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Clustering of Magnetic Ions in Diluted Solid Paramagnets

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A method for studying the magnetic ion cluster forming in magnetically diluted solid paramagnets is proposed based on experimental data on the concentration dependence of the EPR line form and width. As a concrete example, the distribution of the Mn^{2+} ions in the $Mn^{2+}:MgO$ solid solution is considered. Some questions of the EPR concentration dependence in the case of the homogeneous random distribution of the magnetic ions is discussed, too.

Предложен метод изучения кластеризации магнитных ионов в магниторазведённых твёрдых парамагнетиках, базирующийся на использовании экспериментальных данных по концентрационной зависимости формы и ширины линии ЭПР. В качестве примера рассмотрено распределение ионов Mn^{2+} в твёрдом растворе $Mn^{2+}:MgO$. Обсуждаются также некоторые вопросы концентрационной зависимости ЭПР в случае однородного случайного распределения магнитных ионов.

1. Introduction

There are many domains of scientific and technical research (see, for example, [1]) where it is necessary to know the magnetic ion distribution in the crystal lattice of a magnetically diluted crystal (solid solution). For transition ions in diamagnetic crystal such an information may be obtained by means of the concentration dependence study of the electron paramagnetic resonance (EPR). In the first paper [2] on the theory of the concentration dependence of the EPR line shape and width the supposition of a random distribution of magnetic ions has been accepted, i.e. for each site the occupation probability has been considered as equal to the concentration of magnetic ions $C = N_i/N_s$ where N_i is the number of magnetic ions and N_s the number of accessible sites. The same supposition has been used in the following papers [3 to 5]. However, some authors have mentioned the discrepancy between experimental concentration dependence data and theoretical results based on the random distribution supposition — for example, NiO-MgO (see [6] and references therein), in $Mn^{2+}:CdTe$ [7], in $Cr^{3+}:Al_2O_3$ [8], and so on. In the paper presented a method of approximate statistical description of the magnetic ion distribution using some EPR experimental data is proposed and an example of its application is considered. A kind of inversion of the method is discussed, too.

2. Method

To treat the problem in question, the method of moments may be used. Let us consider the case in which the form of the line shape function and its width are due only to the dipolar and exchange interactions. Bearing in mind symmetric lines, let us use the second and the fourth moments. For a powder sample the following expressions have been obtained [9]:

$$M_2^{ad} = \frac{3}{5N} a \sum_{k \neq j} E_{jk}, \quad (1)$$

$$M_4^{\text{ad}} = \frac{1}{5N} a^2 \sum_{m,j,k\neq} \left(\frac{21}{5} E_{jk} E_{jm} - \frac{18}{5} E_{jk} E_{km} \frac{r_{km}}{r_{jm}} + 4I_{jk}^2 E_{jm} + 2I_{jk} I_{km} E_{jm} \right) + \frac{9}{25N} \sum_{k\neq j} \left[\frac{9}{7} \left(\frac{7}{3} a^2 - \frac{1}{2} a \right) E_{jk}^2 + \left(2a^2 - \frac{3}{2} a \right) I_{jk}^2 E_{jk} \right] \quad (2)$$

for weak exchange $I < g\beta H$ (adiabatic case [10]) and

$$M_2^{\text{non}} = \frac{10}{3} M_2^{\text{ad}} \quad (3)$$

for strong exchange $I > g\beta H$ (nonadiabatic case [10]). Here N is the number of magnetic ions, I_{jk} the isotropic exchange constant, $a \equiv S(S+1)$, and $E_{jk} = (g^2\beta^2/r_{jk}^3)^2$, where r_{jk} is the distance between magnetic ions. After rather long calculations, the expression

$$M_4^{\text{non}} = \frac{4}{5N} (3a^2 - 2a) \sum_{k\neq j} I_{jk}^2 E_{jk} + \frac{4}{3N} a^2 \sum_{m,j,k\neq} I_{jk} (2I_{jk} E_{jm} + I_{mk} E_{jm}) \quad (4)$$

for the fourth moment in the case of strong exchange has been found, the terms of the first order with respect to I_{jk} being omitted. All the sums in (1) to (4) must be calculated only for the sites occupied by magnetic ions.

