REVIEWS OF TOPICAL PROBLEMS

Contents

Frustrated lattices of Ising chains

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<u>Abstract.</u> The magnetic structure and magnetization dynamics of systems of plane frustrated Ising chain lattices are reviewed for three groups of compounds: $Ca_3Co_2O_6$, $CsCoCl_3$, and $Sr_5Rh_4O_{12}$. The available experimental data are analyzed and compared in detail. It is shown that a high-temperature magnetic phase on a triangle lattice is normally and universally a partially disordered antiferromagnetic (PDA) structure. The diversity of low-temperature phases results from weak interactions that lift the degeneracy of a 2D antiferromagnetic Ising model on the triangle lattice. Mean-field models, Monte Carlo simulation results on the static magnetization curve, and results on slow magnetization dynamics obtained with Glauber's theory are discussed in detail.

1. Introduction

Magnetic frustrated systems have been extensively studied both theoretically and experimentally for a long time [1-3]. In this review, we will concentrate on a special class of magnetic compounds formed by frustrated Ising chain lattices. The

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Uspekhi Fizicheskikh Nauk **182** (12) 1249–1273 (2012) DOI: 10.3367/UFNr.0182.201212a.1249 Translated by M Sapozhnikov; edited by A Radzig magnetic structure of such systems is determined by a complex hierarchy of magnetic interactions. The strongest of them act along Ising chains, which are treated as basic elements of the magnetic structure. When the chains are oriented along one of the crystallographic axes and are packed into a two-dimensional, most often triangular, lattice in a plane perpendicular to the chain direction, weak antiferromagnetic (AFM) interactions between magnetic ions in adjacent chains lead to frustration. In addition, it is shown that very weak long-range interactions also strongly affect the phase diagram and magnetization dynamics.

We will study systems with triangular Ising chain lattices by the example of three groups of substances. The $Ca_3Co_2O_6$ compound has attracted great attention in the last decade, and therefore a considerable part of the review is devoted to it. One of the most remarkable results obtained for $Ca_3Co_2O_6$ is the low-temperature magnetization curve, in which a sequence of steps equidistant in the magnetic field was found. The number of these steps depends on both temperature and the rate of changing an external magnetic field. In addition, the relaxation of the magnetic moment in $Ca_3Co_2O_6$ occurs unusually extremely slowly, with the relaxation time reaching a few hours or even days. To explain such an unexpected behavior, various theoretical models have been constructed, including the stochastic dynamics and quantum tunneling of the magnetic moment.

To describe the magnetization dynamics in systems with a strong uniaxial anisotropy, it is necessary to go beyond the framework of the static Ising model. At very low temperatures, the quantum nature of magnetism is manifested, and, therefore, the Ising system is treated either as a strongly anisotropic Heisenberg magnet [4] or an open quantum system [5]. Moreover, there is a broad region of moderate and high temperatures, in which the magnetization dynamics is stochastic. In 1963, Roy J Glauber proposed the stochastic theory of the magnetization dynamics in an Ising chain [6]. Later, this theory was extended to two-dimensional and three-dimensional systems and, in particular, was applied to explain the magnetization dynamics in $Ca_3Co_2O_6$ compound. Glauber was awarded the Nobel Prize in Physics 2005 "for his contribution to the quantum theory of optical coherence" [7]. We will see below that he has also managed to solve elegantly 'incoherent' problems such as the stochastic dynamics in the Ising model.

Monte Carlo simulations of the ground state and static magnetization curve of $Ca_3Co_2O_6$ developed dramatically. Earlier work on numerical two- and three-dimensional simulation was performed with the help of the standard Metropolis algorithm. It was then found that this algorithm on a frustrated triangular lattice leads to qualitatively incorrect results, and the new Wang–Landau algorithm should be used for correct calculations.

Apart from Ca₃Co₂O₆, we will discuss two other groups of compounds. CsCoCl₃, CsCoBr₃, and their related compounds were probably the first frustrated systems with triangular Ising chain lattices to have been studied. By now, their properties have been investigated in detail. In addition, a new complex $Sr_5Rh_4O_{12}$ compound, which can be assigned to the third group, was recently synthesized and studied. Note that the magnetic behavior of substances belonging to these three groups has both common features and considerable differences. Because of this, one of the main goals of the review was the development of a unified theoretical model of the magnetic phase diagram.

