Nonlinear Phenomena in Complex Systems, vol. **17**, no. 3 (2014), pp. 306 - 317

Three Levels of Difficulty in Quantitative Analyzing the Results of Real Measuring Regression Experiments

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The description of concepts and methods of the operational regression theory is reported in detail, three levels of difficulty in operational quantitative analyzing the results of real measuring regression experiments are determined and implementation of all three levels into some real magnetochemical experiments, devoted to the study of the magnetic behavior of weak magnetic solid solutions with $3d$-ions versus temperature, is demonstrated.

PACS numbers: 06.20.Dk; 07.05.Kf; 75.20.-g; 75.30.Kz
Keywords: operational regression theory, levels of computational difficulty, magnetic susceptibility, weak magnetic solid solutions, modifications of Curie and Curie–Weiss laws

1. Introduction

The basic computational concepts of classical, operational and regularization approaches to quantitative processing the numerical information of the measuring regression experiments have been discussed in [1]. All related information in [1] was given in a brief concise form. In particular, only four distinctive features in operational quantitative processing of numerical information were mentioned. Namely,

i) *The main problem* of a measuring regression experiment is the investigation of the dependence of a given object characteristic y on a fixed characteristic x. In other words, it is required first to determine the experimental dependence $\{y_n,\ x_n\}$ and then for a given approximative function $F(A,x)$ to find the value of vector parameter A within an error δA where y_n is n-th value of dependent variable, measured within error ε_n, x_n is n-th fixed value of independent variable x ($\{x_n\}$ is *an experiment realization*). Thus, it is assumed initially that (a) the value of the dependent variable is given within some fixed error ε_n; (b) the vector parameter A is to be determined on the experimental dependence $\{y_n,\ x_n\}$ within some fixed error δA or, in other words, in this problem the point estimation of vector parameter A is initially replaced on the interval estimation.

ii) *The operational data analysis model* is distinguished from the classical one $y = F(A, x)+e$ by the presence of a measuring function $g(y)$

$$y_n = g(F(A, x_n) + e_n) \tag{1}$$

where the function g in (1) is necessary to show that n-th value of dependent variable is measured within some error ε_n, $\{e_n\}$ is some noise of the experiments.

iii) If $\varepsilon_n = \varepsilon$ for any n, then the measurement function g coincides with the truncation function

$$\begin{array}{l} g_\alpha(y) = 2\alpha[y/(2\alpha)] + 2\alpha \\ \text{if}\ \ |y - 2\alpha[y/(2\alpha)]| \geq \alpha, \\ \text{else}\ \ g_\alpha(y) = 2\alpha[y/(2\alpha)] \end{array} \tag{2}$$

where the value of $\alpha = \varepsilon$, $[b]$ means the integer part of b.

iv) For the measurement function (2), analytical (operational) solutions of the main fitting problems (see point (i)) can be found by *the algorithm*

1. Find the minimum value $\alpha = \alpha_{\min}$ as a solution of the extreme problem

$$\min_{\alpha} \max_{U} \max_{n} |y_n - g_\alpha(y'_n)|$$

where y'_n is an estimate of n-th value of the dependent variable y, the maximum on U means

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the search for a solution on all U sets of $\{x_U\}$, composed of $N, \ldots, N-n_0$ readings, n_0 is a given integer number, which assigns the maximum level of truncating the initial data array $\{y_n, x_n\}$.

2. Construct a set of equivalent analytical functions $g_\alpha(F(\{P_{m_i}(C'_i, \xi)\},\ x)$ where $\alpha = \alpha_{\min}$ and $P_{m_i}(C'_i, \xi)$ are some polynomials of degree m_i with the variable of ξ ($|\xi| < 1$ or $|\xi| \leq 1$) and the vector parameters of C_i.

3. Compute the value of variance $\delta A'$ by assigning the extreme values of the parameter ξ in the function $F_{\rm a}(A'(\xi), x) = F(\{P_{m_i}(C'_i, \xi)\},\ x)$.

In the next sections the minimal set of concepts and methods of the operational regression theory is significantly expanded, three levels of difficulty in operational quantitative analyzing the results of the real measuring regression experiments are determined and the implementation of all three levels into some real magnetochemical experiments, devoted to the study of the magnetic behavior of weak magnetic solid solutions with $3d$-ions versus temperature, is demonstrated.

2. Expanding the minimal set of concepts and methods of the operational regression theory

2.1. Planning of the measurement process

The measurement experiment, defined in Section 1, shall be called

a) *an active* one, if

i) it is possible to plan the measurement process for this experiment,

ii) the experiment is realized with taking a heed of the measurement process planning results;

b) *a passive* one, if the experiment is realized without taking a heed of the measurement process planning results.

The words "planning of the measurement process" mean an imitation computation procedure, by which for fixed

a) value of vector parameter $A = A_{\rm true}$,

b) experiment realization $\{x_n\}$,

c) estimation method

one is able to find such a maximum value $\varepsilon_{\max}$, that, if the values of dependent variable in the data array $\{y_n,\ x_n\}$ are measured within an error $\varepsilon_{\max}$, then it is still possible to determine the value of the vector parameter A within a given error δA where $y_n = g_{\varepsilon_{\max}}(F(A_{\rm true},\ x_n))$.

If the error δA is not set, then as a value of $\varepsilon_{\max}$ one can select the largest error $\max\limits_n(\varepsilon_n)$ where ε_n is determined in Section 1.

