Mössbauer study of iron in atmospheric air

By MICHAŁ KOPCEWICZ, *Institute of Experimental Physics, University of Warsaw and* BARBARA DZIENIS, *Institute of Geophysics, Polish Academy of Sciences, Warsaw, Poland*

(Manuscript received August 8, 1970, revised version December 19, 1970)

ABSTRACT

Use of the Mössbauer effect has been made for studying iron in atmospheric air. The experiments were performed by observing the absorption of 14.4 keV gamma rays from ^{57}Co by samples consisting of filters through which atmospheric air was pumped. Using the "area method", usually applied in calculations of the recoilless raction (f-factor) the content of natural iron per cubic meter of atmospheric air was found to be 1.4 $\mu g/m^3$. The measurements were carried out at room and liquid nitrogen temperatures. The room temperature spectra show two absorption lines due to quadrupole splitting; the low temperature spectrum shows a central unresolved doublet and, besides it, six lines due to magnetic hyperfine splitting. From the shapes of the Mössbauer spectra obtained it was inferred that iron appears in the Fe_2O_3 compound in the form of ultrafine particles (~ 100 Å) in the superparamagnetic state.

1. Introduction

As is well known, aerosols play a significant role in atmospheric physics although their concentration is much lower than that of the gases. Since, in addition to many other elements and chemical compounds, the aerosols contain also iron, which is a Mössbauer nucleus, it seems possible to study some features of aerosols by means of the Mössbauer effect. The principles, properties and applications of the Mössbauer effect have been described and reviewed extensively in the literature (see e.g.: R. L. Mössbauer, 1958; G. K. Wertheim, 1965; H. Frauenfelder, 1962; R. L. Mössbauer and D. H. Sharp, 1964).

The Mössbauer parameters relevant to the present study are the recoilless fraction (f-factor), electric quadrupole splitting ΔE_Q and the magnetic hyperfine splitting.

In the present paper the results are reported of the, to our best knowledge, first study in which the Mössbauer effect was applied in the field of atmospheric physics. The paper contains the results of the measurements, discussion and conclusions.

2. Determination of the content of a Mössbauer isotope in the sample

Since use is made of the density of the resonant isotope in the sample when calculating the f-factor, the content of the resonant isotope in the absorber can be inferred from the knowledge of the f-factor for the absorbing material. Hence in the present investigation we made use of the method forwarded by Hafemeister & Brooks Shera (1966) for calculation of the f-factor from the measured area under the Mössbauer line.

The formula for the absorption area, given by Hafemeister & Brooks Shera (1966), is

$$A = \frac{\pi}{2} f \Gamma L(t) \tag{1}$$

where

$$t = n\sigma_0 f' \tag{2}$$

is the effective thickness of the absorber consisting of n atoms/cm^2 of the Mössbauer isotope, Γ is the natural linewidth, σ_0 is the cross section for the resonant absorption of gamma rays, f and f' are the recoilless fractions for the source and absorber, respectively, and $L(t)$ is a function of the absorber thickness defined as:

$$L(t) = \sum_{p=1}^{\infty} \frac{(-1)^{p+1}(2p-3)!!\, t^p}{p!\,(2p-2)!!} \tag{3}$$

The $L(t)$ function has been computed numerically, and the data summarized in the paper of Hafemeister & Brooks Shera (1966).

When the experimental Mössbauer spectrum consists of i absorption lines of Lorentzian shape with $\Gamma_{j\,\mathrm{exp}}$ linewidths and with the peak absorption (corrected for the background) $P_{j\,\mathrm{exp}}$, the area under the spectrum is

$$A = \frac{\pi}{2} \sum_{j=1}^{i} \Gamma_{j\,\mathrm{exp}}\, p_{j\,\mathrm{exp}}. \tag{4}$$

By comparing Eqs. (1) and (4) we obtain

$$L(t) = \frac{\sum_{j=1}^{i} \Gamma_{j\,\mathrm{exp}}\, p_{j\,\mathrm{exp}}}{f\Gamma} \tag{5}$$

Eq. (5) permits the evaluation of $L(t)$, and hence also the corresponding value of the effective thickness t.

Using Eq. (2) we finally get,

$$n = \frac{t}{\sigma_0 f'} \tag{6}$$

If the f'-factor for the absorber is known, it is possible to determine experimentally the density of the Mössbauer isotope in the sample.

3. Experimental

In the present study the recoilless resonant emission and absorption have been studied basing on 14.4 keV transition from the first excited level of ^{57}Fe fed in the electron cepture decay of ^{57}Co. The source used was ^{57}Co in platinum of 5 mCi activity.

