Dissymmetric Mössbauer Spectra in Meteoritic Taenite Lamellae (Cape York, III-A)

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ABSTRACT

Room temperature Mössbauer studies have been made on a «mosaic» absorber and three other single absorbers of meteoritic taenite lamellae (Cape York). The lamellae were surface-cleaned by employing the sand-blasting technique.

Our dissymmetric Mösbbauer spectra obtained in each experiment has been interpreted as the superposition of three comonent spectra 1) a paramagnetic single-line spectrum, 2) an asymmetric six-line spectrum with quadrupole splitting, and 3) a symmetric six-line spectrum.

The measured average values of «quadrupole splitting» and «magnetic field of the symmetric spectrum» has been found to be $+0.19 \pm 0.01$ mm/sec and 288 ± 2 kOe, respectively.

ÖZ

Bu çalışmada, bir «mozaik» numune ve üç ayrı meteoritik taenit levha (Cape York) üzerinde, oda sıcaklığında Mössbauer çalışmaları yapılmıştır. Levhalar üzerindeki paslar kum bombardımanı tekniği kullanılarak temizlenmiştir.

Simetrik olmayan Mössbauer spektrumlarının her birinin aşağıdaki üç ayrı bileşen spektrumun üst üste gelmesi sonucu meydana geldiği kabul edilmiştir: 1) paramagnetik tekçizgi spektrumu, 2) «kuadrupol yarılımı» olan bir asimetrik altıçizgi spektrumu, ve 3) simetrik altıçizgi spektrumu.

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Asimetrik altıçizgi spektrumunun birkaç numune için elde edilen ortalama «kuadrupol yarılım» ve «magnetik alan şiddeti» değerleri sırası ile $+0.19 \pm 0.01$ mm/sn ve 288 ± 2 kOe olarak bulunmuştur.

INTRODUCTION

Iron meteorites and laboratory made iron-nickel alloys have been studied by a large number of investigators. Some of the work concerning structural and magnetic investigations in this field using the Mössbauer spectroscopy technique has been reviewed in the folowing two sections.

Palueve and Dautreppe (1) first demonstrated the existence of an ordered phase in polycrystalline and monocrystalline 50% - 50% Fe-Ni alloys irradiated by neutron bombardment in an external magnetic field. Gros and Palueve (2) used the Mössbauer technique to study superstructure in this neutron irradiated alloys. Billard and Chamberod (3) measured quadrupole splitting in their Mössbauer spectra as $+0.23$ mm/sec and magnetic field at room temperature as 288 kOe.

We first dedected the existence of a well defined quadrupole splitting in meteoritic taenite lamellae (Cape York). The Mössbauer parameter on a mosaic sample and three other single absorbers agree with the result obtained by Billard and Chamberod. Our present work led us to the discovery that an ordered phase exist in taenite lamellae.

The work has been started at H. C. Oersted Institute at Denmark an dcontinued at Ege University, İzmir, Turkey. An «Announcement Note» was first published to establish priority in the Physics Letters, Vol. 62A, No. 3, 8 Aug. 1977, by Petersen, J. F., Aydın, M. and Knudjen, J. M. Then a follow-up paper has already been published (Albertsen, J. F., Aydın, M. and Knudsen. J. M., Physica Scripta, Vol. 17, 467-472, 1978.). This is another follow-up paper which covers the part of the research that has not been included in the papers mentioned above.

IRON METEORITES :

Iron meteorites have been worked out systematically by V. F. Buchwald (4). They consist namely of iron and nickel in various proportions, (about 5 to 50 wt. % Ni) with small amount of sulphur, cobalt, phosphorus and carbon.

The three essential constituents of all iron meteorites are kamacite, taenite and fine grained mixture of them called plessite. Kamacite refers to an $\alpha-$phase (ferrite) of a low nickel alloy in which up to 7·5 wt. % Ni, is in solid-solution with iron having b.b.c. structure. The nickel content of the kamacite phase in different octahedrites shows a considerable variation, approximately between 5·5 and 7·5 wt. % Ni. Taenite is a $\alpha-$phase (austenite) Fe-Ni alloy of variable high-nickel composition ranging from 20 to 50 wt. % Ni in different meteorites. With slow cooling from the temperatures at which the meteorite is in $\gamma-$phase, kamacite nucleates along the octahedral planes of the parent taenite.

