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1995 J. Phys.: Condens. Matter 7 4565

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# Natural frequencies of vibration of fine particles and interaction of the particles with electromagnetic radiation

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Received 30 August 1994, in final form 7 February 1995

**Abstract.** The resonant mechanism of high-frequency radiation absorption by fine particles was considered. The natural frequencies of the fine particles arranged on the macroporous carrier were calculated. It was found that the vibration spectra calculated from the temperature dependence of recoilless  $\gamma$ -ray absorption (Mössbauer effect) coincide with those calculated in the present work. On the basis of this research, one could conclude that the fine-particle vibrations give the main contribution to the recoilless absorption of  $\gamma$ -rays.

## 1. Introduction

It is well known that many results of studying fine-particle (FP) ensembles by ferromagnetic resonance (FMR) and nuclear magnetic resonance (NMR) cannot be explained on the base of conventional models of interaction between the bulk solid and an alternating electromagnetic field [1]. So it was found that a sufficient decrease in input radiation power and broadening of the NMR and FMR linewidths occurred. On the other hand, it was supposed that the FPs (e.g. Fe and  $\text{Fe}_2\text{O}_3$ ) could oscillate with frequencies of  $10^5$ – $10^{12}$  Hz. Because of this a sufficient decrease in the probability of  $\gamma$ -ray recoilless absorption was explained [2–8].

In this article the high-frequency radiation (HFR) absorption mechanism is considered in order to investigate the physical properties of the FPs using incident HFR [9]. The conventional model of the harmonic oscillator is accepted as the basis. This model has wide application in molecular and solid spectroscopy.

## 2. Resonant mechanism of interaction between fine particles and high-frequency radiation

Let us consider FPs randomly distributed on the surface of some carriers assuming no contact with each other. Because the average distance between the FPs is large compared with their diameter, vibrational coupling between the particles can be neglected. We assume that the type of carrier is not substantial but it is necessary that the carrier is an isolator; hence it would not absorb and reflect the HFR. The forces which bind the FP to the carrier depend upon the method of synthesis; chemical forces in the case of the salt pyrolysis process, or the London–van der Waals forces when the FPs are formed by the impregnation method (drying the salt on the porous carrier) [10].

Then we assume that the FPs possess either an electrical or a magnetic dipole moment; also FPs must possess a vibration degree of freedom. Thus this model can be applied only to magnetic and ferroelectric materials. The vibration movement of such particles can be described in the first approximation by the following relations.

(a) for the electric dipole,

$$X = \frac{kdE_0}{m(\omega_0^2 - \omega^2)} \sin(\omega t). \quad (1)$$

(b) For the magnetic dipole,

$$X = \frac{kMH_0}{m(\omega_0^2 - \omega^2)} \sin(\omega t). \quad (2)$$

In these equations,  $m$  is the particle mass,  $k$  is the wavevector,  $\omega_0$  is the particle natural frequency,  $\omega$  is the radiation frequency, and  $E_0$  and  $H_0$  are the electric and magnetic field strengths, respectively. From these relations it can be seen that if the incident HFR has the frequency  $\omega \simeq \omega_0$ , then the resonant absorption of HFR is possible as follows: electromagnetic energy  $\rightarrow$  FPs (oscillator) vibration energy  $\rightarrow$  energy in the form of heat at the particle-carrier contact. The frequency of the harmonic oscillator can be written as

$$\omega_0 = \frac{1}{2\pi} \left( \frac{q}{m} \right)^{1/2} \quad (3)$$

where  $q$  is the oscillator force constant and  $m$  is the particle (oscillator) mass.

By varying  $q$  and  $m$ , one can achieve any resonant absorption frequency. It should be noted that both  $q$  and  $m$  are sensitive to the method of production of the FPs. We consider two main methods of the FP production on the carrier, maintaining their vibration degree of freedom.

### 2.1. Method 1: chemical bond

Heat decomposition of salts deposited on a carrier by precipitation or impregnation is carried out. As a result of pyrolysis, metal or oxide particles are formed and then reduced by hydrogen. Such heat treatment leads to the formation of a strong chemical bond between the particles and carrier because of its sintering. The force constant of this bond is essentially determined by the contact area which depends on the shape and orientation of FPs.