We consider a few possible practical applications of compounds with a triangular Ising chain lattice. In particular, a thin nanostructured $Ca_3Co_2O_6$ film is concerned as a possible medium for superdense magnetic data recording [8]. $Ca_3Co_2O_6$ and its related compounds have a very high Seebeck coefficient and good thermal conduction [9, 10], and are treated as promising materials for thermoelements [11]. The only factor preventing their application in this field is too high a specific resistance [10]. The magnetoelectric effect was found in a solid $Ca_3Co_{2-x}Mn_xO_6$ solution [12], and its application is being extensively discussed at present [13].

The layout of the review is as follows. Section 2 is devoted to experimental results. First, we very briefly discuss magnetic systems with isolated Ising chains. Then, we analyze in detail the static and dynamic properties of systems with triangular Ising chain lattices. In Section 3, we consider models of rigid chains and the effective field for a magnetic structure. Section 4.1 contains an introduction to the Glauber theory of the Ising chain dynamics. Then, the Glauber dynamics is applied for numerical two- and three-dimensional simulations of the magnetization dynamics in $Ca_3Co_2O_6$. The results of Monte Carlo simulation of static magnetization curves are the concern of Section 5. In the conclusion, the results and unsolved problems are formulated.

2. Experimental studies of frustrated Ising chain lattices

2.1 Isolated Ising chains

Before proceeding to an analysis of the properties of frustrated Ising chain lattices, it is useful to briefly discuss the behavior of an individual chain. Recent progress in the synthesis of organic magnetic compounds has opened up opportunities for detailed experimental studies of the magnetic properties of isolated low-dimensional elements, including Ising chains. Investigations of molecular magnetism started in the 1980s [14] after the development of theoretical approaches to the fabrication of magnets based on organic compounds [15]. It is remarkable that the presence of organic ligands in compounds often leads to the formation of isolated oligomers, wheel-like structures, and molecular clusters. The role of organic components is reduced in this case to the screening of interactions between magnetic centers.

Researchers became aware of the reality of molecular magnetism early in the 1990s, when the hysteresis in molecular magnetization, tunneling of the magnetic moment, and other very interesting phenomena were revealed in the $[Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4] \cdot 2CH_3COOH \cdot 4H_2O$ compound [16, 17]. It was found that the unusual behavior of this compound is explained by the combination of a strong 'easy-axis' anisotropy and weak intermolecular interactions [18] preventing the passage of a zero-dimensional system to 3D ordering. In this connection, the term 'single-molecule magnet' was proposed.

Later on, based on organic compounds, isolated magnetic structures of different dimensionalities were fabricated, including one-dimensional (1D) systems. In 2001, the team led by D Gatteschi reported the first observation of the slow relaxation of magnetization in a 1D {Co(hfac)₂[NIT(C₆H₄*p*-OM*e*)]} compound (CoPhOM*e*) [19]. An individual chain of this compound has the ferrimagnetic structure and behaves as a whole as a superparamagnetic nanowire. Within a year, the $[Mn_2^{III}(saltmen)_2Ni^{II}(pao)_2(py)_2](ClO_4)_2$ compound was synthesized, which consisted of ferromagnetic chains [20]. At present, there are a few dozen compounds [21] which can be called 'single-chain magnets' (SCMs). Because chains in these substances do not virtually interact with each other, and a strong uniaxial anisotropy manifests itself, the term 'isolated Ising chain' is also applicable.

A slow relaxation of the magnetization is observed in ferromagnetic (FM) [20, 22], ferrimagnetic [19], and noncollinear antiferromagnetic [21] Ising chains. In the absence of a noncollinear structure, relaxation in AFM chains is also possible if a chain contains an odd number of spins [23]. One should, however, take into account that SCM materials generally consist of irregular chains, i.e., a few exchange interaction parameters and several sublattices can be required for their description. The relaxation of magnetization in Ising SCMs is successfully interpreted in terms of the Glauber dynamics [23].

The specific features of the magnetic structure of a single chain can be highlighted by analyzing the temperature dependence of the magnetic susceptibility $\chi(T)$ [21]. For example, it is expected that $\chi \propto T^{-2}$ for an isotropic Heisenberg chain of classical spins with the ferromagnetic exchange interaction between nearest neighbors. In the case of the Ising model or anisotropic Heisenberg model, the longitudinal susceptibility diverges exponentially with decreasing temperature: $\exp(\Delta_{\xi}/k_{\rm B}T)/T$, whereas the transverse susceptibility at low temperatures remains constant and much smaller than the longitudinal susceptibility. The quantity Δ_{ξ} has the physical meaning of the domain wall energy. Depending on the relation between anisotropy and exchange interaction parameters D and J, respectively, the domain wall can be subclassified into sharp $(|D/J| \ge 1)$ or extended.