If the overall nickel content of the meteorite is about 6 wt. % or more and if the cooling temperature of taenite is too low, then the coarse octahedrites are formed, where kamacite and taenite lamellae are arranged with octahedral symmetry giving rise to «Widmanstatten pattern». They usually contain variable amount of plessite as well.

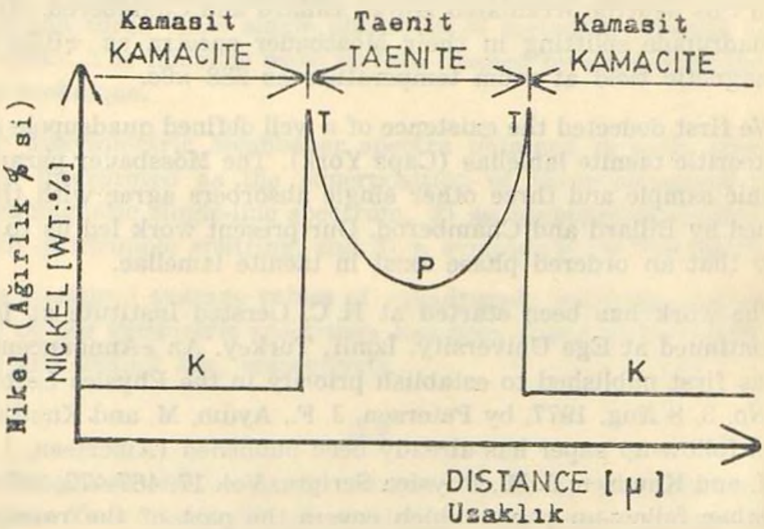

Figure 1 : An illustrative M-Curve about the distribution of nickel in adjacent Kamacite - Taenite - Kamacite region.

Şekil 1 : **Bitişik Kamasit - Taenit - Kamasit ardalanma kesimlerindeki nikel dağılımını gösteren M-Eğrisi.**

It was first pointed out by Perry (5), Smith and Young (6) and later (by using powerful electron probe microanalysers) it has definitely been proved by many investigators (7, 8) that a taenite lamellae is characteristically inhomogeneous from the edge to the center. As shown in Figure 1, the percentage of nickel content in the kamacite phase is quite uniform, but that of taenite is not and it produces the so-called «M-shaped profile» of nickel. Immediately adjacent to kamacite, the taenite is very high in nickel content (about 50 wt. %), but that nickel content decreases rapidly with distance from the interface.

Electron probe investigations of an unannealed taenite lamellae have indicated the following nickel inhomogenities. Traversing from the kamacite/taenite interface inwards, a1-2 μ m wide cream colored layer containing 40-50 wt. % Ni is first encountered. Then follows a blusish brown layer 5-25 μ m wide containing about 40-50 wt. % Ni and a 10-30 μ m wide yellow layer (25-30 wt. % Ni), and next follows a yellowish layer of 20-50 μ m wide layer (25 wt. % Ni) with indistinct martensitic transformation products and a brown-etching layer (<20 wt. % Ni) with a distinctly martensitic product called α_2-phase. At the central area of taenite lamellae, the α_2 structure usually decomposes to a fine grained mixture of α and γ, giving rise to a dark colour. Scott (9) points out that slower cooling had allowed more nickel to diffuse into the taenite so that even mm-wide fields of taenite contained more than 30 wt. % Ni and had not formed fine black plessite inside.