Let $N_{\{qk\}}(C)$ be the number of magnetic ions having q_1 magnetic neighbours on the first coordination sphere possessing Q_1 sites, q_2 magnetic neighbours on the second coordination sphere possessing Q_2 sites, and so on; these numbers are functions of the magnetic ion concentration C . The sums in (1) to (4) may be put down as functions of the concentration by means of $N_{\{qk\}}(C)$. For example,

$$\sum_{k\neq j} E_{jk} = \sum_n \left(\frac{g^2\beta^2}{a_n^3} \right)^2 \sum_{q_1=0}^{Q_1} \dots \sum_{q_k=0}^{Q_k} \dots q_n N_{\{qk\}}(C), \quad (5)$$

where n denotes the coordination sphere and a_n its radius. For the sums which contain three indexes it is necessary to use the average distances \bar{r}_{mn} between the sites of the m -th and n -th coordination spheres. For some lattices these distances are given in Table 1. Now the moments may be put down as follows:

Table 1

Average distances \bar{r}_{mn} between the sites of m -th and n -th coordination spheres ($a_1 = 1$)

lattice	\bar{r}_{11}	\bar{r}_{12}	\bar{r}_{13}	\bar{r}_{14}	\bar{r}_{15}	\bar{r}_{16}	\bar{r}_{22}	\bar{r}_{23}	\bar{r}_{24}	\bar{r}_{25}	\bar{r}_{26}
cubic	1.53	1.66	1.93	2.16	2.38	2.58	2.02	2.12	2.34	2.53	2.72
cubic face centred	1.43	1.66	1.92	2.16	2.38	2.58	2.17	2.12	2.34	2.52	2.73
cubic body centred	1.48	1.46	1.83	2.09	2.16	2.64	1.77	1.91	2.14	2.23	2.69
lattice	\bar{r}_{33}	\bar{r}_{34}	\bar{r}_{35}	\bar{r}_{36}	\bar{r}_{44}	\bar{r}_{45}	\bar{r}_{46}	\bar{r}_{55}	\bar{r}_{56}	\bar{r}_{66}	
cubic	2.56	2.52	2.69	2.85	3.06	2.83	3.01	3.09	3.13	3.38	
cubic face centred	2.39	2.50	2.73	2.85	2.86	2.84	3.00	3.08	3.15	3.62	
cubic body centred	2.33	2.38	2.45	2.86	2.64	2.62	3.00	2.96	3.03	3.47	

$$M_2^{\text{ad}} = \frac{3a}{5N} \sum_n \sum_{q_1=0}^{Q_1} \cdots \sum_{q_k=0}^{Q_k} \cdots N_{\{q_k\}}(C) q_n E_n, \quad (6)$$

$$\begin{aligned} M_4^{\text{ad}} = & \frac{a^2}{5N} \sum_{q_1=0}^{Q_1} \cdots \sum_{q_k=0}^{Q_k} \cdots \left\{ \sum_n q_n(q_n - 1) N_{\{q_k\}}(C) \left[\frac{21}{5} E_n^2 - \frac{18}{5} E_n^2 \left(\frac{a_n}{r_{nn}} \right)^5 + \right. \right. \\ & + 4E_n I_n^2 + 2\bar{E}_n I_n^2 \left. \right] + \sum'_{m,n} q_m q_n N_{\{q_k\}}(C) \left[\frac{21}{5} E_m E_n - \frac{18}{5} E_m E_n \left(\frac{a_n}{r_m} \right)^5 + \right. \\ & + 4E_n I_m^2 + 2\bar{E}_{mn} I_m I_n \left. \right] + \sum_n q_n E_n N_{\{q_k\}}(C) \times \\ & \times \left[\frac{81}{35} \left(\frac{7}{3} - \frac{1}{2a} \right) E_n + \frac{9}{10} \left(4 - \frac{3}{a} \right) I_n^2 \right] \left. \right\}, \quad (7) \end{aligned}$$

$$M_2^{\text{non}} = \frac{2a}{N} \sum_n \sum_{q_1=0}^{Q_1} \cdots \sum_{q_k=0}^{Q_k} \cdots N_{\{q_k\}}(C) q_n E_n, \quad (8)$$

$$\begin{aligned} M_4^{\text{non}} = & \frac{4a^2}{N} \sum_{q_1=0}^{Q_1} \cdots \sum_{q_k=0}^{Q_k} \cdots \left\{ \frac{1}{3} \sum_n q_n(q_n - 1) N_{\{q_k\}}(C) I_n^2 (2E_n + \bar{E}_n) + \right. \\ & + \frac{1}{3} \sum'_{m,n} q_m q_n N_{\{q_k\}}(C) I_n \times \\ & \times (2I_n E_m + I_m \bar{E}_{mn}) + \frac{1}{5} \left(3 - \frac{2}{a} \right) \sum_n q_n N_{\{q_k\}}(C) I_n^2 E_n \left. \right\} \quad (9) \end{aligned}$$

with

$$\bar{E}_n = \left(\frac{g^2 \beta^2}{r_n^3} \right)^2, \quad \bar{E}_{mn} = \left(\frac{g^2 \beta^2}{r_{mn}^3} \right)^2.$$