The Mössbauer effect measurements were performed using a conventional automatic spectrometer with a constant velocity drive and a NaI(Tl) scintillation counter. The Mössbauer investigations were carried out at room and liquid nitrogen temperatures. The samples were prepared using membrane filters[1] which are usually used in measurements of air radioactivity. Atmospheric air was pumped through each filter for 24 hours, and the volume of air passed through the filter was measured by means of a gasometer. The filters were dissolved in acetone, evaporated, and the residue was pressed between two thin aluminium foils. Sample 1 consisted of six filters from Warsaw, obtained from a six day run (May 1967), and sample 2 of filters from Zakopane (February 1969). Both samples were used as absorbers.

[1] The filters were obtained by kind permission of the State Institute of Hydrology and Meteorology (Poland). The pumping of air was performed in the meteorological observatories in Warsaw and Zakopane.

4. Results and discussion

The Mössbauer measurements were carried out at room and liquid nitrogen termperatures for sample 1, and at room temperature only for sample 2. The Mössbauer spectra obtained are shown in Figs. 1, 2 and 3. The parameters of the spectra were computed by least square method fitting the Lorentzian shape to the experimental data. The lines observed are approximately Lorentzian with a width of $\Gamma_{\mathrm{exp}} = 3.1 \times 10^{-8}$ eV (0.64 mm/s). The Mössbauer spectra obtained at 300°K for samples both from Warsaw and Zakopane consists of two absorption lines due to quadrupole splitting. The quadrupole splitting ΔE_Q and isomer shift δ were

$$\Delta E_Q = 0.63 \text{ mm/s}$$

$$\delta = -0.12 \text{ mm/s}$$

The liquid nitrogen temperature spectrum shows a central unresolved doublet (due to quadrupole splitting) of a much smaller intensity than that obtained at room temperature and six lines due to magnetic hyperfine (hf) splitting. The two middle lines are weak, and the four external lines are very pronounced. The position of the lines of the magnetic fraction of the spectrum correspond to the line positions of the bulk α-Fe_2O_3 spectrum (Fig. 4). The magnetic properties of α-Fe_2O_3 have been the subject of numerous investigations (K. Ono & A. Ito, 1962, O. C. Kistner & A. W. Sunyar, 1960). The Mössbauer spectra of ^{57}Fe in α-Fe_2O_3 have been also measured as a function of particle size and temperature (T. Nakamura & S. Shimizu, 1964; T. Nakamura et al., 1964; W. Kündig et al., 1966). The bulk α-Fe_2O_3 spectrum obtained at 300°K and 78°K consists of six lines of magnetic hf splitting. In the papers by T. Nakamura & S. Shimizu (1964), T. Nakamura et al. (1964) and W. Kündig et al. (1966) it has been found that the α-Fe_2O_3 particles of a size of about 50 Å–300 Å (ultrafine particles) have at room