Hooke's law allows us to write the following relation:

$$q = E \frac{S}{\Delta l} \quad (4)$$

where  $E$  is Young's modulus of the sintering area,  $S$  is the contact area and  $\Delta l$  is the deformation (in the harmonic oscillator model it is equivalent to a spring).

The basis of calculation by this relation is very difficult since Young's modulus of the sintering area, the contact area and the deformation value are not known. However, in order to set limits on possible values of the natural frequency, one can carry out a calculation using estimates. For instance let us consider the iron FPs produced by pyrolysis of iron (III) nitrate and applied to the macroporous carrier on the base of  $\text{SiO}_2$ . Young's modulus of the sintering area can be varied from its value for iron ( $2 \times 10^{11}$  Pa) to its value for quartz ( $6.5 \times 10^8$  Pa), the contact area from  $0.1r^2$  to  $r^2$ , and the deformation value  $\Delta l$  from 5, to 10, to 20 Å. The calculated (by equations (3) and (4)) vibration frequencies are given in figure 1, curves a and b. It can be seen that values of  $\gamma$  and  $m$  exist which allow us to choose frequencies within the HFR region.

The process of production of FPs on the carrier mentioned above is very promising, but by varying the salt and the pyrolysis behaviour one can change the particle size, its force constant and consequently the frequency vibration range. We emphasize that for absorption of HFR the particles must possess a magnetic dipole moment.

