C of EETA79001. This glass is dark brownish-black in color and closely resembles the terrestrial glass-like material hisingerite, postulated to occur on Mars[6]. However, Mossbauer analysis failed to detect any Fe^{+3} phases at all; instead, a doublet corresponding to Fe^{+2} in the glass phase appeared in addition to the peaks attributable to lith A, which was impossible to entirely separate from lith C. The absence of ferric-bearing glass is in contrast to the assumptions made in various microprobe analyses of lith C already performed which report Fe as Fe_2O_3, partly to compensate for low totals[4]. These analyses will need to be recalculated, as there is now no support for this assumption.

At this stage, it is important to address the question of the identity of the ferric phase or phases. Mossbauer analysis was thought to be an especially good tool for this determination, since many of the weathering products proposed in the literature would be easy to identify--goethite, hematite, and magnetite all have six-line spectra at room temperature which are easily identifiable and distinguishable from the overlapping paramagnetic peaks. However, it is interesting to note that no magnetic peaks were detected in *any* sample, other than the original troilite and FeNi peaks.

The absence of additional sextets seemed to rule out any of these oxides; however, because the weathering products bear a

resemblance to rust in thin section, there was a possibility that the beta- or gamma-FeOOH minerals akaganeite and lepidocrocite were present. These minerals have been found as weathering products of certain kinds of meteorites not directly related to the SNC's. Moreover, the room temperature spectra of these FeOOH polymorphs comprise one ferric doublet. Alternatively, it was possible that the rust product was microcrystalline FeOOH (<200A). Other possibilities included Fe-sulfates, Fe-rich clays or other aluminosilicates.

In order to distinguish betweem these various possibilities, it was necessary to make use of XRD and low temperature Mossbauer spectroscopy. Results of these experiments are described in the following two chapters.

References:

1. Lipschutz, M. E., personal communication

2. Herr and Skerra (1968) Mossbauer spectroscopy applied to the classification of stone meteorites Meteorite Research (P. M. Millman, ed.) Austria p106-122

3. Gooding (1986) Clay-mineraloid weathering products in Antarctic meteorites GCA Vol 50 p2215-2223

4. LPI Technical Report 86-01 (1986) International Workshop on Antarctic Meteorites Johnson Space Center, Houston

5. Gooding, Wentworth, and Zolensky (1987) Martian (?) calcite and gypsum in shergottite EETA79001 Lunar and Plan. Sci. XVIII (abstract)

6. Burns (1986) Hisingerite and iddingsite: Deuteric alteration products of basalts on Mars Lunar and Plan. Sci. XVII p93-94 (abstract)

Chapter 7. X-ray Diffraction

X-ray diffraction experiments were run with two purposes in mind: to help identify the weathering product(s) present in the Antarctic specimens, and to search for unusual phases in the glass-rich lith C. Six chondritic specimens were measured including one A and one C sample from each of the three meteorite classes in which C samples were available--H, L3, and L6. In addition, lithologies A and C from EETA79001 were run.

X-ray powder diffraction measurements were obtained using a Phillips X-ray generator and DeBye-Scherrer cameras. Cobalt radiation was used, with an Fe filter. Experiments were run for a minimum of 12 hours, and XRD patterns recorded on film.

Unfortunately, these experiments were on the whole inconclusive. No extra lines could be detected in either the glass phase or in weathered C samples. However, a number of possibilities were ruled out -- no lines corresponding to any of the FeOOH polymorphs were found. This left as possible ferric phases either microcrystalline FeOOH polymorphs, which do not appear in XRD, or clay-like silicates, whose XRD lines would be obscured by the predominant minerals in the meteorite and whose Mossbauer parameters would be similar to those recorded in Table 2. However, diagnostic 7 and 10 angstrom lines were missing from the XRD pattern, implying that sheet silicates were not present.

Chapter 8. <u>Liquid Nitrogen Mossbauer Spectroscopy</u>

In order to distinguish between the ferric alternatives left to us, Mossbauer spectra were obtained at liquid nitrogen temperature (77K). If the ferric phase present were in fact microcrystalline FeOOH, magnetic six-line spectra would be expected to appear at low temperatures.

The Neel temperature for pure, well-crystallized goethite is ~400K, well above room temperature. Akaganeite has a Neel temperature of 293K, and lepidocrocite, 73K. Thus, one would normally expect to see a sextet at room temperature in the Mossbauer spectrum of goethite, and doublets in that of akaganeite and lepidocrocite. However, there are various factors which can lower the Neel temperature of goethite, sometimes below room temperature. The most important of these effects relate to non-stoichiometry, small particle size, and the presence of structural defects[1]. For instance, substitution of Al for Fe beyond the 10% level reduces the Neel temperature of goethite to below room temperature; particle sizes below 200A have the same effect. (It is important to note here that such particle sizes are not large enough to allow coherent scattering of an X-ray beam, thus no lines will appear in XRD.)

All of these effects disrupt the antiferromagnetic coupling along the c-axis, causing the magnetic peaks to distort, and in some cases disappear altogether, with the corresponding appearance of a paramagnetic doublet in the ferric region. However, the Neel temperature is not lowered very far below room temperature, and

liquid nitrogen temperatures should cause a reappearance of the magnetic lines. These lines are still not as sharp as in the spectra of perfectly crystalline goethite, but rather are broadened and asymmetrical[1]. In addition, it has been shown, using microcrystalline hematite, that the appearance of the magnetic sextet as the temperature is lowered is a gradual effect--the paramagnetic peaks are not lost entirely until nearly 20K[2].