2.2. Searching for a set of optimal estimation methods

Before beginning any active measuring experiment, let one find $\{\varepsilon^{(q)}_{\max}\}$ (see Section 2.1) for a set of estimation methods having numbers $q = 1, \ldots, Q$ and $\varepsilon^* = \max\limits_q(\varepsilon^{(q)}_{\max})$. In this case one forms a set of best estimation methods from the methods with $\varepsilon^{(q)}_{\max} = \varepsilon^*$. Any estimation method included in the mentioned set of best methods shall be called *optimal*.

2.3. Determining the contamination level of the initial data array

As a rule, full control of the operational situation of a measurement experiment is impossible in practice. For this reason, even for an active measurement experiment, nobody can ensure that the contamination level in the initial data array $\{y_n, x_n\}$ does not exceed the permissible value $\varepsilon_{\max}$ (see Section 2.1). For determination of the contamination level of the dependent variable in the initial data array $\{y_n, x_n\}$, it is suggested to use virtual device (VD) method, mentioned in point 1 of the corresponding algorithm from the Section 1.

It should be noted that

a) since the value $\alpha_{\min}$ is determined by VD-method from the worst suitable variant, the value $\alpha_{\min}$ is directly proportional to the value $\max\limits_n |e_n|$ in (1) and, consequently, one can indeed estimate the contamination level of the dependent variable in the initial data array $\{y_n, x_n\}$ by the value

$\alpha_{\min}$;

b) due to the interpretation of the contamination level of the dependent variable in the initial data array $\{y_n, x_n\}$, which is given in the point (a), it is evident that for determination of the discussed contamination level one can also use some methods, elaborated in the frame of the "guaranteed approach" to solving approximative problems [2–5].

2.4. Classification of active measurement experiments and their properties

An active measurement experiment is

i) *a precision* if

$$\alpha_{\min} \le \varepsilon_{\max}. \tag{3}$$

In this case the determination of the values A' within an error δA can be made on any subset of $\{x_i\}$, contained not less than $M+1$ different elements of $\{x_n\}$ where M is the dimension of the vector parameter A of the approximative function $g(F(A,x))$ (see (1));

ii) *a local non-precision* if it is precision only on a truncated sets $\{x_i\} \subset \{x_n\}$ and the number of elements in $\{x_i\}$ exceeds $M+1$. Thus, one can simply bring this case to the case (i) by deleting all outliers from the initial array $\{y_n, x_n\}$;

iii) *a global non-precision* if the number of elements in $\{x_i\}$ (see point (ii)) does not exceed $M+1$. In this case one must solve tasks on revealing the parameters values of the (global) inadequate fitting models $F(A,x)$. This task is solved if one can find new fitting models $G(B,x)$ for which the condition $\alpha_{\min} \le \varepsilon_{\max}$ is satisfied [6].

This classification system (see points (i)-(iii) and Figure 1) clearly reflects all three levels of difficulty in operational quantitative analyzing the results of real measuring regression experiments. The bottom right rectangle is marked in Figure 1 with Greek letter "Θ" because it is the only case when, by using the methods of the operational regression theory, one can not extract any useful information from the initial data array $\{y_n, x_n\}$.

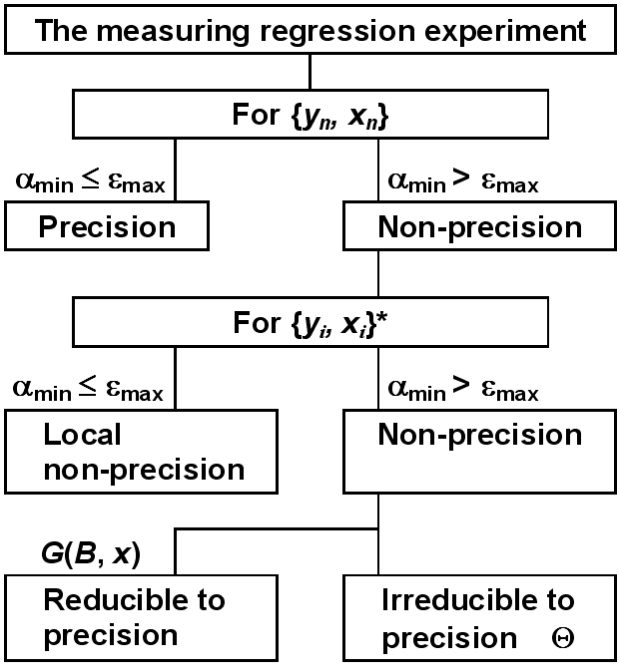

FIG. 1. Levels of computational difficulty in the operational regression.

2.5. Testing the adequacy of approximative models

It is suggested to use the condition (3) as a test of adequacy of the approximative function $g(F(A,x))$. Indeed, the condition (3) is connected with the concept of the "precision experiment" that is equivalent to the concept of the "best even-approximating function", used in approximation theory [7–9] and, accordingly, the concept of "inadequacy of approximative function" $g(F(A,x))$ does not disagree with the same concept, accepted in design experiment and regression analysis theories [10–12].

2.6. Set of equivalent approximative functions

"In practice, as the rule, neither prior information about the probability nature of processed data, nor the knowledge of physical mechanism of investigated phenomenon do not give us, just the same, enough arguments, by

which one could establish rigorously the choice of some model or other..." [13].