Such a drastic difference in the behavior of the abovementioned models arises from the nature of magnetic excitations allowable in each of them. The spectrum of excitations in the Heisenberg model is continuous, whereas low-energy excitations in the Ising 1D model represent extended ordered domains separated by sharp domain walls and exhibit a discrete energy spectrum.

At temperatures close to absolute zero, the magnetization relaxation time can reach a few hours. The temperature dependence of the relaxation time has an activation nature and obeys the Arrhenius equation $\tau(T) = \tau_0 \exp(\Delta_{\tau}/k_{\rm B}T)$ [21]. The energy Δ_{τ} is determined by the domain wall and anisotropy energies Δ_{ξ} and Δ_{a} , respectively, and by the relationship between the correlation length ξ and the chain segment size L: at high enough temperatures, $\Delta_{\tau} = \Delta_{a} + 2\Delta_{\xi}$, the segment is divided into domains, and new domains are generated inside old ones. On the other hand, ordering occurs inside the entire segment in the low-temperature limit, while the generation of new domains is displaced to its boundaries, $\Delta_{\tau} = \Delta_{a} + \Delta_{\xi}$. Thus, the presence of defects in the system give rise to a break in the plot of the temperature dependence of the relaxation time in $\ln(\tau)$ and 1/T coordinates, resulting in a change in the straight line slope. The break corresponds to a crossover between the above-mentioned formation modes of new domains. By analyzing the temperature dependences of the susceptibility and relaxation time, we can numerically estimate characteristic interactions inside the system (exchange interaction and anisotropy parameters) and also the chain segment length between two defects.

The uniqueness criteria for the magnetization relaxation mechanism are the Cole–Cole plots [21] representing the dependence of the imaginary part χ'' of the magnetic susceptibility on its real part χ' . It was found experimentally that the Glauber dynamics in certain SCMs, which will be discussed below, comprises the only relaxation process.

In ferromagnetic single-chain systems [21, 24] residing in an external magnetic field applied along the anisotropy direction, broad hysteresis loops with a large coercive force (up to 2.75 T at temperatures below 0.4 K) are observed. The area of hysteresis loops increases with decreasing temperature and upon increasing the field change rate. In specific cases, hysteresis loops can exhibit steps [19].

Detailed information and comprehensive references can be found in reviews devoted to the strategy of synthesis of these compounds [25], the adjustment of the intermolecular interaction [23], theoretical and experimental descriptions of the magnetization dynamics [21], and the general development of studies in this field [14].

2.2 Ca₃Co₂O₆: the electronic structure

Although the Ca₃Co₂O₆ compound has been known for quite some time [26], systematic studies of its low-temperature magnetic properties were initiated only in the middle of the 1990s [27-30]. The crystalline structure of this compound is formed by Co₂O₆ chains oriented along the crystallographic c-axis (Fig. 1). Calcium ions are located between chains and are not involved in magnetic interactions. Cobalt ions in chains are resided in two alternating positions: at the centers of octahedra (CoI) and trigonal prisms (CoII) formed by oxygen ions and sharing faces with each other. The Co_2O_6 chains are packed into a regular triangular lattice in the ab plane. Here, we should point out that adjacent chains are displaced relative to each other along the *c*-axis by 2/3 of the cell size (Fig. 1b), resulting in a complex topology of the Ca₃Co₂O₆ magnetic subsystem. The strongest bonds between cobalt ions in adjacent chains are realized via oxygen bridges, with the minimal bond length between oxygen ions, as shown in Fig. 1b. Such bonds between chains form double spiral paths along the *c*-axis in the magnetic subsystem of the compound.

The valent and spin states of cobalt ions in $Ca_3Co_2O_6$ have been discussed for a long time. For example, it was assumed that cobalt can be tetravalent and bivalent in positions CoI and CoII, respectively [27]. However, it has now been reliably established by the methods of X-ray photoemission spectroscopy [31], X-ray magnetic circular dichroism (XMCD) and X-ray absorption spectroscopy (XAS) [32], and nuclear magnetic resonance (NMR) [33] that the cobalt ion is trivalent (Co³⁺) in both positions.