Evidence for microcrystalline weathering products of Martian rocks has been recently presented by Agresti and Morris[2,3]. They noted that many of the features of reflectance spectra of Martian surface rocks are very closely correlated with the features of microcrystalline hematite spectra. Although this interpretation is controversial, it at least provides some evidence that Martian rocks could weather to microcrystalline compounds. Synthetic hematite was produced on silica gel, which provides spaces small enough to harbor the microcrystals. It might be mentioned at this point that some of the SNC meteorites are described in thin-section as having porous groundmasses (see pg 20). As for the mineralogy, it does not seem too surprising that the terrestrial weathering product might be the more hydrous Fe oxide, goethite.

Mossbauer spectra of the three most weathered (C) samples were taken at 77K and compared to the previous room temperature runs. These spectra all showed a significant (~50%) decrease in the intensity of the paramagnetic ferric doublet; these spectra appear in Figures 34-41. The room temperature spectrum appears first, then the 77K spectrum in each case. Unfortunately, the size of the ferric doublet compared to the baseline scatter makes it very difficult to

Figures 34-41

These figures show the reduction of the ferric doublets at 77K. This reduction is most easily noticed in the region between 0 and 1 mm/sec.
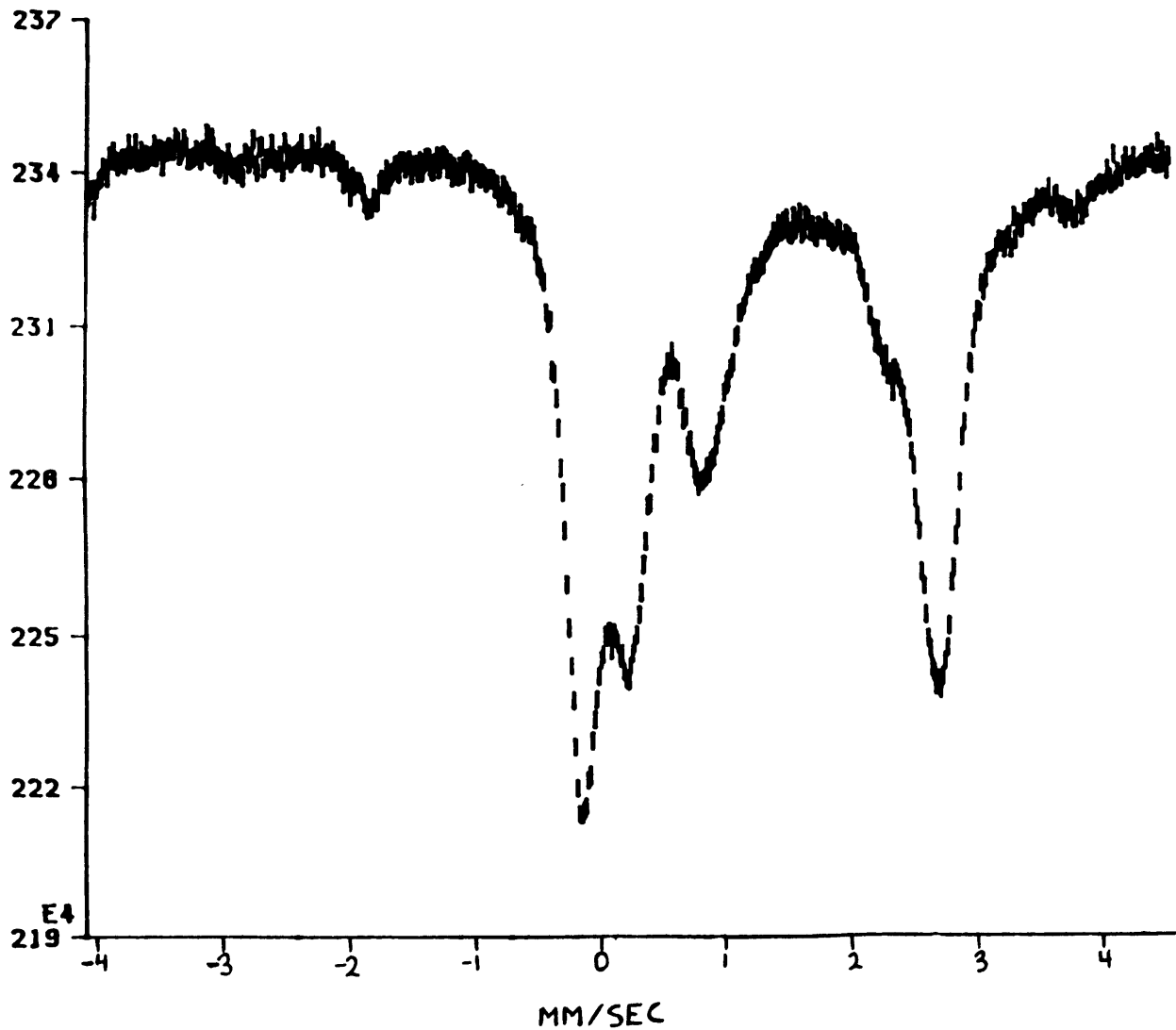
Figures 34, 35: L3 C normal scale. RT, 77K