Continuous on interval $[x_{\min}, x_{\max}]$ analytical functions $g(F_1(A_1, x))$ and $g(F_2(A_2, x))$ shall be called *equivalent approximative functions*, if for any x_i of $\{x_n\}$

$$g_\alpha(F_1(A'_1, x_i)) = g_\alpha(F_2(A'_2, x_i)) \qquad (4)$$

where $x_{\min}$ and $x_{\max}$ are respectively minimum and maximum values of the independent variable x on the experiment realization $\{x_n\}$, A'_1 and A'_2 is some estimates of the vector parameters A_1 and A_2; $g_\alpha(y)$ is a measurement function (2).

3. Different implementations of three computational levels in some real magnetochemical experiments

Magnetochemistry is a branch of physical chemistry that examines the interrelationship between a magnetic field and different paramagnetic ions embedded in diamagnetic structures [14–16].

3.1. Operational modification of the Curie and Curie–Weiss laws

According to [14–17], experimental temperature dependencies of the specific magnetic susceptibility χ for magnetically dilute solid solutions, containing $3d$ ions, obey the Curie $F_1 = C/T$ or Curie–Weiss $F_2 = C/(T - \theta)$ laws where T is the temperature, K; θ is the Weiss constant, K; C is the Curie constant, the value of which is proportional to the square of an effective magnetic moment of a $3d$ ion.

However, F_i-models are inadequate if

a) $\chi = \chi_0 + F_i$ where $i = 1, 2$, χ_0 is a temperature independent part of the specific magnetic susceptibility that consists of the structure diamagnetism and paramagnetism of Van Vleck and Pauli;

b) investigated samples are magnetic heterogeneous.

Let us discuss *some advantages* of modified models $F_i^* = \chi_0 + F_i$.

i) If $\chi_0 \neq 0$ then using models F_i^* *allows to avoid the "global non-precision" situations* in real magnetochemical experiments with magnetically dilute solid solutions.

ii) In real magnetochemical experiments [18–28] an inconsistent parametric approach is used to determine the value of χ_0. The essence of this approach is to calculate values of χ_0 by using some tables containing information about the contribution to value χ_0 of each individual element forming the chemical formula of the solid solution. Obviously, the inconsistent parametric approach goes beyond the operational approach to conducting scientific experiments, as it ignores the following two operational requirements: (a) main experimental information must be obtained only within the confines of a given experiment, (b) all operational conditions of a given experiment should be included into approximation (theoretical) models as some parameters or functions [29–33]. Since models F_i^* satisfy simultaneously both conditions (a) and (b), the use of models F_i^* are *more preferable* compared with models F_i. It is naturally assumed in this case that quantitative processing experimental arrays $\{\chi_n, T_n\}$ is carried out by techniques of operational regression theory (see Sections 1, 2).

iii) For more than 70 years, the representation of experimental dependencies $\chi(T)$ of magnetically diluted systems is made by diagrams $1/\chi$–T. And, for many investigated weak magnetic materials, *a set of kinks* or significant deviations from the linear dependencies $1/F_i$ $(i = 1, 2)$ are observed in these diagrams [18–28].

It is generally known, that alignment of a curvilinear part of the dependence $1/\chi(T)$ is often successful by subtracting the temperature-independent term χ_0 from the experimental dependence $\{\chi_n, T_n\}$. Discussion of the physical sense of the constant χ_0 for a set of metals, alloys and magnetic diluted systems one can find in [34, 35]. But still it is not clear how to process and interpret experimental curves $1/\chi(T)$ with a set of kinks. In the discussed sort of physical-chemical experiments, the presence

of a set of kinks on diagrams $1/\chi$–T is often connected with changing the type of exchange interactions between paramagnetic ions or with manifesting some phase transitions, and analyzing magnetic behavior of weak magnetic substances is usually carried out separately for low and high temperature regions of the dependencies $1/\chi(T)$ with using models F_i. This approach may not be acceptable, so in 1940 B. Cabrera had established (see [22]) that for many salts a set of kinks on diagrams $1/\chi$–T passes into nothingness, when F_2 fitting models were replaced by F_2^* ones. To support B. Cabrera's idea, let us prove the correctness of the following Proposition 1.

Proposition 1. *For magnetically homogeneous diluted systems, a set of kinks on diagrams $1/\chi$–T has no relation to any real physical phenomena, but it connects with a complex of operational errors, which are an integral part of the considered type of experiments. In particular, it connects with wrong decomposition of measured values $\{\chi_n\}$ on temperature-dependent (F_2) and temperature-independent (χ_0) parts, measuring errors ε_n (see Sections 1, 2) and the discreteness of measurements.*

Proof If the structural formula of a substance is wrong or the correction on temperature-independent paramagnetism contributes significantly to the value of χ then using the inconsistent parametric approach (see point (ii)) gives the dependency

$$1/(\chi + \chi_d^{(\mathrm{calc})}) = 1/(\chi_{pd} + F_2) \qquad (5)$$

on diagram $1/\chi$–T instead of the temperature-dependent part, obeyed Curie–Weiss law where χ is an experimental dependence of the specific magnetic susceptibility ($\chi = \{\chi_n\}$); $\chi_d^{(\mathrm{calc})}$ is a calculated amount of the diamagnetic corrections from each atom of the chemical formula of the solid solution; χ_{pd} is an unaccounted parts of corrections on temperature-independent para- and diamagnetism of the solid solution.