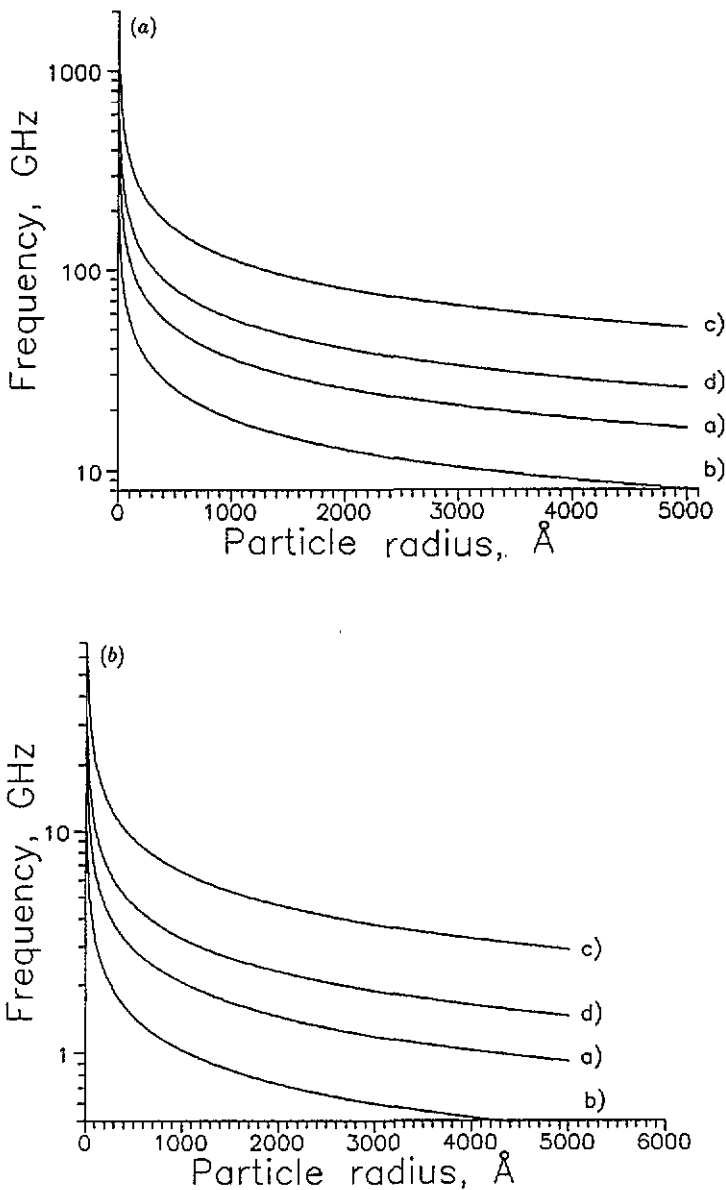


Figure 1. FP natural frequencies calculated from equations (3) and (4) for (a)  $E = 2 \times 10^{11}$  Pa and (b)  $E = 6.5 \times 10^8$  Pa: curves a,  $S = 0.1r^2$ ,  $\Delta l = 5$  Å; curves b,  $S = 0.1r^2$ ,  $\Delta l = 20$  Å; curves c,  $S = r^2$ ,  $\Delta l = 5$  Å; curves d,  $S = r^2$ ,  $\Delta l = 20$  Å.

2.2. Method 2: the London–van der Waals bond

This is a method of impregnation of the porous carrier by ferroelectric solutions. The choice of a ferroelectric is due to the presence of electric dipole moment in these particles. In this case the particles are bound to the carrier by the London–van der Waals forces.

The London–van der Waals force theory has been developed rather completely and it is easy to derive the analytical relations for the force constant [11, 12]: for spherical particles with radii  $r_1$  and  $r_2$ ,

$$q = \frac{H4r_1r_2[3R^2 + (r_1 + r_2)^2]}{6[R^2 - (r_1 + r_2)^2]^3} + \frac{4r_1r_2[3R^2 + (r_1 - r_2)^2]}{[R^2 - (r_1 - r_2)^2]^3} - \frac{2R^2 + 2(r_1 + r_2)^2}{[R^2 - (r_1 + r_2)^2]^2} + \frac{2}{R^2} \quad (5)$$

and, for a spherical particle of radius  $r$  and a plate with infinite depth,

$$q = \frac{64Hr^3(x + 2r)}{3x^3(x + 4r)^3} \quad (6)$$

where  $H$  is Hamaker's constant,  $x$  is the distance between particle and carrier and  $R$  is the distance between the particle centres.

However, Hamaker's constant is not known, but as an estimation it can be accepted according to [12] that  $H = 10^{-18}$ – $10^{-20}$  J and that  $x$  is 1–10 Å. The curves calculated from equations (3) and (6) are plotted in figure 2. It can be seen that in the case when the particle sizes are 30–10 000 Å the values of natural frequency are in good accordance with HFR range.

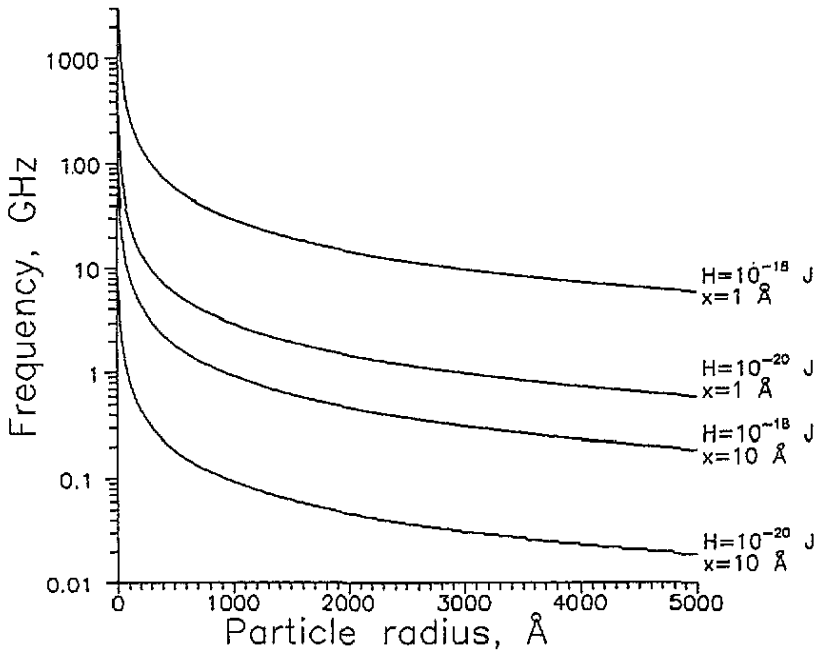


Figure 2. FP natural frequencies from equations (3) and (6).