IRON-NICKEL ALLOYS :

In the study of iron meteorites the metastable states occuring in the Fe-rich FeNi alloys have a great deal of importance. The formation of the metastable structural states of the FeNi alloys vary widely according to the composition and heat treatment. In the case of alloys annealed for long duration at a temperature in the $\alpha+\gamma$ region, the two phase transformation in austenite ($\gamma \rightarrow \gamma + \alpha$) takes place. When the alloy cools down in a short time, the γ-phase transforms to a new structure called α_2-phase by a diffusionless martensitic prcces. It is a supersaturated solution having the same composition as the γ-phase. Alloys containing up to approximately 30 at. % Ni and quenched from temperatures above 500°C are all converted ito the α_2-phase. However, for alloys having higher nickel content and treated in the same way, the γ-phase is predominantly retained (10).

It has been shown by Johnson et al. (11) that alloys containing less than at. % Ni, they are body-centered cubic and for more than 34 at. % Ni they are face-centered cubic. Within the composition range of 26 and 32 at. % Ni, the alloys show inhomogeneous physical structure and corresponding magnetic inhomogenity.

The magnetic properties of the γ-phase iron-nickel alloys are found to be quite complicated, especially near the invar region (about 34 at. % Ni). Johnson et al. first studied the magnetic properties of the whoole iron-nickel alloy system by means of the Mössbauer effect. As shown in Figure 2, they found that the magnetic hyperfine field at Fe^{57} nuclei in these alloys seems to be constant with respect to nickel concentration.

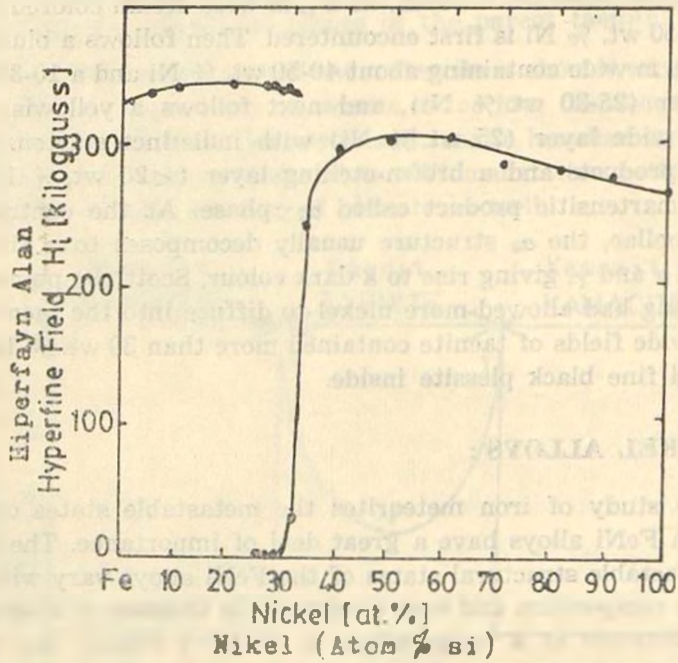

Figure 2 : Variation of the internal magnetic field at tha site of Fe^{57} nucleus in iron-nickel alloys. (11).

Şekil 2 : Demir-Nikel alaşımları içindeki Fe^{57} çekirdeklerinin bulundukları yerlerdeki iç magnetik alan değişimi. (11).

The average value of the field at a given concentration is about 300 *k0e*, expect for the vicinity of 30 at. % Ni. In the body-centered cubic phase the field varies slowly and the experimental data is a well resolved six-line Mössbauer spectra indicating that the internal field is ferromagnetic. The Mössbauer effect spectrum of the face-centered alloys containig about 30 at. % Ni at room temperature gives a single, relatively narrow peak which is characteristic of paramagnetism. As the nickel

30 at. % Ni to the high values), the magnetic field increases rapidly to the value of about 300 kOe and thereafter decreases slowly.

Following Johnson et al., the f.c.c. phase iron-nickel alloys with 30, 32 and 34 at. % Ni were obtained Nakamura et al. (12). At liquid nitrogen temperature they observed a Mössbauer spectrum consisting of two sets of obsorption lines. One of them is six symmetric absorption lines characteristic of ferromagnetic materials with the internal magnetic field of 330 kOe, and the other is a single narrow peak characterestic of paramagnetic materials. Thus, it has been concluded that in this composition range the alloys consist magnetically of two phases, namely ferromagnetic and antiferromagnetic.