Neutron diffraction studies of a polycrystalline sample [27] showed that the spin states of cobalt ions are different: the magnetic moment is $0.08 \pm 0.04 \,\mu_{\rm B}$ and $3.00 \pm 0.05 \,\mu_{\rm B} \,(\mu_{\rm B}$ is the Bohr magneton) in CoI and CoII positions, respectively. Later on, the presence of magnetic and nonmagnetic cobalt was confirmed by XMCD, XAS [32], and NMR [33] data. However, the detailed analysis by XMCD and XAS methods gave a higher estimate of the total magnetic moment in the CoII position amounting to $5.3 \,\mu_{\rm B}$. Simultaneously, the orbital part of the magnetic moment proved to be anomalously large $(1.7 \,\mu_{\rm B})$.



Figure 1. (See in color online). $Ca_3Co_2O_6$ crystal structure: (a) view along the *c*-axis (solid and dashed lines show the rhombic cell and hexagonal cell, respectively, and (b) adjacent Co_2O_6 cells (cross section along the long diagonal of the rhombic cell), solid and dashed lines show two types of interactions between CoII ions in adjacent chains.

The resistivity of Ca₃Co₂O₆ has the semiconducting nature and decreases from $5 \times 10^3 \Omega$ cm at T = 4.2 K [34] to $8 \times 10^{-3} \Omega$ cm at T = 1073 K [35] in single-crystal samples as a current flows along chains (along the c-axis). Mobile current carriers are assumed to be localized on Co³⁺ ions. At low temperatures (T < 25 K), the exponent v in the temperature dependence of the resistivity $\rho(T) = \rho_0 \exp(T_0/T)^{\nu}$ is 0.5, which is interpreted as the result of the Efros-Shklovskii variable range hopping type conduction mechanism [34]. In the range of room temperatures, the exponent increases to $v \approx 1$ because of the probable involvement of various conduction mechanisms, for example, the activation of the mobility edge, the increase in the hopping range, etc. [34]. Also, a strong difference between the conductivities of single crystals along the *c*-axis and polycrystals, which reached two orders of magnitude at room temperature, was pointed out [35]. This effect is probably related to the strong conduction anisotropy and resistance at grain boundaries in polycrystals. Measurements of the optical spectrum give the band gap estimate of 1.35 eV [36].

The high-temperature magnetic susceptibility obeys the Curie–Weiss law $\chi(T) = C/(T-\theta)$ [27] with temperature $\theta = 28 \pm 3$ K, which means that the interaction is predominantly ferromagnetic. This gave the estimate of the magnetic moment of the CoII ion as $5.7 \pm 0.02 \,\mu_{\rm B}$. On the other hand, the low-temperature saturation magnetic moment is about $5 \mu_{\rm B}$ per formula unit [37, 38]. As a whole, the magnetic moment values of the CoII ion measured from the magnetization saturation, from the Curie-Weiss dependence, and by the XMCD and XAS methods well agree with each other, whereas the estimate made from neutron diffraction measurements [27] seems understated. Below 100 K, a small deviation from the Curie–Weiss dependence is observed, and Ca₃Co₂O₆ passes to the magnetic ordered state at $T_{C1} = 24$ K. In the paramagnetic phase, extremely strong uniaxial magnetic anisotropy is observed: the ratio of the longitudinal and transverse magnetic susceptibilities at temperatures below 50 K reaches 100 [39]. Therefore, it is obvious that Ca₃Co₂O₆ is a pronounced Ising system. The anisotropy energy estimated from the low-temperature dependence of the magnetic susceptibility is $D \approx 200$ K [39, 40].

Before proceeding to a discussion of the properties of $Ca_3Co_2O_6$ in the ordered phase, it is useful to discuss theoretical models of the electronic structure of this compound. Earlier calculations of the electronic structure were performed by the methods of the density functional theory (DFT) with the employment of the local spin density approximation (LSDA) and generalized gradient approximation (GGA) [41-44]. All these methods gave an erroneous semimetallic or metallic ground state. In particular, it was stated that this compound could be the first 1D ferromagnetic semimetal. The Fermi level in LSDA calculations lay in a narrow (1 eV) band formed by the 3d electrons of the CoII ion. As a result, taking into consideration of the subatomic Coulomb interaction in the LSDA+U and GGA+U approximations led to the passage to a state of a Mott-Hubbard insulator with a band gap of ~ 1 eV, consistent with experimental data [36, 44, 45]. Optical measurements have shown that the Hubbard energy of the intrasite interaction approaches 5.6 eV [36].