If χ_{pd} is a non-zero constant then, using mathematical analysis methods, it is easy to prove, that the curve (5) is continuous and smooth at all values T except for the value $T_{\mathrm{cr}} = \theta - C/\chi_{pd}$, and character of its concavity depends on a sign of the constant χ_{pd}. Consequently, for the discussed experiments, if $\chi_{pd} \neq 0$ then some monotone concavo or convex curves will be shown on the diagram $1/\chi$–T. To finish the proof it remains to add, that it is always possible to approximate any monotone curvilinear dependence, determined on a discrete set of $\{T_n\}$ within a given error, by a set of lines with kinks, except for the single case when $\chi_{pd} = 0$ and the simple linear dependence $1/\chi = (1/C)T - (\theta/C)$ is shown on the diagram $1/\chi$–T. ■

To demonstrate the practical importance of Proposition 1, let us compare "the authors interpretations" of curves $1/\chi(T)$ for solid solutions $LaMeO_3$ – $LaAlO_3$ (Me = Ti, Mn, V, Fe) investigated in [20, 21, 24] with the proved results about the connection of a set of kinks on diagrams $1/\chi$–T with the presence of a temperature-independent magnetism in dependencies $\chi(T)$. The mentioned dependencies are shown in Figure 2(a, b, c, d) where $\chi_{\mathrm{Me}}^{\mathrm{para}}$ is the paramagnetic component of the specific magnetic susceptibility for systems $LaMeO_3$ – $LaAlO_3$ (Me = Ti, V, Mn, Fe). Namely, (a) — $LaTi_xAl_{1-x}O_3$ (x = 0.077 (1); 0.111 (2)); (b) — $LaV_xAl_{1-x}O_3$ (x = 0.023 (1); 0.041 (2); 0.080 (3)); (c) — $LaMn_xAl_{1-x}O_3$ (x = 0.009 (1); 0.059 (2); 0.113 (3)); (d) — $LaFe_xAl_{1-x}O_3$ (x = 0.011 (1); 0.033 (2); 0.066 (3)). For all listed solid solutions, experimental arrays of $\{\chi_n, T_n\}$ are given in [36].

1) As it is stated in [20, 21, 24] "solid solutions $LaMeO_3$ – $LaAlO_3$ (Me = Ti, Mn) are characterized by the presence of a temperature-independent magnetism in magnetic susceptibility". Comparing this explanation of all curves on diagrams (a) and (c) (see Figure 2), with one of the proved statement we may conclude that *both explanations are identical.*

2) By comparing curves on diagrams (b) and (d) with curves on diagrams (a) and (c), the authors of [20, 21, 24] conclude, that in distinction from systems, listed in point 1, "for solid solutions, containing $LaVO_3$ and $LaFeO_3$, a kink is observed on curves $1/\chi(T)$. In solid solutions $LaVO_3$ – $LaAlO_3$ (see diagram (b)), this kink can be

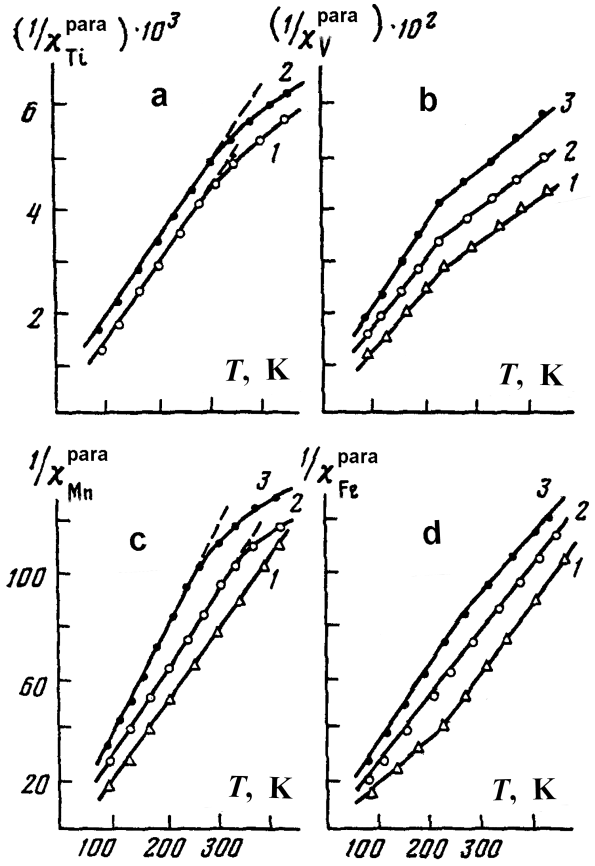

FIG. 2. Dependencies $1/\chi_{\mathrm{Me}}^{\mathrm{para}}(T)$ for solid solutions $LaMeO_3$ – $LaAlO_3$

explained by partial withdrawal of exchange interactions of antiferromagnetic type between vanadium atoms. In solid solutions $LaFeO_3$ – $LaAlO_3$ (see diagram (d)) the position of the kink points and angles between high and the low temperature of the straight lines depends on the solution composition... One may reasonably assume that, at increasing concentrations of $LaFeO_3$, not only character but a sign of exchange between iron atoms is also changed".

In reality (see the proof of Proposition 1)

α) From the graphical information, presented in Figure 2, one can not see any difference between curves on diagrams (b) and (d) and curves on diagrams (a) and (c). Namely, in all these cases curves may be presented as dependencies $1/\chi(T)$ with kinks. Thus, no one can say with the authors of [20, 21, 24] that the distinction between curves on all four diagrams (see Figure 2) is a symptom of "the internal periodicity of the magnetic properties of solid solutions" $LaMeO_3$ – $LaAlO_3$ (Me = Ti, V, Mn, Fe).