In order to investigate the effect of structural and magnetic inhomogenities in invar alloys, more precise Mössbauer work has been done by Tomiyoshi et al. (13). They studies the distribution of the internal magnetic field and its temperature dependence of Fe^{57} nuclei in γ-phase iron-nickel alloys with composition ranging from 31.8 to 65.6 at. % Ni. Their spectra have been interpreted to show first the existence of only one magnetic phase, i.e., ferromagnetic, and second inhomogeneous nature of the magnetic order. Close to the invar region, the alloys were regarded to the first approximation as an assembly of ferromagnets with different magnetic characteristics.

DISSYMMETRIC MÖSSBAUER SPECTRA IN 50 % - 50 % Fe-Ni ALLOYS :

The structural and magnetic inhomogenities in the Fe-Ni alloys have been extensively studied by many investigators. Some of this work has been discussed briefly above.

Paluevé and Dautreppe (1) first showed the existence of an ordered phase in polycrystalline or monocrystalline 50 % - 50 % Fe-Ni laboratory made alloys ,irradiated by neutron bombardment in an external magnetic field. They showed that this ordering process induces a very high magnetic anisotropy in the sample. By using the X-ray difraction technique, Paluevé et al. (14) discovered that this long range ordered structure is of —the tetragonal— *AuCu* (*L* 10) type, and its order-disorder transition occurs at 320°C.

Gros et al. (2) used Mössbauer technique to study superstructure in neutron irradiated 50 % - 50 % Fe-Ni alloys. They studied the internal field anisotropy both experimentally and theoretically. They observed quadrupole splitting in their specta indicating the existence of superstructure in the neutron irradiated 50 % - 50 % Fe-Ni polycrystalline and monocrystalline samples.

Using the Mössbauer technique Billard and Chamberod (3) studied the dissymmetry of Mössbauer spectra in iron-nickel alloys. They showed that the spectra of an irradiated monocrystal must be composed of two elementary spectra of six lines. Each component spectrum has different quadrupole splitting and corresponds to a different magnetic field. In the spectra of a 50 % - 50 % Fe-Ni ordered monocrystal, they measured the quadrupole splittings as $+0.23$ mm/sec and -0.12 mm/sec and the magnetic field at room temperature as 288 and 327 $k0e$, respectively.

EXPERIMENTAL :

The Mössbauer absorption spectra of Fe^{57} in untreated meteoritic taenite lamellae have been measured by using the Standard Transmission Mössbauer Spectroscopy Technique. The spectra were recorded keeping the absorber fixed and moving the source. The single-line Co^{57} in-Pd source and absorbers were kept at room temperature at all times. The value of Mössbauer parameters, such as magnetic hyperfine field H_i and quadrupole splitting were obtained by an iterative curve fitting technique using a «RC 4000» computer.

Absorbers :

Different size non-corroded taenite lamellae picked up from the rusty kamacite of Cape York Meteorite were used as absorbers. We first chose many small shining pieces of taenite lamellae, each having approximately 1 mm^2 area, and put the together in a layer on a thin plastic holder to make a «mosaic» absorber. Next we chose three larger size taenite lamellae having about the area of 80 mm^2 and thickness of 150 μm, designated as L-1, L-2 and L-3.

Mössbauer Spectra in Untreated Taenite Lamellae :

The room temperature Mössbauer spectra of the mosaic absorber together with those of a taenite lamellae L-1, a «crust» absorber, and $\alpha-$Fe as reference are presented in Figure 3. Here we are interested only in the Mössbauer line positions of the specta and not the amount of relative absorption of each line. The line position are measured in terms of channel numbers.