Let the site occupation probability for the first coordination sphere be $f_1(C)$, for the second sphere $f_2(C)$, and so on. Then the mean values of the numbers $N_{\{q_k\}}$ are

$$N_{\{q_k\}}(C) = N \prod_k [C_{Q_k}^{q_k} (f_k(C))^{q_k} (1 - f_k(C))^{Q_k - q_k}] \quad (10)$$

and the moments can be expressed in terms of $f_k(C)$. Of course, the pair space correlations between different ions can practically be essential only at short distances. Usually such correlations are to be taken into account only for the first and, sometimes, the second coordination spheres [1]. For all the other spheres we may put $f_k(C) = C$. Our task is to find the function $f_1(C)$ (and, may be, $f_2(C)$). Let the EPR absorption line experimentally obtained be approximated by some functions containing as many parameters as line moments are available. This is practically always the case and makes it possible to express the parameters mentioned in terms of the line moments. On the other hand, the line characteristics such as linewidth, the amplitude, and so on are functions of the line parameters in question. The symmetric EPR absorption lines in solids may usually be approximated by functions having a form intermediate between rectangular and Gaussian or between Gaussian and Lorentzian. In the first case the Abragam's function [10]

$$f_A(\omega) = \frac{1}{4b} \operatorname{erf} \frac{b + (\omega - \omega_0)}{\sqrt{2} d} + \frac{1}{4b} \operatorname{erf} \frac{b - (\omega - \omega_0)}{\sqrt{2} d} \quad (11)$$

may be used for which b and d are parameters and

$$M_2 = d^2 + \frac{b^2}{3}, \quad M_4 = 3d^4 + 2d^2b^2 + \frac{b^4}{5} \quad (12)$$

which gives

$$d^2 = M_2 - \sqrt{\frac{5}{2} M_2^2 - \frac{5}{6} M_4}, \quad b^2 = 3 \sqrt{\frac{5}{2} M_2^2 - \frac{5}{6} M_4}. \quad (13)$$

The half-width of this line may be obtained as the solution of the equation

$$\operatorname{erf} \frac{b + \frac{1}{2} \Delta\omega_{1/2}}{\sqrt{2} d} + \operatorname{erf} \frac{b - \frac{1}{2} \Delta\omega_{1/2}}{\sqrt{2} d} = \operatorname{erf} \frac{b}{\sqrt{2} d}. \quad (14)$$

Using the power and asymptotic series to represent the function erf [11] we have obtained

$$\Delta\omega_{1/2} = \begin{cases} 2b + \frac{2d^2}{b} \exp\left(-\frac{b^2}{2d^2}\right), & \frac{b}{d} \geq 1.9, \\ d \left(2.34 + 0.44 \frac{b^2}{d^2}\right), & 1.9 \geq \frac{b}{d} \geq 0.7, \\ 2d \sqrt{2 \ln \frac{12d^2}{6d^2 - b^2}}, & 0.7 \geq \frac{b}{d} > 0 \end{cases} \quad (15)$$

as a result of the numerical solution and the interpolation in the intermediate region, the approximation error being not more than 2%.

In the second case, i.e. the Lorentz-Gauss form (which usually is the case of a small magnetic ion concentration or a strong exchange) the mixed function

$$f_{L-G}(\omega) = \frac{\sqrt{A}}{\pi} \varphi\left(\frac{C}{A}\right) \frac{\exp\{-C(\omega - \omega_0)^2\}}{1 + A(\omega - \omega_0)^2} \quad (16)$$

is useful having the moments

$$M_2 = \frac{\varphi\left(\frac{C}{A}\right)}{\sqrt{\pi A}} \left[\frac{1}{\sqrt{C}} - \sqrt{\frac{\pi}{A}} \frac{1}{\varphi\left(\frac{C}{A}\right)} \right], \quad (17)$$