β) For the system $LaV_xAl_{1-x}O_3$ (x= 0.041), curves of $1/(\chi + \chi_2)(T)$ are shown in Figure 3(a, b, c) where χ_2 is equal 0.5, 0.094 and -0.1 respectively for the diagrams (a), (b) and (c).

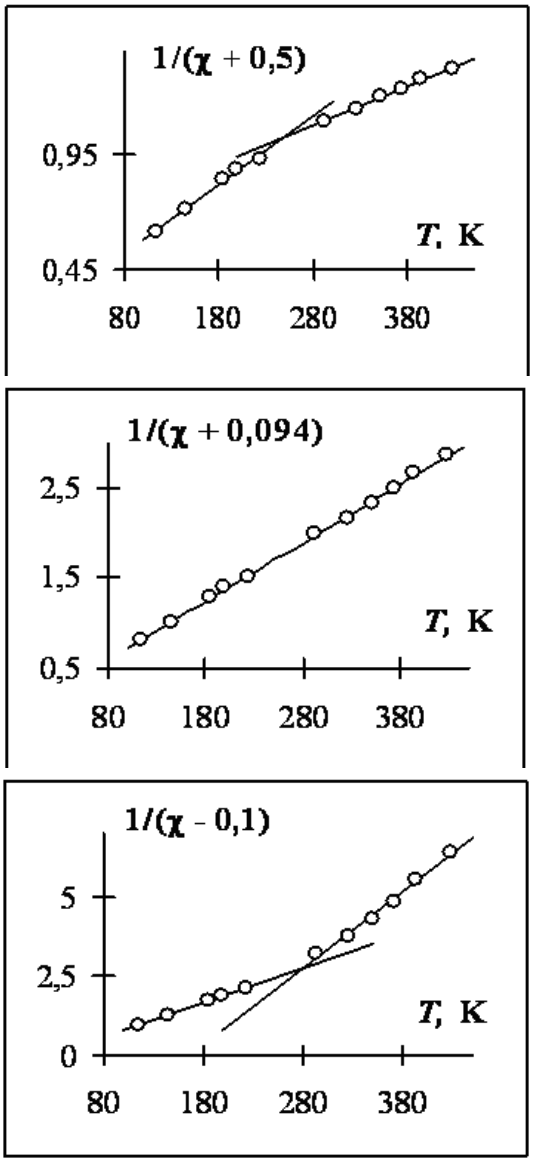

FIG. 3. Dependencies $1/(\chi + \chi_2)(T)$ for solid solution $LaV_xAl_{1-x}O_3$ (x = 0.041).

Analysis of these three graphs allows us to conclude that dependencies, shown in Figure 2(b, d), have the same simple explanation as one in the proved Proposition, and, consequently, different interpretations, which are given in [20, 21, 24] for curves $1/\chi(T)$ of solid solutions $LaMeO_3$ – $LaAlO_3$ (Me = V, Fe), are incorrect.

Since the temperature dependence of many physical properties of solids (eg, magnetic and electrical susceptibility, conductivity, dielectric constant, thermal expansion coefficient, etc.) obey the Curie–Weiss law, *the scope of Proposition 1 is much wider* than that provided in this item. In particular, experimental curves with a set of kinks are given in [37] — the logarithm of the bulk conductivity, in [38] — the electrical susceptibility, in [39] — the specific conductivity.

iv) In this item a set of experimental arrays of $\{\chi_n,\ T_n\}$, investigated in [19, 20, 21, 24, 28] for weak magnetic systems $Me_xAl_{1-x}O_{1.5}$ (Me = V), $LaMe_xAl_{1-x}O_3$ (Me = V, Fe), $LaSrMe_xAl_{1-x}O_4$ (Me = Fe) and $YCaMe_xAl_{1-x}O_4$ (Me = Fe) are tested by VD-method (see Section 2.3). For all listed solid solutions, experimental arrays of $\{\chi_n, T_n\}$ are given in [36].

The obtained computational results are adduced in Table 1. In Table 1, k is the serial number of the analyzed data array, x is concentration of Me in the analyzing solid solution with number k, mole fractions; N is the general number of readings in the experimental data array $\{\chi_n, T_n\}_k$; $\varepsilon_{\max}$ is the largest measurement error of the dependent variable χ (see Section 2.1);
$\alpha_{\min}$ is a parameter whose value is determined by VD-method (see Section 2.3) with using model F_2^* and data array $\{\chi_n,\ T_n\}_k$; n_{out} is a number of such outliers, that after their removing of the data array $\{\chi_n,\ T_n\}_k$, the operational situation "inadequacy of model F_2^* on the plane $\{\chi_n,\ T_n\}_k$" (see condition (3) in Section 2.4) goes into the operational situation "precision experiment on the plane $\{\chi_i, T_i\}_k$, containing no outliers"; $\alpha^*_{\min}$ is a parameter whose value is determined by VD-method (see Section 2.3) with using model F_2^* and data array $\{\chi_i, T_i\}_k$.

Using criteria (3), one can ensure that computational results, presented in Table 1, demonstrate the local inadequacy of the approximating model F_2^* except for systems $LaV_xAl_{1-x}O_3$ having $k = 5$ and 6. Therefore, in the next section, the main efforts will be focused on revealing the reasons for inadequacy of this model and adaptation of models F_i^* to operational situations of some real magnetochemical experiments.