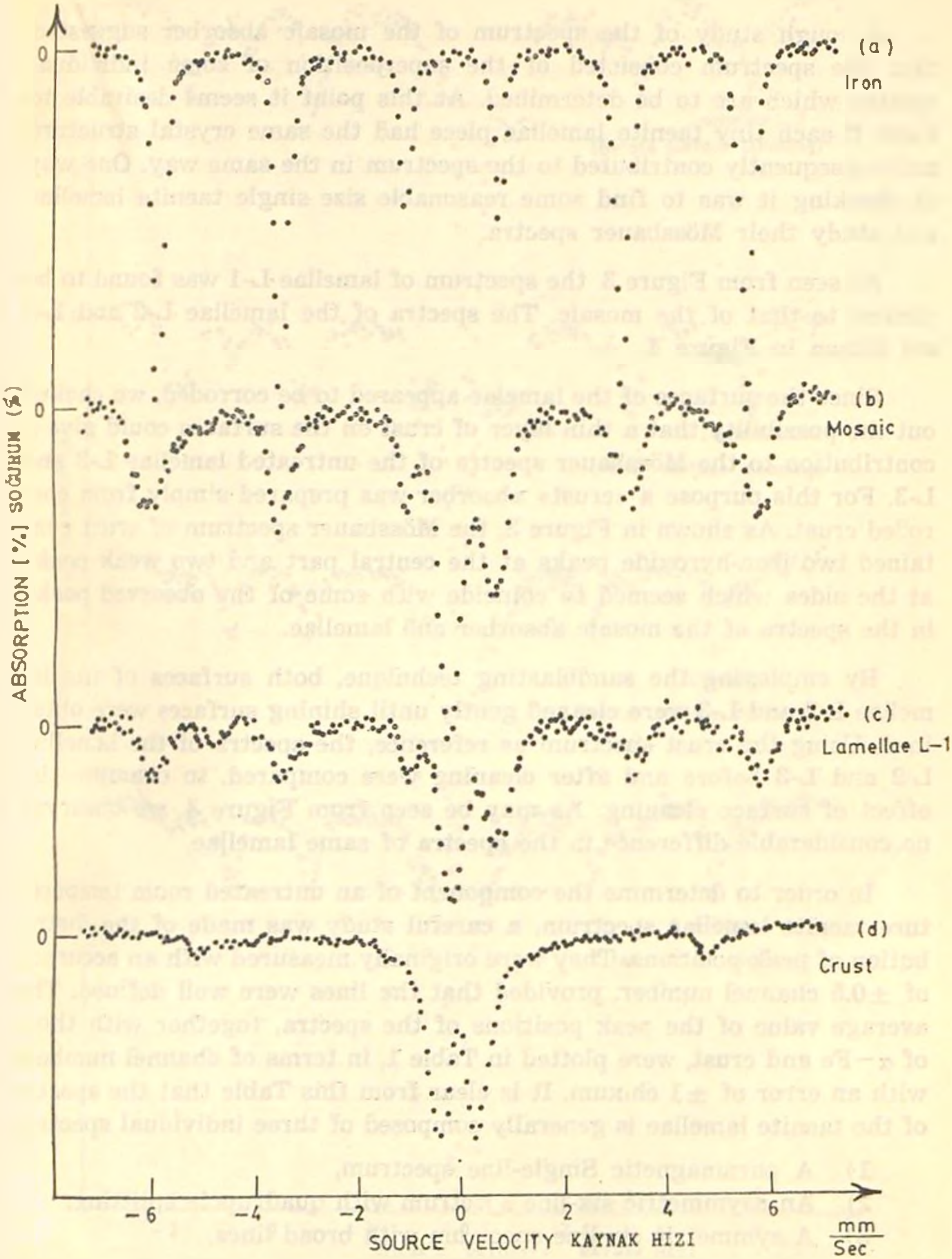

Figure 3 : Room temperature spectra of (a) iron-foil, (b) mosaic absorber, (c) taenite lamellae L-1 and (d) crust absorber.