$$M_4 = \frac{\varphi\left(\frac{C}{A}\right)}{\sqrt{\pi AC}} \left[\frac{1}{2C} - \frac{1}{A} + \frac{1}{A \varphi\left(\frac{C}{A}\right)} \sqrt{\frac{\pi C}{A}} \right],$$

where $\varphi(C/A) = \exp(-C/A) (1 - \operatorname{erf} \sqrt{C/A})^{-1}$. The parameters A and C are tied with moments for which we got the formulae by using series for function erf [11], numerical solution, tables [12], and interpolation:

$$\frac{C}{A} = \begin{cases} \frac{1.63}{\sqrt{1-3x}} + \frac{1.86}{1.22 + 3.39\sqrt{1-3x}}, & \frac{1}{3} > x \geq 0.323, \\ 2.18 \times 10^{16} x^{31.25}, & 0.323 \geq x \geq 0.300, \\ 802 x^{5.55}, & 0.300 \geq x \geq 0.198, \\ 3.4 x^{2.18}, & 0.198 \geq x \geq 3.56 \times 10^{-4}, \\ 0.79 x^2, & x \leq 3.56 \times 10^{-4}, \end{cases} \quad (18)$$

where $x \equiv M_3^2/M_4$,

$$A = \begin{cases} \frac{1}{2M_2y} \left(1 - \frac{1}{y} + \frac{1.37}{y^2} \right), & y > 10, \\ \frac{0.32}{M_2} y^{-0.844}, & 1 \leq y \leq 10, \\ \frac{0.32}{M_2} y^{-0.662}, & 0.1 \leq y \leq 1, \\ \frac{1}{M_2 \sqrt{\pi y}} (1 - 0.64 \sqrt{y} + 0.25y), & y \leq 0.1, \end{cases} \quad (19)$$

where $y \equiv C/A$. The half-width of the line (16) is

$$\Delta\omega_{1/2} = \begin{cases} \frac{2}{\sqrt{A(1+2y)}}, & y \leq 0.1, \\ \frac{2}{\sqrt{A}} (0.61 - 0.19 \ln y - 0.03 \ln^2 y), & 0.1 \leq y \leq 1, \\ \frac{2}{\sqrt{A}} (0.61 - 0.19 \ln y + 0.02 \ln^2 y), & 1 \leq y \leq 10, \\ \frac{1.66}{\sqrt{A(1+y)}}, & y \geq 10. \end{cases} \quad (20)$$

The lines (11) and (16) are normalised by the condition $\int_{-\infty}^{\infty} f(\omega) d\omega = 1$.

The formulae given above may be used for processing the experimental data on the EPR line shape and width. Given the magnetic ion position probability distribution, formulae (4) to (10) make it possible to obtain the absorption line moments. Contrarily, the EPR line characteristics experimentally obtained can be used to find the probability distribution mentioned (which is more interesting and important).

3. Example: Distribution of the Ions Mn^{2+} in MgO

The experimental data on the concentration dependence of the EPR line width in $Mn^{2+}:MgO$ in the concentration range $0.01 < C < 1$ [13, 14] (see Fig. 1) could not be explained on the basis of the supposition of equal site occupation probabilities [5]. The exchange parameters are [15]: $I_1 = (19 \pm 3) \text{ cm}^{-1}$, $I_2 = (1 \pm 0.1) \text{ cm}^{-1}$ for the Mn^{2+} ions in the first and second coordination spheres, respectively; so, this is the non-

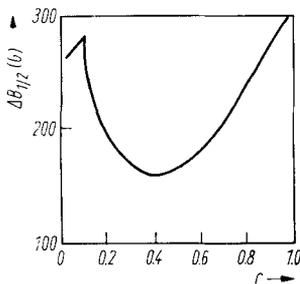


Fig. 1. The experimental data on the concentration dependence of the EPR line width in $Mn^{2+}:MgO$ [13, 14]

adiabatic case ($I_1/g\beta H \approx 10$). Let us take the simplest case in which only the influence of the presence of a magnetic ion at each occupied site on the site occupation probabilities for the first coordination sphere is accounted for. In this case the probabilities are equal to C for all the sites except those of the first coordination sphere and to $f(C) \equiv f_1(C) \neq C$ for the sites of the first sphere. According to that using formulae (8), (9), and (10) we get

$$M_2^{\text{non}} = 2a \left(Q_1 f(C) E_1 + C \sum_{n=2}^{\infty} Q_n E_n \right), \quad (21)$$