Figures 36, 37: L3 C expanded scale. RT, 77K

Figures 38, 39: L6 C expanded scale. RT, 77K

Figures 40, 41: H6 C expanded scale. RT, 77K
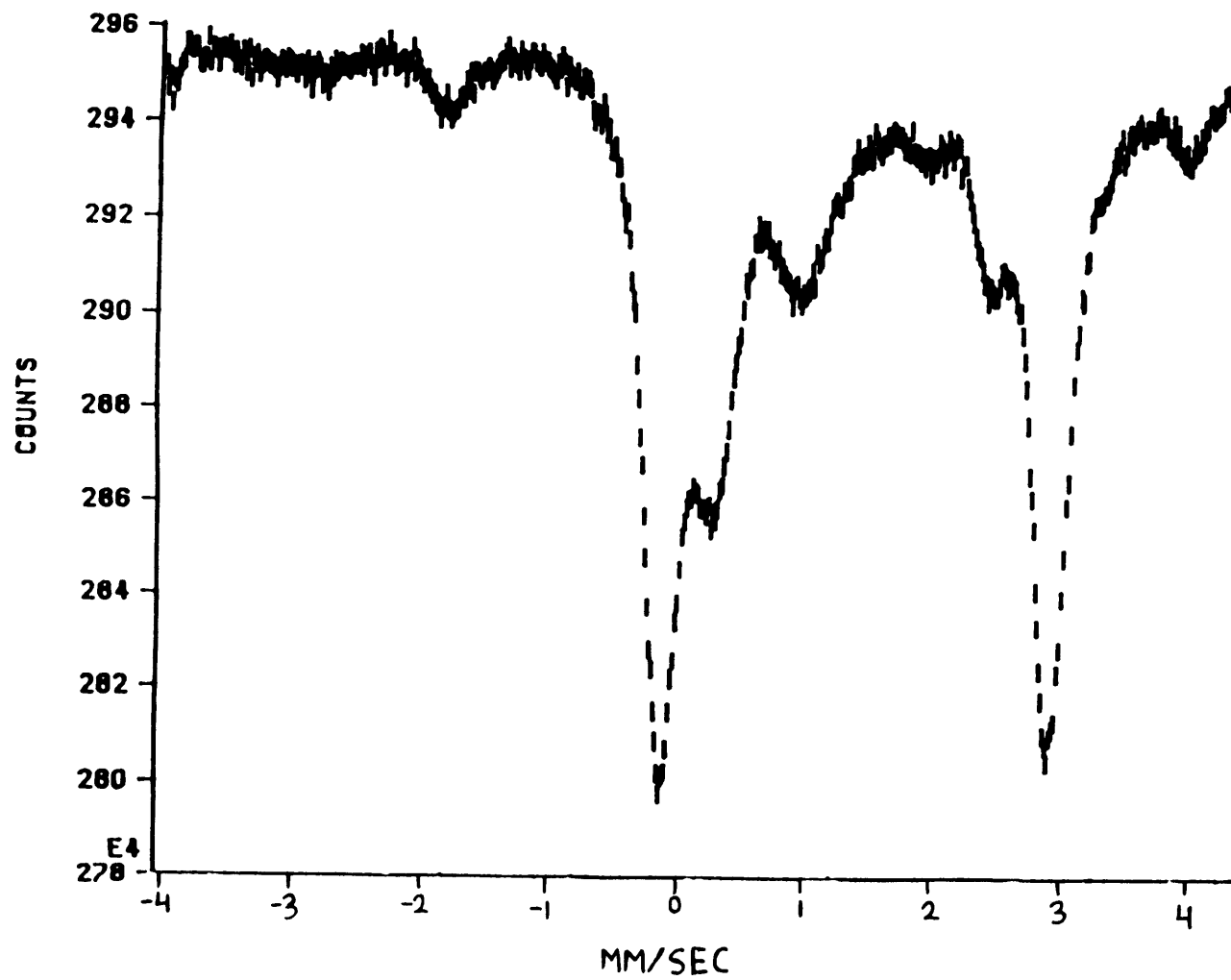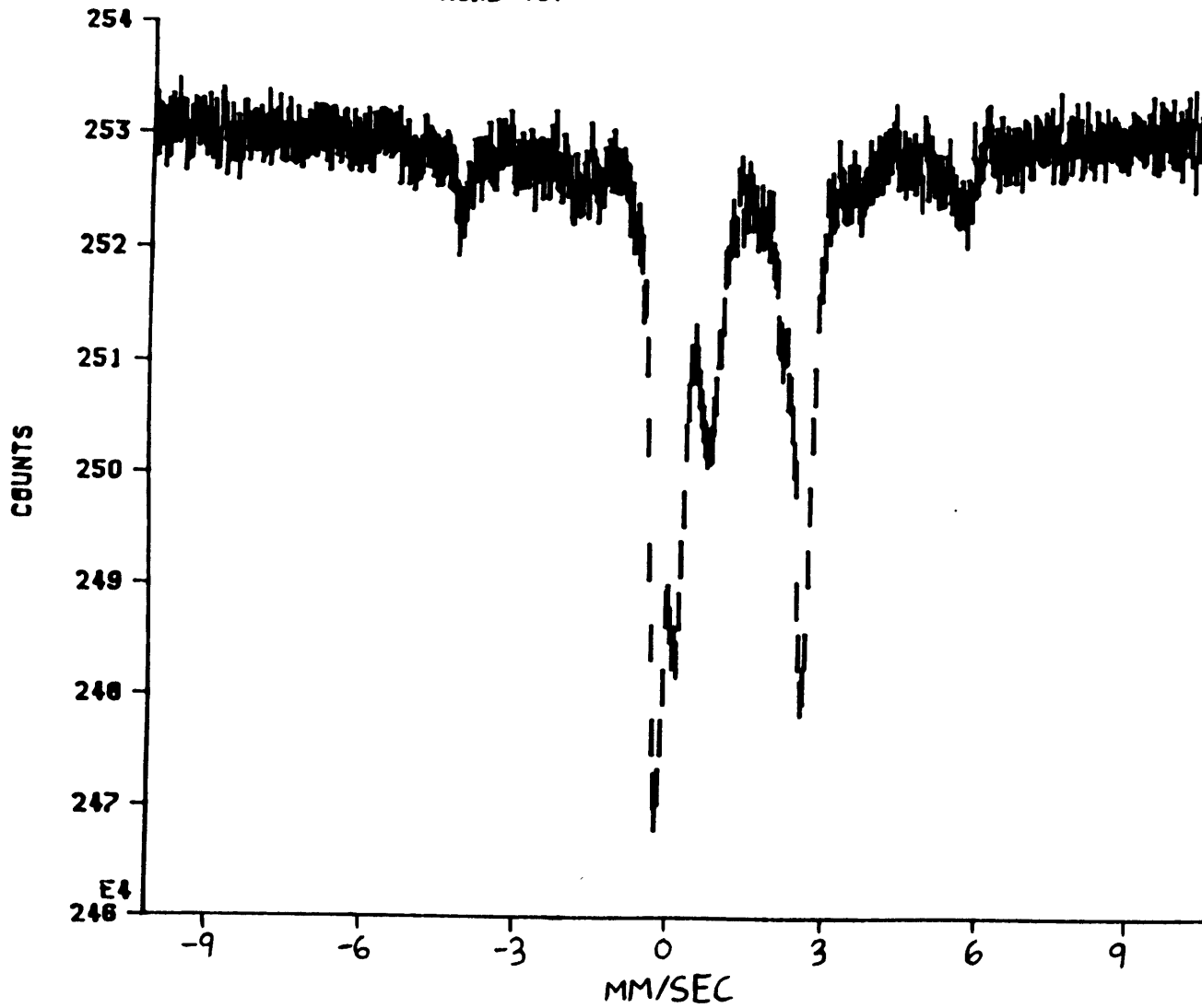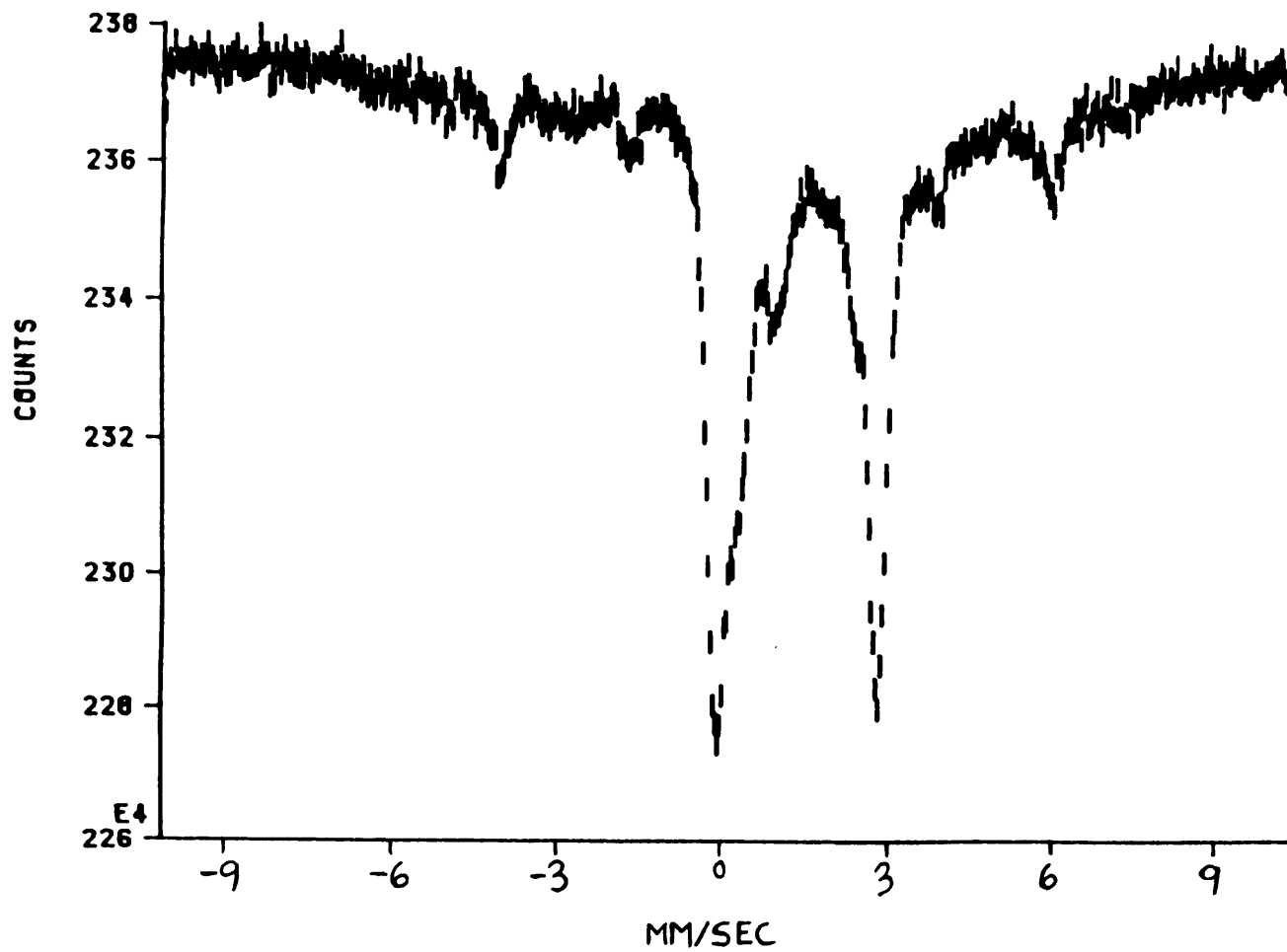
ALHA77214   L3 C