Şekil 3 : **(a) Demir levha'nın, (b) mozaik soğurucunun, (c) taenit L-1 lamelinin ve (d) kabuk soğurucu'nun oda sıcaklığındaki Mössbauer spektrumları.**

A rough study of the spectrum of the mosaic absorber suggested that the spectrum consisted of the superposition of some individual spectra which are to be determined. At this point it seems desirable to know if each tiny taenite lamellae piece had the same crystal structure and consequently contributed to the spectrum in the same way. One way of checking it was to find some reasonable size single taenite lamellae and study their Mössbauer spectra.

As seen from Figure 3 the spectrum of lamellae L-1 was found to be similar to that of the mosaic. The spectra of the lamellae L-2 and L-3 are shown in Figure 4.

Since the surfaces of the lamelae appeared to be corroded, we chcked out the possibility that a thin layer of crust on the surfaces could give a contribution to the Mössbauer spectra of the untreated lamellae L-2 and L-3. For this purpose a «crust» absorber was prepared simply from corroded crust. As shown in Figure 3, the Mössbauer spectrum of crust contained two iron-hyroxide peaks at the central part and two weak peaks at the sides which seemed to coincide with some of the observed peaks in the spectra of the mosaic absorber and lamellae.

By employing the sandblasting technique, both surfaces of the lamellae L-2 and L-3 were cleaned gently until shining surfaces were obtained. Using the crust spectrum as reference, the spectra of the lamellae L-2 and L-3 before and after cleaning were compared, to examine the effect of surface cleaning. As may be seen from Figure 4, we observed no considerable difference in the spectra of same lamellae.

In order to determine the component of an untreated room temperature taenite lamellae spectrum, a careful study was made of the distribution of peak positions. They were originally measured with an accuracy of ± 0.5 channel number, provided that the lines were well defined. The average value of the peak positions of the spectra, together with those of $\alpha-$Fe and crust, were plotted in Table 1, in terms of channel numbers with an error of ± 1 ch.num. It is clear from this Table that the spectra of the taenite lamellae is generally composed of three individual spectra:

1) A paramagnetic Single-line spectrum,
2) An asymmetric six-line spectrum with quadrupole splitting,
3) A symmetric six-line spectrum with broad lines.

The most intense central paramagnetic line has been observed in all spectra and it has always been a well defined strong peak. We cannot