$$\begin{aligned} M_4^{\text{non}} = 4a^2 & \left\{ \frac{1}{3} f^2(C) Q_1(Q_1 - 1) I_1^2(2E_1 + \bar{E}_1) + \right. \\ & + \frac{1}{3} C^2 \sum_{n=2}^{\infty} Q_n(Q_n - 1) I_n^2(2E_n + \bar{E}_n) + \\ & + \frac{2}{3} C f(C) Q_1 \sum_{n=2}^{\infty} Q_n (I_1^2 E_n + I_n^2 E_1 + I_1 I_n \bar{E}_{1n}) + \\ & + \frac{1}{3} C^2 \sum'_{m,n=2} Q_m Q_n I_n (2I_n E_m + I_m \bar{E}_{mn}) + \\ & \left. + \frac{1}{5} \left(3 - \frac{2}{a} \right) \left[Q_1 f(C) I_1^2 E_1 + \sum_{n=2}^{\infty} Q_n C I_n^2 E_n \right] \right\}. \quad (22) \end{aligned}$$

The line shape being almost Lorentzian in the whole concentration range [13, 14], formulae (18), (19), and (20) with $M_2^2/M_4 \ll 1$ give

$$\Delta\omega_{1/2} = 2.52 \sqrt{M_2^3/M_4}. \quad (23)$$

For the parameter values given above, one obtains

$$\Delta B_{1/2}(C) = (240 \pm 35) \sqrt{\frac{[4.9f(C) + C]^3}{14f^2(C) + (3C + 1)f(C) + 3C^2}}. \quad (24)$$

Here $\Delta B_{1/2}(C)$ is the absorption line half-width experimentally obtained (in field units $\Delta B_{1/2} = (\hbar/g\beta) \Delta\omega_{1/2}$). Using a set of values of this quantity (see Fig. 1) and solving (24) numerically, one gets the function $f(C)$ shown in Fig. 2. This function possesses a minimum at $C_{\text{min}} \approx 0.4$ with $f(C \ll C_{\text{min}}) \gg C$ which reveals the tendency to cluster formation for small concentration values. In the concentration range $C \lesssim 0.1$ our results cannot be valid because of the fact that they lead to probability values exceeding unity. To get rid of this discrepancy, one has to take into account the next pair correlations and the exchange interactions inside the coordination spheres.

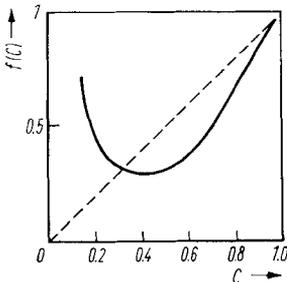


Fig. 2. The concentration dependence of the site occupation probability for the first coordination sphere $f(C)$. Dashed line: probability for the random distribution

The fact that different values of the parameters in question (especially of I_2) have been given by different authors (see [16]) does not affect our qualitative conclusion that the Mn^{2+} ion clusters in MgO are more numerous than it follows from the equal probability hypothesis.

4. Inversion of the Method: Equal Probability Case in Dipolar System

The method proposed allows to predict a concentration dependence of the shape and width EPR lines on condition that some suppositions are accepted for the distribution of the magnetic ions. Let us consider the simple case (which has been considered before by other authors [2 to 4]) in which the EPR line shape is defined by the dipole-dipole interactions of randomly distributed magnetic ions. The problem is to calculate the sums entering the formulae for the moments (or the type (1), (2)) only for the sites occupied by magnetic ions. Kittel and Abrahams [2] assumed that the sums may be calculated for all the sites and then multiplied by the concentration C for the two-indexes sums and by C^2 for the three-indexes ones. Then the line will be quasi-Lorentzian (if the concentration is small) and the linewidth proportional to C .

In our notation, the random distribution means that $f_k(C) = C$ in formula (10) for all values of k . Using (10), (6), and (7) we have got

$$M_2 = aCS_1, \quad M_4 = a^2C^2S_2 + C(14a^2 - 3a)S_3, \quad (25)$$

where

$$\begin{aligned} S_1 &= \frac{3}{5} \sum_n Q_n E_n, \\ S_2 &= \frac{3}{25} \left[\sum_n Q_n(Q_n - 1) E_n^2 \left(7 - 6 \left(\frac{a_n}{r_{nn}} \right)^5 \right) + \sum'_{m,n} Q_m Q_n E_m E_n \left(7 - 6 \left(\frac{a_n}{r_{mn}} \right)^5 \right) \right], \\ S_3 &= \frac{27}{350} \sum_n Q_n E_n^2. \end{aligned} \quad (26)$$

The sums S_1, S_2, S_3 have been calculated for some lattices and are given in Table 2.