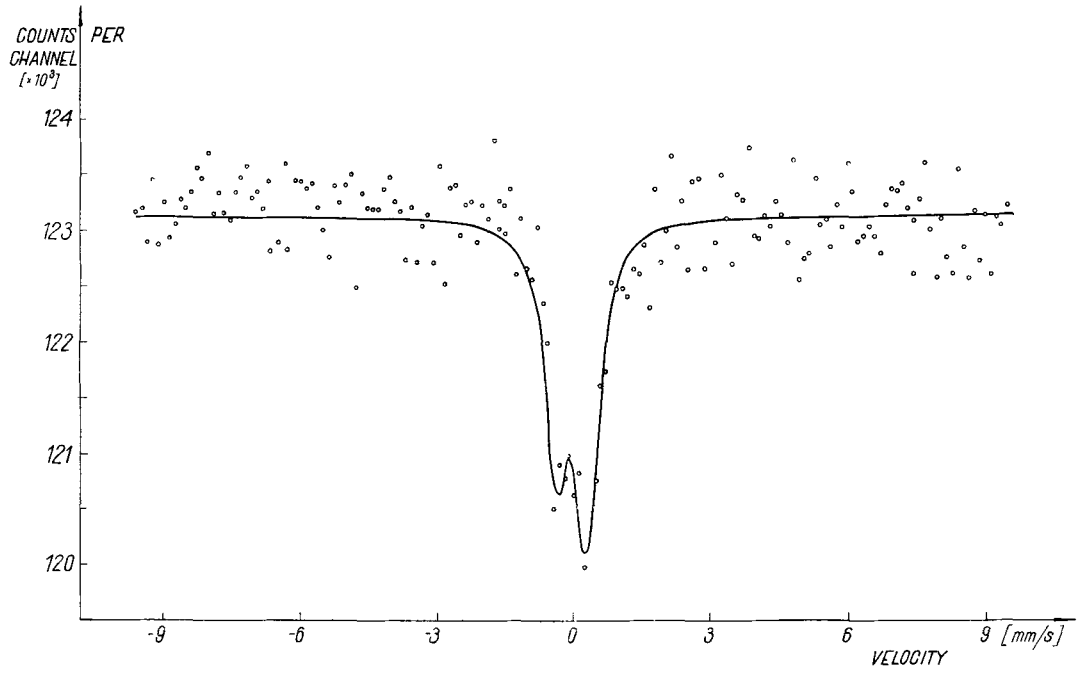

Fig. 1. Mössbauer spectrum for sample 1 at 300°K. The solid curve was computed by the least square fitting of the Lorentzian shapes to the experimental data.

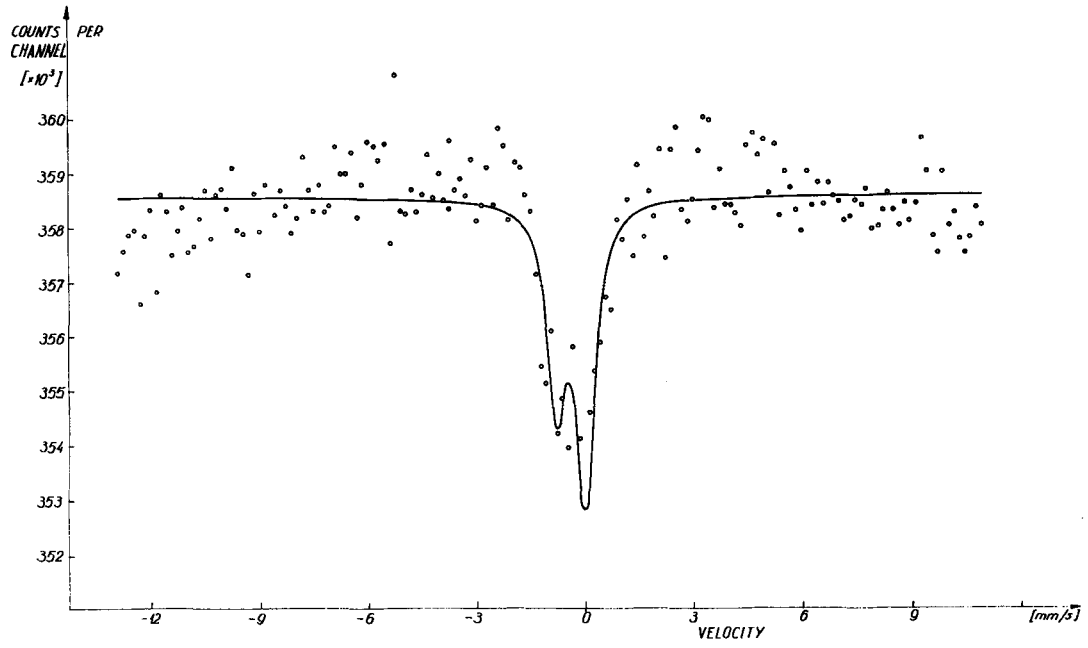

Fig. 2. Mössbauer spectrum for sample 2 at 300°K.