3.2. Adaptation of modified Curie and Curie–Weiss laws to operational situations of some real magnetochemical experiments

i) Among all the samples listed in Table 1(A), the sample number 6 has the largest number of readings ($N = 23$). For this reason, it is selected as the best sample with experimental dependence (see [19, 36]) $\{\chi_n\} = (10.97, 8.06, 6.94, 5.56, 5.11, 4.75, 4.62, 4.00, 3.79, 3.31, 3.20, 3.06, 3.00, 2.78, 2.67, 2.56, 2.48, 2.46, 2.42, 2.28, 2.12, 2.02, 1.97)$ and $\{T_n\} = (80, 121, 144, 182, 202, 214, 220, 267, 292, 351, 360, 385, 401, 438, 464, 486, 501, 512, 523, 559, 601, 651, 668)$.

Using the model F_2^* and array $\{\chi_n, T_n\}$, let us construct

a) a standard regression solution for estimating the values of the parameters $\chi_0,\ C,\ \theta$

$$\chi_0{=}0.54{\pm}0.06,\ C{=}997{\pm}29,\ \theta{=}-14.9{\pm}2.7, \quad (6)$$

obtained by Marquardt's nonlinear estimator (see formula (15) in [1]) with $\max\limits_n |\chi_n - \chi_0 - C/(T_n - \theta)| \le 0.18524$;

b) a set of the equivalent analytical functions $F_2^*(A(\xi), T)$ as it is mentioned in algorithm of Section 1 and in Examples of [1, 40]

$$F_2^*(A(\xi), T) = 0.5286 + 0.0117\xi + (1002.75 - 9.03\xi)/(T + 14.79 - 1.17\xi) \quad (7)$$

where $-1 \le \xi \le 1$, $\max\limits_n |\chi_n - F_2^*(A(\xi), T_n)| < 0.185$ and consequently $\chi_0 = 0.529 \pm 0.012,\ C = 1002 \pm 9,\ \theta = -14.8 \pm 1.2$.

Using the same fitting model and the truncated array $\{\chi_i, T_i\}$, that is different from the initial data array $\{\chi_n, T_n\}$ by the absence of the

Table 1. The computational results on analyzing experimental data arrays $\{\chi_n,\ T_n\}_k$ for some magnetically dilute solid solutions.

A. Polycrystal systems $V_xAl_{1-x}O_{1.5}$

k	x	N	ε_{max}	α_{min}	n_{out}	α^*_{min}
1	0.0096	11	0.01	0.017	2	0.01
2	0.019	11	0.01	0.05	2	0.01
3	0.045	10	0.01	0.03	3	0.005
4	0.059	11	0.01	0.15	3	0.01
5	0.069	12	0.01	0.15	5	0.01
6	0.078	23	0.01	0.16	5	0.03
7	0.142	21	0.01	0.23	6	0.05
8	0.195	22	0.01	0.30	5	0.05

B. Polycrystal systems $LaV_xAl_{1-x}O_3$

k	x	N	ε_{max}	α_{min}	n_{out}	α^*_{min}
1	0.011	8	0.001	0.0054	1	0.0018
2	0.017	7	0.001	0.015	2	0.004
3	0.023	10	0.001	0.016	2	0.0024
4	0.035	11	0.001	0.07	1	0.006
5	0.041	11	0.01	0.009	0	0.009
6	0.057	10	0.01	0.01	0	0.01
7	0.080	14	0.01	0.22	5	0.03
8	0.113	11	0.01	0.12	4	0.008

C. Monocrystal systems $YCaFe_xAl_{1-x}O_4$

k	x	N	ε_{max}	α_{min}	n_{out}	α^*_{min}
1	0.0027	9	0.001	0.015	3	0.0008
2	0.0027	9	0.001	0.0054	2	0.0012
3	0.0054	12	0.001	0.034	2	0.0024
4	0.0055	12	0.001	0.027	3	0.0026
5	0.0060	12	0.001	0.020	2	0.001
6	0.060	9	0.001	0.026	3	0.002
7	0.0126	12	0.001	0.035	3	0.008
8	0.0148	12	0.001	0.02	4	0.001

D. Polycrystal systems $YCaFe_xAl_{1-x}O_4$

k	x	N	ε_{max}	α_{min}	n_{out}	α^*_{min}
1	0.0037	9	0.001	0.009	3	0.001
2	0.0039	9	0.001	0.011	2	0.002
3	0.0062	12	0.001	0.027	3	0.004
4	0.0066	11	0.001	0.095	2	0.003
5	0.0119	12	0.001	0.049	3	0.006

E. Polycrystal systems $LaFe_xAl_{1-x}O_3$

k	x	N	ε_{max}	α_{min}	n_{out}	α^*_{min}
1	0.0115	8	0.01	0.037	3	0.008
2	0.0173	10	0.01	0.12	4	0.0008
3	0.0219	11	0.01	0.34	4	0.03
4	0.0327	17	0.01	0.66	5	0.1
5	0.0439	9	0.01	0.28	3	0.02
6	0.065	17	0.01	0.56	6	0.08
7	0.088	14	0.01	0.76	6	0.04
8	0.102	13	0.01	0.79	6	0.06
9	0.122	12	0.01	0.94	4	0.12
10	0.176	8	0.01	2.1	3	0.19