82

ALHA 77214   77K   L3 C

83

296

294

292

290

288

COUNTS

286

284

282

280

E4
278

-4   -3   -2   -1   0   1   2   3   4

MM/SEC

ALHA 77214   L-3 CHOND (C)

84

ALHA 77214   77K   L3   C

85

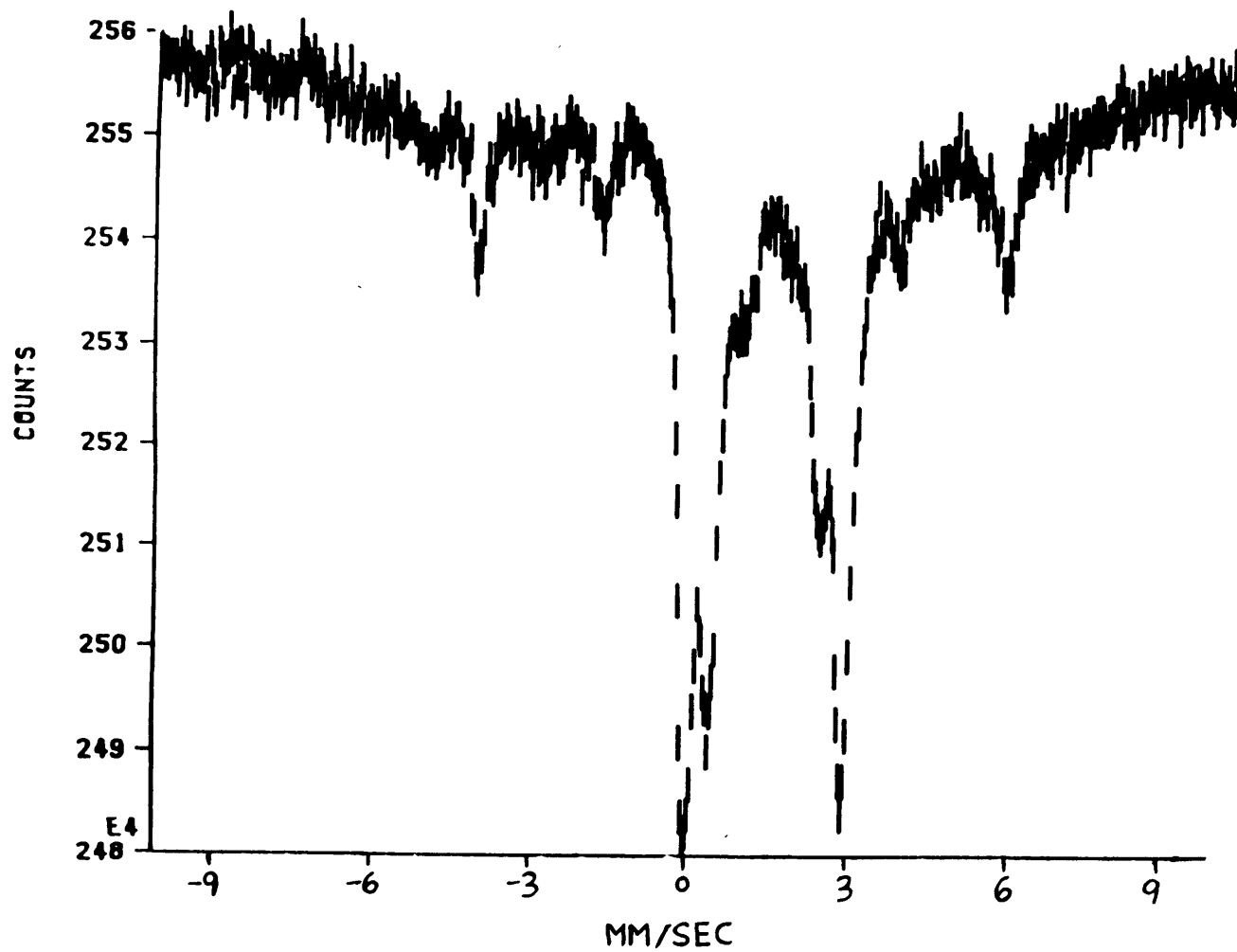ALHA 81027   L-6 CHOND (C)

COUNTS

MM/SEC

86

ALHA 81027   77K   L6 C

87

ALMA 77271   H-6 CHOND (C)