The vibration of a loosely dispersed FP system can be described by equation (5) if the FPs are connected with each other by the London–van der Waals forces. As well as in the previous case, one can calculate the spectrum of natural frequencies of particles in this sample. This was the case described in [4–6].

It is necessary to emphasize that, in order to let the system of FPs absorb HFR, the particles must possess both a vibration degree of freedom and a dipole moment. Otherwise, HFR absorption is impossible. If these two conditions are realized, one could vary the frequency range in wide limits by changing the force constant (e.g. by sintering FPs with a carrier); also another free parameter is the particle size.

### 3. Results and discussion

For absorption experiments, two different types of sample have been synthesized.

First, samples of ferromagnets and ferrimagnets were produced by method 1. These FPs were produced by heat decomposition of Fe, Ni, Co and Cu nitrate aqueous solutions, pre-applied onto a  $\text{SiO}_2$  carrier. This carrier possesses a large surface (porosity about 95%). After decomposition the metallic oxides have been reduced by hydrogen. TEM and x-ray investigations showed that a polydisperse mixture of randomly arranged FPs formed with sizes of 100–5000 Å. Also samples containing  $\text{Fe}_3\text{O}_4$ ,  $\text{NiFe}_2\text{O}_4$  and  $\gamma\text{-Fe}_2\text{O}_3$  have been synthesized by the above technique with different temperatures and calcination times. More details on this technique will be published elsewhere.

Second, ferroelectric FPs were produced by impregnation of the carrier with ferroelectric solutions (potassium iron cyanide ( $\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$ ) and Rochelle salt ( $\text{K}_2\text{NaC}_4\text{H}_4\text{O}_6 \cdot 6\text{H}_2\text{O}$ )). We used the same carrier to produce both types of FP. In this method, ferroelectric FPs with sizes from 30 to 10 000 Å were produced. For details of the production of these FPs and their physical properties see [10].

In the absorption experiments the absorption was obtained as a function of frequency. The frequency range was 5–12 GHz. It was found that the samples containing FPs with a dipole moment (Fe, Ni, Co,  $\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$  and  $\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 6\text{H}_2\text{O}$ ) absorbed up to 90% of the incident HFR. The results of these investigations are presented in figures 3–5. In our opinion, the rather smooth type of absorption curves arises because there are many particles with different sizes, contact areas, sintering areas, etc, and each can absorb only one frequency; hence the total curve, consisting of many single curves, is smooth.

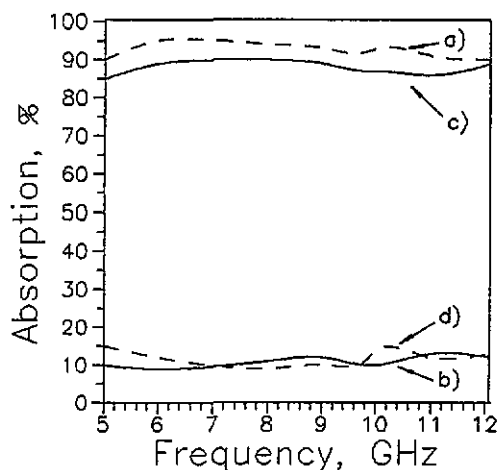


Figure 3. HFR absorption versus frequency: curve a, Fe+ $\text{SiO}_2$ ; curve b, Fe+ $\text{SiO}_2$  after impregnation; curve c, Ni+ $\text{SiO}_2$ ; curve d, Ni+ $\text{SiO}_2$  after impregnation.

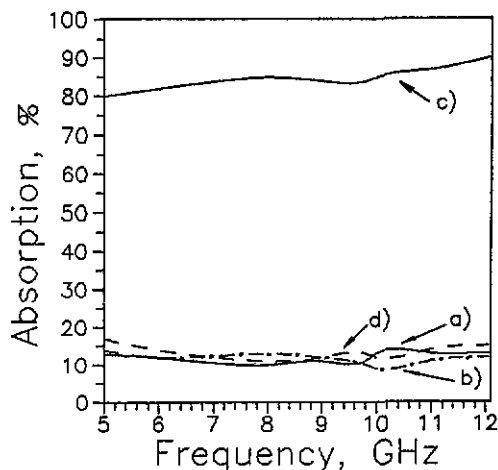


Figure 4. Absorption versus frequency: curve a, Cu+ $\text{SiO}_2$ ; curve b, Cu+ $\text{SiO}_2$  after impregnation; curve c,  $\text{NiFe}_2\text{O}_4$ + $\text{SiO}_2$ ; curve d,  $\text{NiFe}_2\text{O}_4$  after impregnation.