F. Polycrystal systems $LaSrFe_xAl_{1-x}O_4$

k	x	N	ε_{max}	α_{min}	n_{out}	α^*_{min}
1	0.0042	18	0.001	1.3	5	0.07
2	0.0047	12	0.001	0.050	1	0.004
3	0.0058	12	0.001	0.023	2	0.008
4	0.0074	12	0.001	0.037	5	0.003
5	0.0098	9	0.01	0.040	3	0.003
6	0.0113	12	0.01	0.044	5	0.0022
7	0.0126	12	0.01	0.036	4	0.01
8	0.0131	12	0.01	0.05	3	0.0054
9	0.0169	12	0.01	0.23	4	0.05
10	0.0312	12	0.01	0.22	4	0.009
11	0.0490	12	0.01	0.55	6	0.01
12	0.0645	13	0.01	0.47	5	0.06
13	0.0902	12	0.01	0.6	5	0.01

first five (anomalous) readings and, thus, restores the operational situation "precision experiment on the plane $\{\chi_i, T_i\}_{k=6}$, containing no outliers" (see Table 1(A) and text after the Table 1(F)), one is able to get the undistorted values of the parameters $\chi_0,\ C,\ \theta$

c) the new Marquardt's nonlinear estimator solution is

$$\chi_0{=}0.141{\pm}0.073,\ C{=}1386{\pm}67,\ \theta{=}-88.7{\pm}10.5 \quad (8)$$

with $\max_n |\chi_n - \chi_0 - C/(T_n - \theta)| \le 0.03889$;

d) the new operational analytical solution

reads

$$F_2^*(A(\xi),T) = 0.0855 + 0.0043\xi \\ +(1441.08 - 4.58\xi)/(T + 97.49 - 0.79\xi) \quad (9)$$

where $-1 \le \xi \le 1$, $\max\limits_n |\chi_n - F_2^*(A(\xi),T_n)| < 0.040$ and consequently $\chi_0 = 0.0855 \pm 0.0043$, $C = 1441.1 \pm 4.6$, $\theta = -97.5 \pm 0.8$.

ii) As it is stated in [19, 41], the polycrystal solid solutions $V_xAl_{1-x}O_{1.5}$ exist "at vanadium concentrations $0.01 \le x \le 0.195$ and $0.79 \le x \le 1.0$"; metallic V_20_3 have the magnetic phase transition "about 160 K" and "a large temperature-independent orbital susceptibility". Using these facts and the computational results presented in Table 1(A), it is naturally to expect that for the systems $V_xAl_{1-x}O_{1.5}$

a) at high vanadium concentrations, the dependencies $\chi(T)$ should not differ greatly from the dependency of vanadium oxide or, in other words, experimental dependencies $\chi(T)$ are to have a sigma-shaped form and to be described by the equation [33, 42]

$$\chi = \chi_1 \tanh(a_1(T - T_1)) \quad (10)$$

which is the analogue of "the activation function", proposed in [43] for the description of the so called "the blurred phase transitions".

In (10), χ is the experimental magnitude of the specific magnetic susceptibility; T is the absolute temperature, K; χ_1, a_1, T_1 are parameters of a sigma-shaped dependence; $\tanh(z)$ is the hyperbolic tangent;

b) at low vanadium concentrations, dependencies $\chi(T)$ should be rather hyperbolic type and, thus, they must be well approximated by the modified models F_2^*. The implicit confirmation of this prediction correctness is the finding a set of kinks on the diagrams $1/\chi$–T for discussed systems in [19] (see the proof of Proposition 1 in the previous section);

c) It is easy to establish that all n_{out} anomalous readings of experimental arrays, listed in Table 1(A), are in the temperature range $(78 \div 220)$ K. Thus, one can assume that all anomalous readings can be connected with "the blurred phase transitions", observed in magnetically concentrated solid solutions $V_xAl_{1-x}O_{1.5}$. If so, then the following model

$$\chi(T) = F_2^*(T) + \chi_1 \tanh(a_1(T - T_1)) \quad (11)$$

must have good approximating properties for the discussed systems with both low and high vanadium concentrations.

One can estimate the fitting quality of the equation (11) by analysing the dependencies $\delta\chi(T) = \chi - F_2^*(T)$, shown in Figure 4(a,b,c) for different vanadium concentrations of the systems $V_xAl_{1-x}O_{1.5}$.

Namely, for systems with high vanadium concentrations, curves $\delta\chi(T)$ are adduced in Figure 4(a) for the values x = 0.788 (1), 0.848 (2), 0.908 (3), 1.0 (4); for systems with middle vanadium concentrations — in Figure 4(b) for the values x = 0.078 (1), 0.142 (2), 0.195 (3); for systems with low vanadium concentrations — in Figure 4(c) for the values x = 0.010 (1), 0.019 (2), 0.045 (3), 0.059 (4), 0.069 (5). In graphs 4(a,b,c), circles and triangles — the values of $\chi_2 + \chi_n - \chi_0 - C/(T_n - \theta)$, continuous curves — dependencies $\chi_2 + \chi_1 \tanh(a_1(T - T_1))$ where χ_2 — some auxiliary constants by which curves are located in the diagrams so that they do not overlap.

iii) As it is stated in [28], for the investigated monocrystal and polycrystal weak magnetic systems $YCaFe_xAl_{1-x}O_4$

a) "the dependencies $\chi(T)$ are well fitted by Curie–Weiss law $F_2 = C/(T - \theta)$ and hence they do not have any features on diagrams χ–T or $1/\chi$–T";

b) "if the concentrations of iron ions in weak magnetic systems $YCaFe_xAl_{1-x}O_4$ are the same, then it is impossible to distinguish between the monocrystal and polycrystal samples by means of analyzing the experimental curves $\chi(T)$ or $1/\chi(T)$".