88

ALHA 77271   77K   H6   C

89
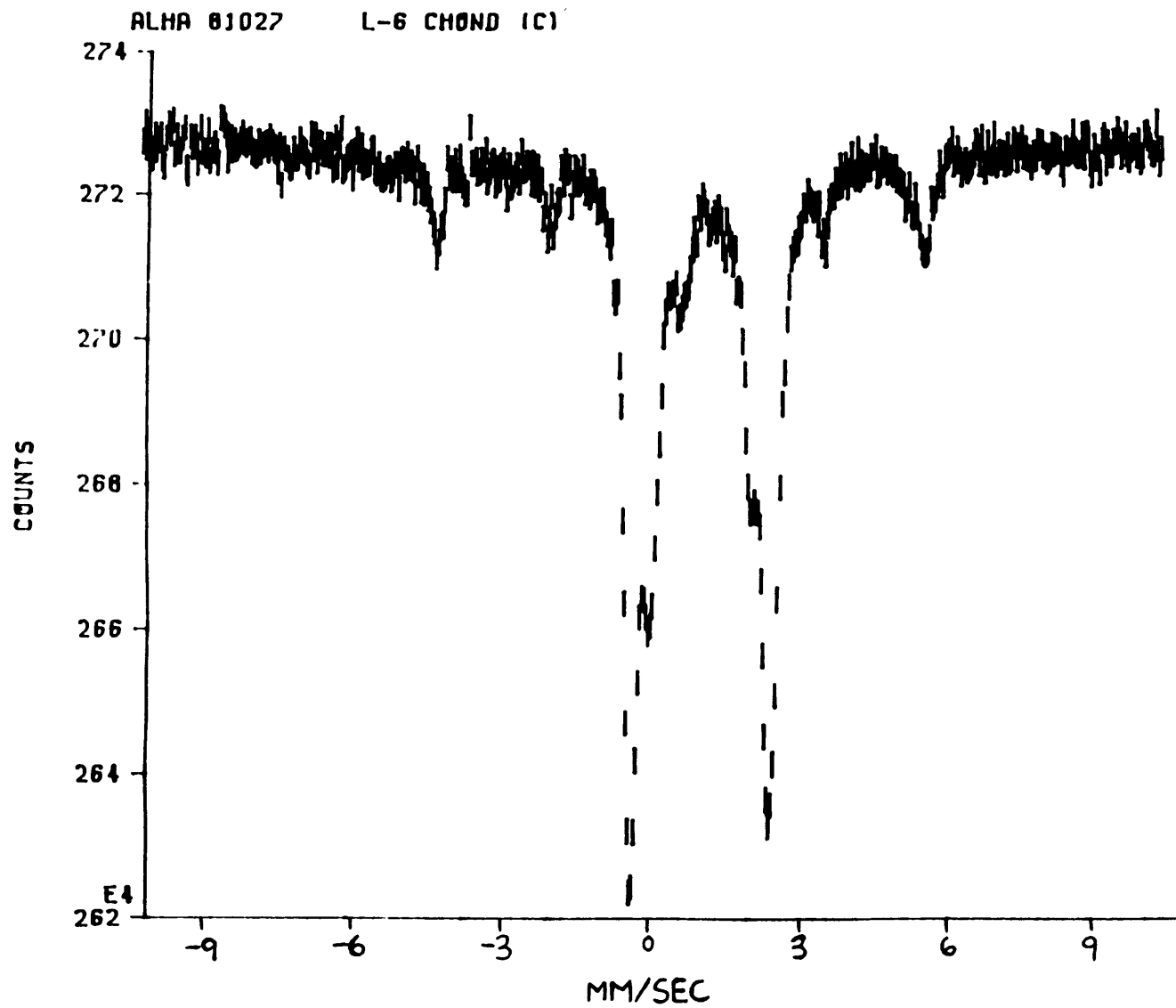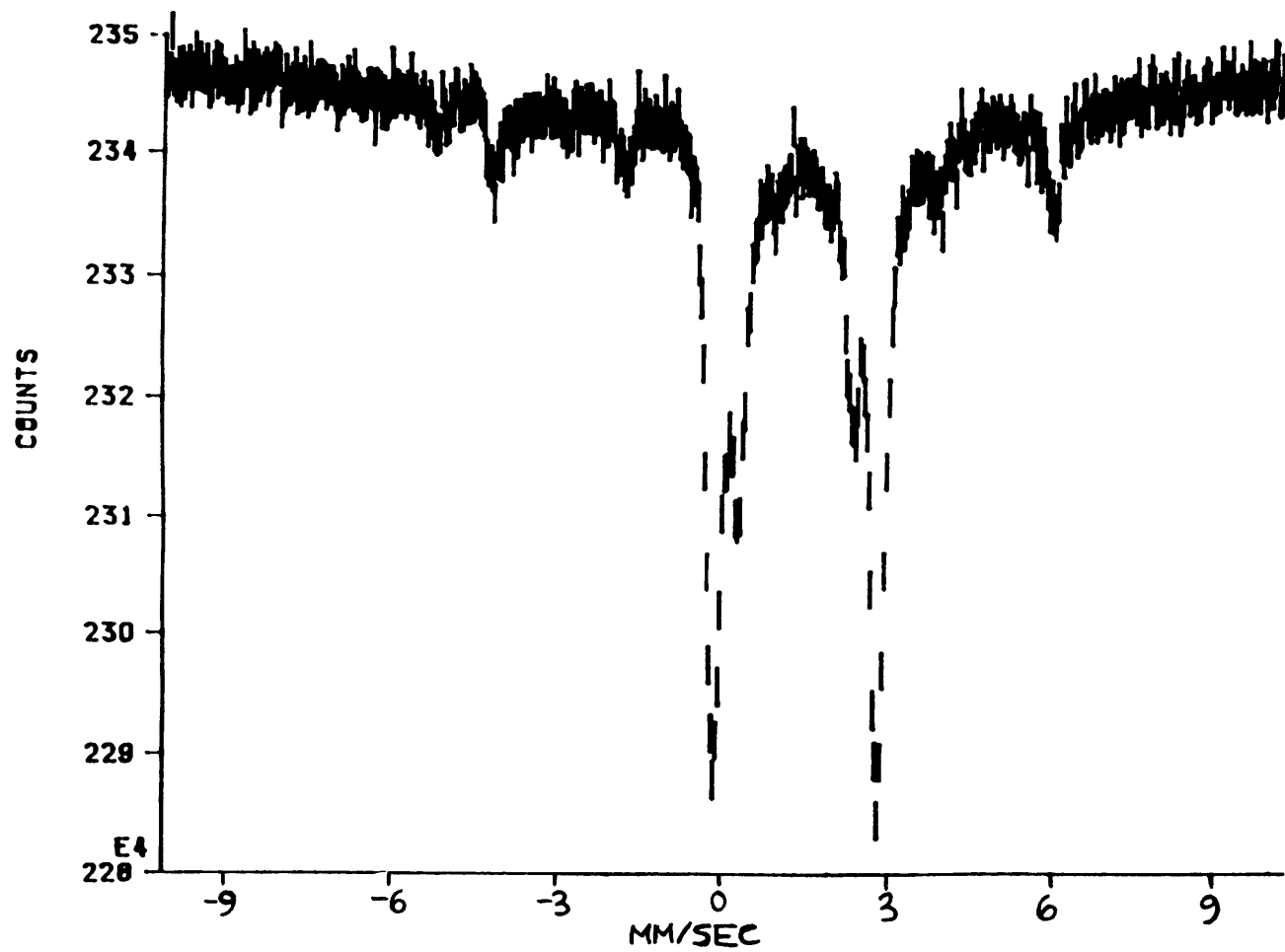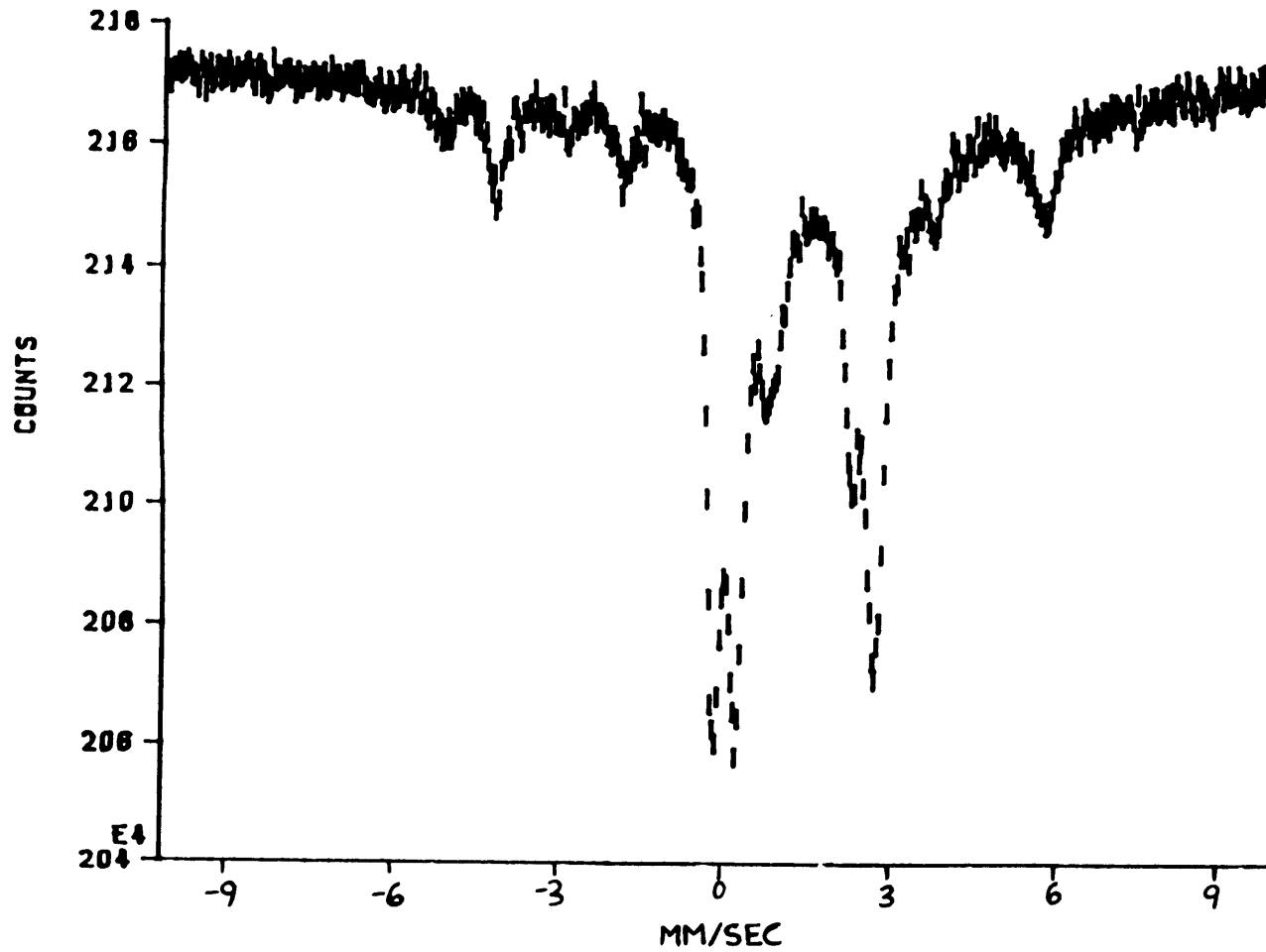
determine whether corresponding magnetic peaks have appeared, especially since the area lost under the paramagnetic doublet must be spread out among six magnetic peaks. However, there appears to be no other plausible explanation for the 50% disappearance of these peaks. The FeOOH polymorph lepidocrocite can now be ruled out, since its Neel temperature is so low that one would not expect to see significant disappearance of its doublet at 77K. The paramagnetic parameters of the ferric doublet (see Table 2) are consistent with either paramagnetic goethite or akaganeite, and on the basis of these studies these two possibilities cannot be distinguished between.