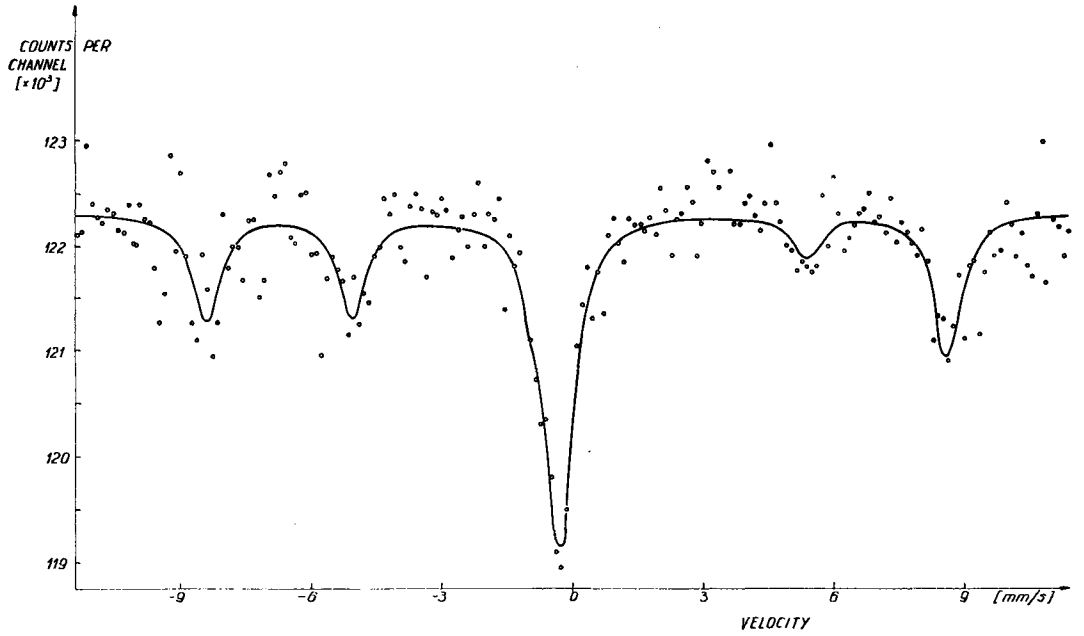

Fig. 3. Mössbauer spectrum for sample 1 at 78°K .

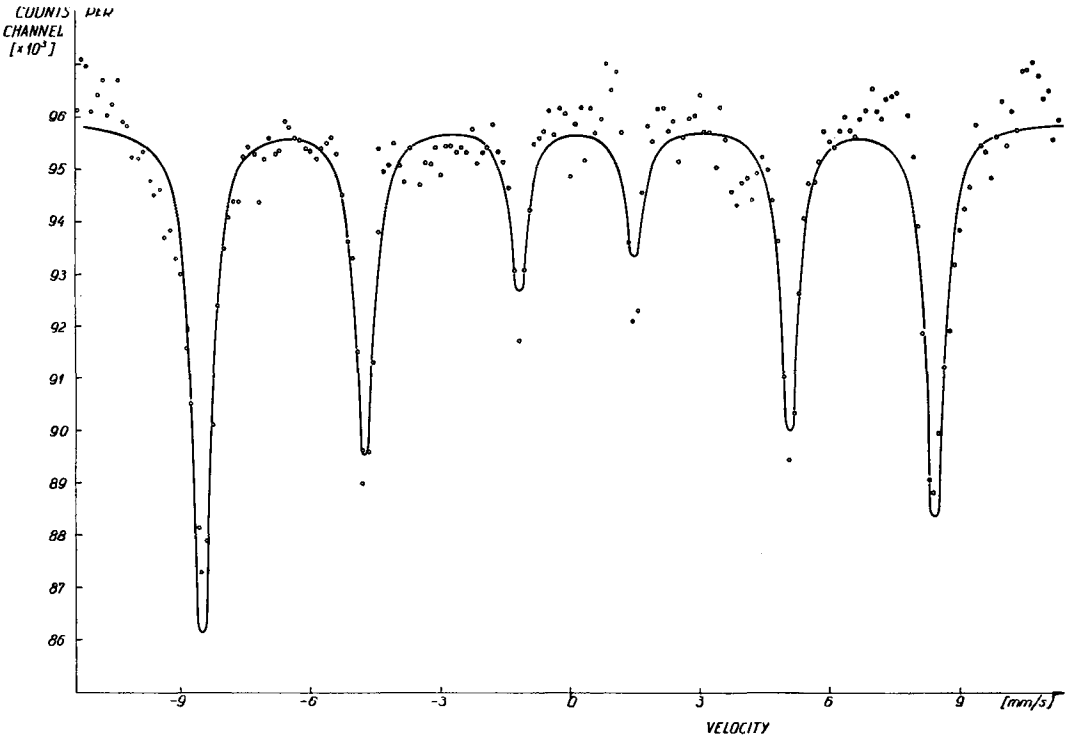

Fig. 4. Mössbauer spectrum for bulk α-Fe_2O_3 at 300°K.