One can make sure

a) by using criteria (3), that computational results, presented in Tables 1(C) and 1(D), demonstrate the local inadequacy of the approximating model $F_2^*(T)$ for all investigated magnetic systems $YCaFe_xAl_{1-x}O_4$;

b) by analyzing the curves $\delta\chi(T) = \chi -$

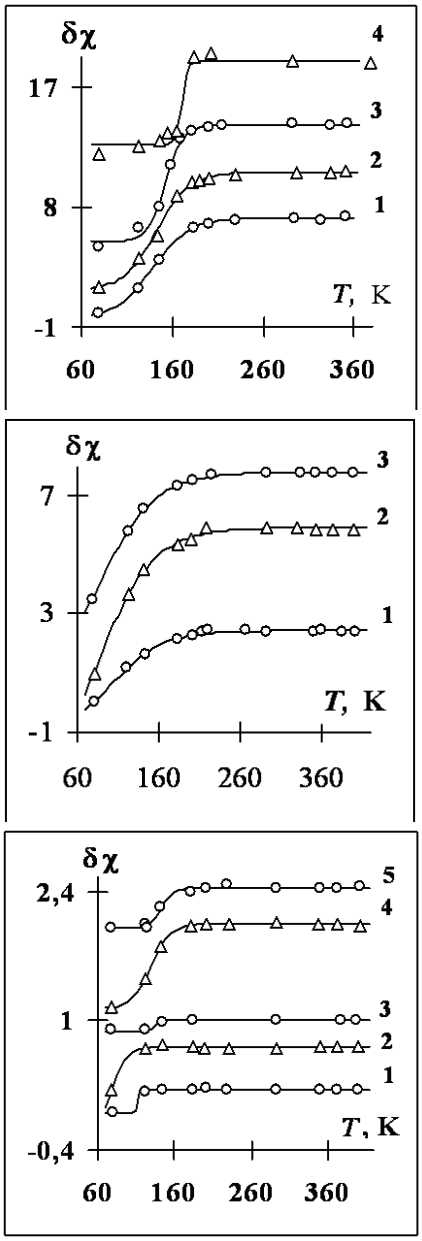

FIG. 4. Dependencies $\delta\chi(T)$ for solid solutions $V_xAl_{1-x}O_{1.5}$.

$F_2^*(T)$ of systems $YCaFe_xAl_{1-x}O_4$ shown in Figure 5(a, b), that the experimental curves $\chi(T)$ have the same "features on diagrams χ–T" as the experimental curves $\chi(T)$ of systems $V_xAl_{1-x}O_{1.5}$, investigated in point (ii). For monocrystal systems $YCaFe_xAl_{1-x}O_4$, curves $\delta\chi(T)$ are adduced in Figure 5(a) for the values x = 0.0027 (1), 0.0054 (2), 0.0055 (3), 0.060 (4), 0.0060 (5), 0.0126 (6), 0.0148 (7). For polycrystal systems — in Figure 5(b) for the values x = 0.0037 (1), 0.0039 (2), 0.0062 (3), 0.066 (4), 0.0119 (5);

c) by analyzing the curves $\delta\chi(T) = \chi - F_2^*(T)$ of systems $YCaFe_xAl_{1-x}O_4$ with the equal concentration of iron ions (see Figure 5(a, b)), that *it is possible* "to distinguish between the monocrystal and polycrystal samples by means of analyzing the experimental curves $\chi(T)$" *in low temperature regions*. This result is in a good agreement with the conclusions of [44]: the investigated "LiV_2O_4 samples, that were prepared in slightly different ways, show the differences in behavior dependencies $\chi(T)$ at low T".

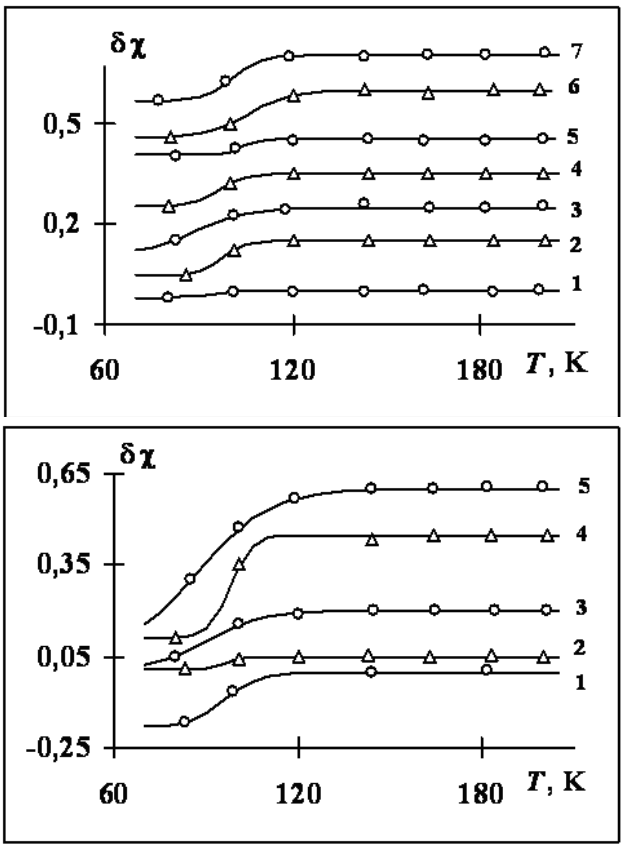

FIG. 5. Dependencies $\delta\chi(T)$ for solid solutions $YCaFe_xAl_{1-x}O_4$.

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