The possibility still exists that some of the remaining ferric phase is a form of ferric-rich clay-silicate, which could be expected to have parameters similar to those obtained. (Although there has been no work substantiating the existence of a microcrystalline clay, there is no reason to rule it out). This is likely, in view of the fact that in all of these samples the spectra are thought to contain two ferric phases. However, there is probably a paramagnetic FeOOH component left over as well, since the paramagnetic peak should not entirely disappear until a lower temperature.

References:

1. Murad (1982) The characterization of goethite by Mossbauer spectroscopy Amer. Min. 67 p1007-1011

2. Agresti, Newcomb, and Morris (1987) Mossbauer study of ultramicrocrystalline hematite Lunar and Plan. Sci. XVIII p7-8 (abstract)

3. Morris et al (1987) <u>Ultramicrocrystalline hematite: Properties and occurrence on the Martian surface</u> Lunar and Plan. Sci. **XVIII** p668-669 (abstract)

Chapter 9. Summary and Conclusions

This project represents the first large-scale study of iron oxidative weathering in Antarctic meteorites, and leads to several important conclusions. Contrary to previous belief, nearly all Antarctic meteorites are weathered, containing at least 1% and up to 30% or more ferric Fe. Furthermore, this weathering occurs throughout the meteorites, even in the center.

Quantitative guidelines for weathering can be applied to the ABC system currently in use, with some modifications. The largest group of samples, chondrites from the Allan Hills area, have the following characteristics: "A" samples contain 4-5% ferric phases, "B" samples 7-10%, and "C" samples up to 30% or more. The Allan Hills chondrites are the most severely weathered of all the Victoria Land specimens.

Achondrites tend to have lesser degrees of weathering, probably because the first phases to weather (metallic FeNi, troilite) are much less abundant in these meteorites. In addition, meteorites from other localities in Antarctica are less weathered. This phenomenon is best explained by differences in ice-sheet flow causing the meteorites to spend varying amounts of time buried in the ice. The evidence supports the theory that it is possible for weathering to occur during burial as well as on the surface of the ice. However, it is also possible that these meteorites have different terrestrial ages, and thus experienced different periods of weathering. These factors cause anomalies in the ABC classification

system, and should be taken into account by researchers interested in Antarctic meteorites.

It has been determined that oxidation of meteorites in the museum environment is a definite problem. Specimens classified as falls contain 0.5-4% ferric Fe, well above the range of detectability we must work with when studying SNC meteorites. Museum curators should become aware of this problem; ideally, meteorite falls should all be handled as carefully in the future as the Antarctic specimens are. At the very least, researchers should be warned of this inherent error in compositional calculations.

The identity of the ferric phase or phases has been narrowed down significantly. Normal crystalline hematite, goethite, and magnetite have all been ruled out, as they would be expected to produce six-line spectra, which were not observed. XRD eliminated other crystalline FeOOH polymorphs from the list of possibilities. Two legitimate candidates remain: microcrystalline FeOOH and Fe-rich clay-silicates. Since both have similar Mossbauer parameters and neither was identifiable by XRD, a final determination could not be made. It is probable that both exist, since two ferric-bearing phases were distinguished in samples containing over 8% ferric Fe. The Fe-oxide phase would be expected to appear first, resulting from weathering of the metallic Fe, but the clay-like phase may be more predominant in the achondrites where little metal is present. In both cases, H_2O and O_2 (now OH in microcrystalline phases) must have permeated the meteorites.

The existence of so much ferric Fe presents a particular problem with respect to study of the SNC meteorites thought to have

their origin on Mars. All three samples studied here, one fall (Nakhla) and two shergottites from Allan Hills and Elephant Moraine, were found to contain only 1.5-2% ferric phase. This lies at or below the possible error for these samples due to on-site or museum weathering, and indicates that preterrestrial oxidation cannot be conclusively shown by compositional studies alone. Rather, petrologic evidence from SEM studies is needed to confirm its presence.

The phase of special interest is lith C of EETA79001, due to the presence in it of trapped Martian gases, interesting silicate minerals, and possible preterrestrial compounds. However, no evidence for ferric phases were found within it.

On the basis of these studies, it can be concluded that these SNC meteorites do not contain any significant percentage of Martian surface material, but must have their origin in the crust or upper mantle of Mars.

The discoveries made in this thesis open up many promising avenues for further research. It seems that oxidation of metallic Fe in meteorites is a much faster process than previously realized, both inside and outside of museums. The weathering classification of meteorites in Antarctica badly needs revision; the implementation of an instrumental method of characterization would be helpful to many researchers. In addition, further study to help prevent museum weathering would be of use.

This work helps define some of the questions surrounding ice-sheet weathering. The implication seems to be that weathering can occur under the ice sheet, and that properties of ice flow differ at

the various sites sufficient to create variations in weathering patterns. It would be interesting to study meteorites that are still entirely encased in ice; these samples have been spotted, but none have been excavated. Further studies of Antarctic meteorites classed by locality may also give clues to help understand the ways ice sheets are moving in Antarctica.