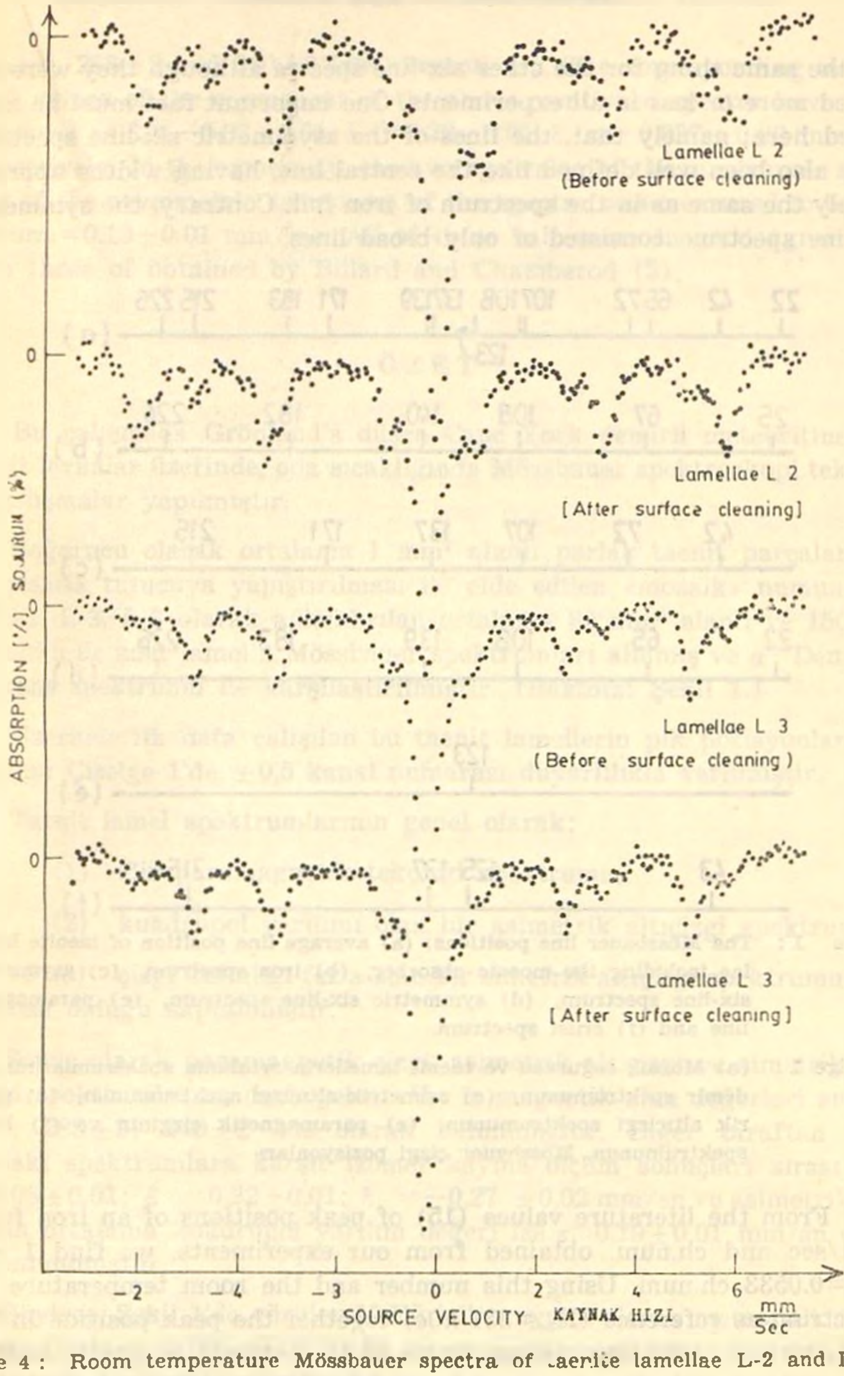

Figure 4 : Room temperature Mössbauer spectra of taenite lamellae L-2 and L-3, before and after surface cleaning.

Şekil 4: L-2 ve L-3 taenit lamellerinin, yüzey temizleme işleminden önce ve sonra alınan oda sıcaklığındaki Mössbauer spektrumları.

say the same thing for the other six-line spectra although they were observed more or less in all experiments. One important fact must be mentioned here; namely that, the lines of the asymmetric six-line spectrum have also been well defined like the central line, having widths approximately the same as in the spectrum of iron foil. Contrary, the symmetric six-line spectrum consisted of only broad lines.

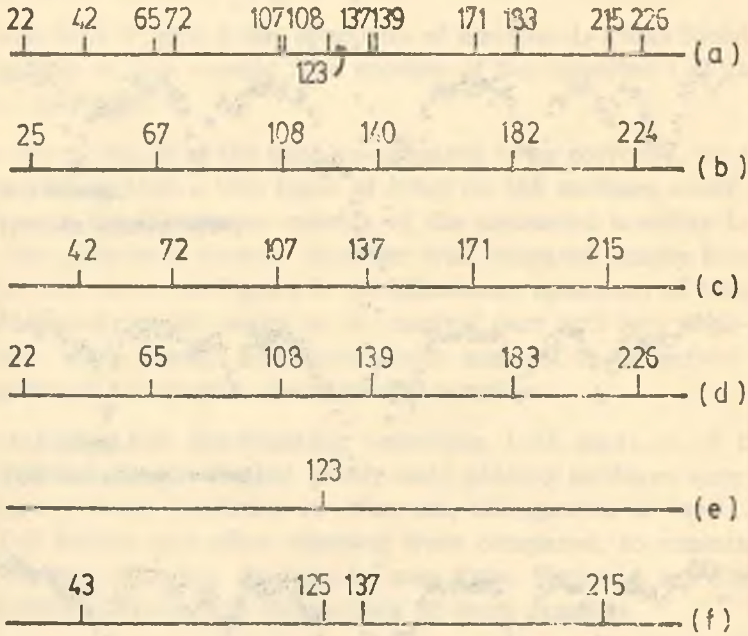

Table 1 : The Mössbauer line positions: (a) average line position of taenite lamellae including the mosaic absorber, (b) iron spectrum, (c) asymmetric six-line spectrum, (d) symmetric six-line spectrum, (e) paramagnetic line and (f) crust spectrum.