temperature a Mössbauer spectrum which consists of a doublet similar to that obtained in the present study. The ultrafine α-Fe_2O_3 particles show a weak ferromagnetism and therefore the liquid nitrogen temperature spectrum consists of six lines. Such changes in the Mössbauer spectra can be due to magnetic spin relaxation effects. When the ferromagnetic or antiferromagnetic particles are very small (~ 100 Å), the magnetization vector can at a certain temperature become unstable due to thermal agitation. Then their behaviour is paramagnetic as if they had a large magnetic moment. Such a state is called "superparamagnetic". The transition from the ferromagnetic to superparamagnetic phase caused either by the decrease of particle size or the increase of temperature has been quantitatively studied by Kündig et al. (1966), and the dependence of quadrupole splitting, isomer shift and magnetic fraction intensity on the particle size was clearly demonstrated. In the present study the Mössbauer spectra obtained at 78°K and 300°K correspond to the respective spectra shown by Kündig et al. (1966). From our results and the data reported by Nakamura & Shimizu (1964), Nakamura et al. (1964) and Kündig et al. (1966) we could infer that in the investigated sample the ^{57}Fe isotope is contained in Fe_2O_3 in the superparamagnetic state. The disappearence of the magnetic fraction of the spectrum when the temperature increases (from liquid nitrogen to room temperature) can be interpreted as the motional narrowing due to relaxation of ferromagnetic spins. When the spin relaxation time becomes smaller than the nuclear Larmor precession time, the particles become superparamagnetic and the magnetic splitting disappears.

The line positions in the magnetic fraction of the 78°K spectrum of sample 1 are almost identical with these for bulk α-Fe_2O_3 at room temperature. This is in good agreement with the results of Kündig et al. (1966).

From the investigations of the temperature dependence of the ratio of the superparamagnetic fraction of Fe_2O_3 particles to the ferromagnetic fraction, the particle size distribution can be obtained as was done by Kündig et al. (1966). This could not be done in the present study, because the Mössbauer absorption was too small due to the small concentration of iron in the sample. However, taking into account the quadrupole splitting value only, measured in the present study, and the results of Kündig et al. (1966), it was possible to estimate roughly the size of those particles which dominate in the sample. This size was estimated to be in the range of ca 100 Å. It follows from general considerations that the size of particles is probably not uniform and some of the iron oxide may consist of particles large enough to show a magnetic hf splitting even at room temperature. The absence of such lines at room temperature in the present experiment (Figs. 1 and 2) indicates however, that the number of large particles is probably too small to produce measurable absorption lines.

In the present study the content of iron in atmospheric air was determined using the method described in section 2. When calculating the content of iron in the sample it was necessary to determine f'-factor for Fe_2O_3. The f'-factor determined in the present study for bulk $\alpha - Fe_2O_3$ at 300°K (using the "area method" reported by Hafemeister & Brooks Shera (1966)) is 0.83. All the factors used in our calculations (see Eqs. (1), (2), (5) and (6)) are summarized in Table 1.

Table 1.

Factor	Value
Γ, natural linewidth	0.45×10^{-8} eV
σ_0, total cross section	22×10^{-19} cm^2
f_s, factor for ^{57}Co in Pt Mössbauer source	0.90
f'_s, factor for bulk Fe_2O_3 at 300°K	0.83

Using the values listed in Table 1 and the absorption area computed from the spectrum obtained for sample 1 at 300°K, the content of the ^{57}Fe isotope in that sample was calculated. We obtained 1.97×10^{17} atoms which is equivalent to 18.8×10^{-6} g. Our sample was prepared using six filters, 100 m^3 of air being pumped through each filter. Hence, the concentration of ^{57}Fe in atmospheric air is 3.1×10^{-2} $\mu g/m^3$. If we assume that the composition of iron in atmospheric air is natural, and consider that natural iron contains 2.19 % of the ^{57}Fe isotope, the content of natural iron in atmospheric air, as measured in our experiment, is 1.4 $\mu g/m^3$. This value is probably underestimated due to following reasons:

1. As mentioned above, the probably existing large particles (which would give the magnetic splitting at room temperature) were not taken into account.

2. The f-factor for Fe_2O_3 used in the calculations was not corrected for small partcle size. It was indicated (Nakamura & Shimizu, 1964), that for ultrafine particles the recoilless fraction should be affected by the particle size and should decrease with decrease of the particle size. However, the systematic investigations of this effect were not reported, and only very rough values were given. In this situation we have not corrected our results for this effect.

As we know, the content of iron in atmospheric air was investigated by chemical methods several years ago and the results are discussed by Junge (1965). The particles of aerosols were collected on glass filters during the period of over one year and then investigated by chemical analysis. Among many other metallic elements iron was also found. The average values of the content of natural iron for several American towns varies from 2.4 to 5.1 $\mu g/m^3$.