Table 2
The lattice sums S_1, S_2, S_3

lattice	$S_1 \left/ \left(\frac{g^2 \beta^2}{a_1^3} \right)^2 \right.$	$S_2 \left/ \left(\frac{g^2 \beta^2}{a_1^3} \right)^2 \right.$	$S_3 \left/ \left(\frac{g^2 \beta^2}{a_1^3} \right)^2 \right.$
cubic	5.1	43.3	0.48
cubic face centred	8.7	135.7	0.94
cubic body centred	7.4	96.4	0.70

In order to get an additional control, we have performed the numerical calculation of the concentration dependence of the sum $S = \sum_{j,k} r_{jk}^{-6}$, which differs from (1) only by a constant multiplier. The scheme of the calculation is the following: A fixed number $N = 90$ of ions has been distributed randomly by the computer inside the cube containing n^3 lattice sites. The sum S has been found for each of a large number of distributions, n being the same. Using Student's statistical distribution (see, for example, [17]), the value of S for a given concentration $C = N/n^3$ and the standard deflection ΔS have been obtained for the reliability 0.9. Table 3 shows the results of the calculation. These results are in agreement with formula (25).

Table 3

The results of computer calculation of the concentration dependence of the sum S (random distribution)

n	C	number of versions	S	ΔS
45	0.0010	300	0.72	0.10
21	0.0097	186	6.76	0.36
14	0.0328	185	22.08	0.66
12	0.0521	180	33.92	0.82
11	0.0676	180	45.04	1.02

For concentrations small enough the line is exactly Lorentzian, and for its width (18), (19), (20), and (25) give

$$\Delta\omega_{1/2} = C \frac{2.50a}{\sqrt{14a - 3}} \sqrt{S_1^3/S_3}, \tag{27}$$

i.e. the width is proportional to the concentration. For large concentrations according to (11), the line shape is intermediate between rectangular and Gaussian for $M_2^2/M_4 > 1/3$ and Gaussian for $M_2^2/M_4 = 1/3$. The concentration which corresponds to the Gaussian line is

$$C_{\text{Gauss}} = \left(1 - \frac{3}{14a}\right) \frac{14S_3}{3S_1^2 - S_2}. \tag{28}$$

Its values for spin 1/2, 1, 3/2, 2, 5/2 are given in Table 4.

Table 4

The values of concentration which corresponds to a Gaussian line defined by dipole-dipole interactions (random distribution)

lattice	spin				
	1/2	1	3/2	2	5/2
cubic	0.14	0.17	0.18	0.19	0.19
cubic face centred	0.10	0.13	0.14	0.14	0.14
cubic body centred	0.10	0.13	0.14	0.14	0.14

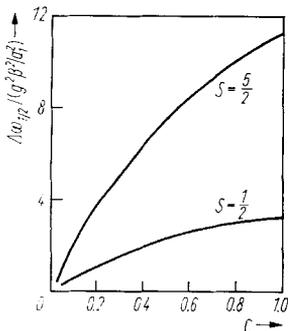


Fig. 3. The concentration dependence of the linewidth for spin $S = 1/2$, $S = 5/2$, for random distribution

Using formulae (11) to (20), we have found the linewidth for $S = 1/2$ and $S = 5/2$. This dependence may be approximated by the expression $\Delta\omega_{1/2} \approx C^\alpha$, where $\alpha = 1.0$ for $C \lesssim 0.05$, $\alpha = 0.9$ for $0.05 < C \lesssim 0.3$, and $\alpha = 0.7$ for $C > 0.3$ (see Fig. 3).

5. Conclusions

It seems that the method developed could be useful for the study of the magnetic ion distribution in solid solution — in some cases, more useful than the methods traditionally applied. The mere fact of magnetic ion clustering in magnetically diluted crystals is well known; see, for example, [6] and [18] where Ni^{2+} and Fe^{3+} clusters in MgO are considered, respectively. In the survey [1] causes and consequences of the clustering effect are discussed thoroughly. As to the paper presented, its purpose is to call one's attention to some new aspects of the statistical approach to the clustering effect.

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