Çizelge 1 : (a) Mozaik soğurucu ve taenit lamellerin ortalama spektrumlarının, (b) demir spektrumunun, (c) asimetrik altıçizgi spektrumunun, (d) simetrik altıçizgi spektrumunun, (e) paramagnetik çizginin ve (f) kabuk spektrumunun, Mössbauer çizgi pozisyonları.

From the literature values (15) of peak positions of an iron foil in mm/sec and ch.num. obtained from our experiments, we find 1 mm/sec=0.0533 ch.num. Using this number and the room temperature iron spectrum as reference (H_{Fe}=331 kOe) together the peak position in Table 1, we computed the average value of the internal magnatic field for the paramagnetic line, asymmetric six-line and symmetric six-line spectra as 0, 288 ± 2 and 340 ± 2 kOe, respectively. The corresponding isomer shift values of the component of the above mentioned spectra have been measured as $\delta_s = -0.08 \pm 0.01$, $\delta = 0.22 \pm 0.01$, $\delta = -0.027 \pm 0.02$ mm/sec respectively. In the same way, the average value of the quadrupole splitting of the asymmetric component of the spectra was measured to be 3.5 ch.num. $= 0.19 \pm 0.01$ mm/sec. All of these values are in good agreement with those of obtained by Billard and Chamberod (3).

ÖZET

Bu çalışmada Grönland'a düşen Cape York demirli meteoritine ait taenit levhalar üzerinde, oda sıcaklığında Mössbauer spektroskopi tekniği ile çalışmalar yapılmıştır.

Soğurucu olarak ortalama 1 mm^2 alanlı parlak taenit parçalarının bir plastik tutucuya yapıştırılması ile elde edilen «mozaik» numunenin ve L-1, L-2, L-3 olarak adlandırılan ortalama 80 mm^2 alanlı ve 150 μm kalınlıklı üç adet lamelin Mössbauer spektrumları alınmış ve $\alpha-$Demirin referans spektrumu ile karşılaştırılmıştır. (Bakınız: Şekil 1.)

Üzerinde ilk defa çalışılan bu taenit lamellerin pik pozisyonlarının dağılımı Çizelge 1'de $\pm 0,5$ kanal numarası duyarlılıkla verilmiştir.

Taenit lamel spektrumlarının genel olarak;

(1) Bir paramagnetik tekçizgi spektrumu,

(2) kuadrupol yarılımı olan bir asimetrik altıçizgi spektrumu

ve (3) çizgi kalınlığı fazla olan bir simetrik altıçizgi spektrumunun bileşkesi olduğu saptanmıştır.

Sonuç olarak paramagnetik çizgi, asimetrik altıçizgı ve simetrik altıçizgi spektrumlarına denk gelen «H_i» iç magnetik alan değerleri sırası ile 0; 288 ± 2; 340 ± 2 kOe olarak bulunmuştur. Diğer taraftan yukarıdaki spektrumlara karşıt izomer kayma ölçüm sonuçları sırası ile $\delta_s = 0,08 \pm 0,01$; $\delta = 0,22 \pm 0,01$; $\delta = -0,27 \pm 0,02$ mm/sn ve asimetrik bileşenin ortalama kuadrupol yarılım değeri ise $\varepsilon = 0,19 \pm 0,01$ mm/sn olarak bulunmuştur.

Böylece, Şekil 1'de görülen M-Eğrisi'ne uygun olarak meteoritik taenit lamellerinde % 50 - % 50 Fe-Ni içeren, ardalanmalı bir süperstrüktürün varlığı gözlenmiş olmaktadır.

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