Comparing the results of the present study with those reported by Junge (1965), and taking into account that the particles of aerosols were collected in different periods of time and in different parts of the world and investigated by quite different methods it can be inferred that the results obtained are in satisfactory agreement.

5. Conclusions

The study reported in the present paper shows evidently that the Mössbauer effect is a valuable tool in investigations of the content of Mössbauer isotopes, especially iron. Although chemical methods are as accurate as this method, the Mössbauer spectra permit under favourable conditions not only to determine the content of the Mössbauer isotope in the sample, but also to identify the chemical compound in which the Mössbauer isotope appears and sometimes even to evaluate the average size of the particles in which it is contained. Apart from that the Mössbauer method has several advantages over the chemical ones, viz. no other nuclides interfere with the resonant absorption of the Mössbauer isotopes; it does not affect the chemical form of the samples; it is more convenient.

Further Mössbauer investigations using absorbing materials from different places and taking into account meteorological conditions, may also throw some light on the origin of iron in atmospheric air.

Acknowledgments

The authors are indepted to Professor B. Buras and Professor R. Teisseyre for their kind interest in this investigation. Thanks are also due to Mrs J. Orlicz and Mr R. Tomaszenko from the State Institute of Hydrology and Meteorology (Poland) for making available the filters. The authors wish to thank Mr S. Fijałkowski for his technical assistance.

REFERENCES

Frauenfelder, H. 1962. *The Mössbauer effect*. W. A. Benjamin, New York.

Hafemeister, D. W. & Brooks Shera, E. 1966. Calculations of the Mössbauer absorption areas for thick absorbers. *Nucl. Instr. and Methods 41*, 133–134.

Junge, C. E. 1965. *Air chemistry and radioactivity* (Russian translation) pp. 209–215. Izdat. "Mir", Moscow.

Kistner, O. C. & Sunyar, A. W. 1960. Evidence for quadrupole interaction of Fe^{57m}, and influence of chemical binding on nuclear gamma-ray energy. *Phys. Rev. Letters 4*, 412–415.

Kündig, W., Bömmel, H., Constabaris, G. & Lindquist, H. R. 1966. Some properties of supported small α–Fe_2O_3 particles determined with the Mössbauer effect. *Phys. Rev. 142*, 327–333.

Mössbauer, R. L. 1958. Kernresonanzfluoreszenz von gammastrahlung in Ir^{191}. *Z. Physik 151*, 124–143.

Mössbauer, R.L. 1958. Kernresonanzabsorption von γ-Strahlung in Ir^{191}. *Naturwissenschaften 45*, 538–540.

Mössbauer, R. L. & Sharp, D. H. 1964. On the theory of resonant scattering of gamma rays by nuclei bound in crystals. *Rev. Mod. Phys. 36*, 410–417.

Nakamura, T. & Shimizu, S. 1964. Experimental study on the Mössbauer effect of Fe^{57} in several iron compounds. *Bull. Inst. Chem. Res. Kyoto Univ. 42*, 299–318.

Nakamura, T., Shinjo, T., Endoh, Y. Yamamoto, Y., Shinga M. & Nakamura, Y. 1964. Fe^{57} Mössbauer effect in ultrafine particles of α-Fe_2O_3. *Phys. Letters 12*, 178–179.

Ono, K. & Ito, A. 1962. A Mössbauer study of the internal field at Fe^{57} in α-Fe_2O_3. *Journal Phys. Soc. Japan 17*, 1012–1017.

Wertheim, G. K. 1965. *Mössbauer effect: principles and applications*. Academic Press, New York and London.

РЕЗЮМЕ

В исследованиях наличия железа в атмосферном воздухе применен эффект Месбауэра. Опыты производились путем исследования поглощения 14,4 кев р-лучей ^{57}Co употребляя пробы состоящие из фильтров, через которые пропускался атмосферный воздух. Используя «метод поля» обыкновенно применяемый к расчету безотдачной частицы (f-фактор) установлено что содержание натурального железа в кубическом метре атмосферного воздуха составляет 1,4 $\mu г/м^3$.

Измерения производились в комнатной температуре и температуре жидкого азота. Спектр полученный в комнатной температуре состоял с двух линий поглощения квадрупольного расщепления, спектр полученный в низкой температуре состоял из центрального неразделенного дублета и шести линий магнитного расщепления. С формы полученных месбауэровских спектров сделано вывод, что железо выступает в составе Fe_2O_3 в виде ультра малых частиц (~ 100 Å) в суперпарамагнитном состоянии.