Also samples containing the metal oxides under consideration were investigated by incident HFR. It was found that absorption by these samples was about 5–10% which might be attributed to the effect of percolation. The same results were obtained during our Cu samples investigations. Its absorption was about 10%.

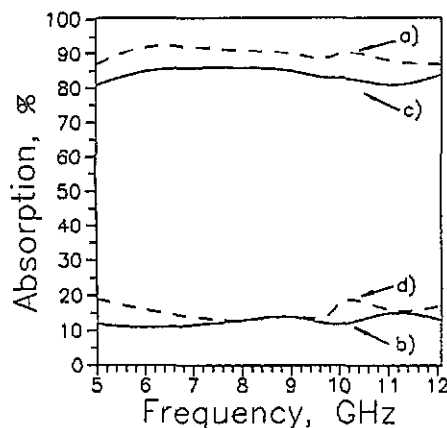


Figure 5. HFR absorption versus frequency: curve a,  $K_4(Fe(CN)_6) \cdot 3H_2O + SiO_2$ ; curve b,  $K_4(Fe(CN)_6) \cdot 3H_2O + SiO_2$  after impregnation; curve c,  $KNaC_4H_4O_6 \cdot 6H_2O + SiO_2$ ; curve d,  $KNaC_4H_4O_6 \cdot 6H_2O + SiO_2$  after impregnation.

It is interesting that after impregnation of such samples by chemically inert polymers, which filled out the pores completely, the HFR absorption value decreased to several per cent. In our opinion this phenomenon is explained in the following way: in this case the FPs have no vibration degree of freedom and hence no ability to vibrate and to be in resonance with the HFR. It should be pointed out that the above-mentioned method of FP production does not allow us to explain this phenomenon in conventional ways (skin effect or resistance loss). It should be noted that absorption depends strongly upon the sample density and uniformity of FPs distribution in the carrier volume. Heat treatment in vacuum leads to a shift in the absorption frequency spectrum to a shorter wavelength. This is in full accordance with the suggested theory of resonant absorption, i.e. the force constant increases with increasing natural frequency of the particles.

Thus the FP vibration spectra of the ferromagnets and ferroelectrics on the porous carrier were calculated on the basis of the suggested resonant mechanism. These spectra fall into the vibration region from  $10^7$  to  $10^{10}$  Hz which coincides with FP vibration frequencies calculated on the basis of the temperature dependence of recoilless absorption of  $\gamma$ -rays (Mössbauer effect) [2–8]. Therefore the main reason for the decreasing recoilless fraction in comparison with the value calculated on the basis of the Debye continuum theory is the high vibration frequencies of FPs.

In our opinion the next step in this research could be the simultaneous Mössbauer study of the above-described FP samples under incident HFR. On the basis of the data obtained, one might estimate the force constant value for particle–carrier connection and the vibration amplitude. This in turn allows us to specify the data used for the vibration spectrum calculation in the harmonic oscillator approximation.

#### 4. Conclusions

The method of HFR absorption by the FP system was proposed. The resonant mechanism of HFR absorption was theoretically proved and was experimentally confirmed.

The natural frequencies of FPs arranged on the macroporous carrier were calculated.

It was shown that the frequency spectrum obtained from the temperature dependence of the  $\gamma$ -ray recoilless absorption coincided with that calculated from HFR absorption ( $10^7$ – $10^{10}$  Hz).

On the basis of this research, one could conclude that the FP vibrations give the main contribution to the recoilless absorption.

### Acknowledgments

Financial support from the Scientific Council of Investigations in Electronics and Radio Engineering is gratefully acknowledged. One of us (V A Muratov) would like to acknowledge M I Mendeleev for a helpful and fruitful discussion.

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