Of most interest in model calculations are studies of the charge and spin states of cobalt ions and of magnetic interactions between them. The distance between the cation and ligands in the CoI octahedral position is 191.6 pm, while



Figure 2. Structure of the 3d levels of the Co^{3+} ion in $Ca_3Co_2O_6$ compounds: (a) in the octahedral crystal field (CoI), and (b) in the trigonal prism field (CoII).

this distance for CoII is noticeably greater (206.2 pm) [27]. For this reason, the crystal field on the CoI ion proves to be strong but is weak on the CoII ion [27]. The octahedral field splits the 3d level into the t_{2g} (d_{xy} , d_{xz} , d_{yz}) triplet and e_g ($d_{x^2-y^2}$, d_{z^2}) doublet. Six electrons in the strong crystal field occupy the t_{2g} states and produce the nonmagnetic configuration of the CoI ion with the total spin S = 0, as shown in Fig. 2a.

A more complicated and interesting situation is observed with the triangular surrounding of the cobalt ion in the CoII position. The expected structure of the 3d levels in a trigonal prism should be as follows [27, 46, 47]: the lowest-lying level should be the d_{z^2} level, the $d_{x^2-y^2}$, d_{xy} doublet is located slightly higher, and the highest-lying energy level is the strongly split off d_{xz} , d_{yz} doublet. LDA calculations confirm this picture as a whole, although the d_{z^2} level and the $d_{x^2-v^2}, d_{xv}$ doublet are interchanged (Fig. 2b) [46, 47]. The crystal field proves to be weak, i.e., in accordance with the first Hund rule, at first five electrons occupy all the spin-up levels, while the remaining sixth spin-down electron remains in the lower orbital. It was pointed out in paper [45] that, although this picture is consistent with experimental data, it does not answer two important questions: what are the reasons for the strong Ising anisotropy and the great orbital contribution? It was shown [45, 48] that the inclusion of the spin-orbit interaction in the LDA+U calculations (the LDA+U+SOC method) gives the answer to these questions. The spin-orbit interaction splits the $d_{x^2-v^2}$, d_{xv} doublet into d_2 and d_{-2} levels, as shown in Fig. 2b. Then, the sixth spindown electron is found in the lower d₂ orbital, which leads to the total CoII spin S = 2 and the total orbital momentum L = 2. The value of the orbital momentum agrees well with the value $1.7 \mu_{\rm B}$ presented above. Some decrease in the experimental value of the orbital momentum is explained by the cation-ligand hybridization. It is important that the spinorbit splitting energy (70 meV) in the LDA+U+SOC calculations proved to be much smaller than the gap between the group of $d_{z^2}, d_{x^2-y^2}, d_{xy}$ levels and the d_{xz}, d_{yz} doublet, which was on the order of 1 eV. As a result, the $d_2 \rightarrow d_1$ type transitions can be neglected, and terms $\hat{l}_+\hat{s}_- + \hat{l}_-\hat{s}_+$ in the spin-orbit interaction Hamiltonian can be excluded, which finally leads to the strong Ising anisotropy [45]. Other theoretical schemes of the d-orbital splitting in cobalt were also studied, in particular, taking into account the mixing of CoI and CoII states [9].

Two mechanisms of interaction of magnetic CoII ions via nonmagnetic CoI along chains are possible: either due to a direct exchange between CoI and CoII ions or due to the exchange between CoI and CoII ions via oxygen ions. The relative strength of these interactions is estimated variously by different authors [45–47]. In paper [45], the anomalously strong cobalt–oxygen hybridization in Ca₃Co₂O₆ is pointed out, which suggests that the second mechanism dominates. As a whole, the theoretical estimates of the exchange interaction parameter in both cases well agree with the magnetic susceptibility [28] and thermal capacity [49] data, and the temperatures of transition, 17 K [45] and 23 K [46], to the ordered phase.

Recent detailed NMR studies of the ⁵⁹Co nucleus [50] have given an unexpected result contradicting the mechanisms of exchange along chains under discussion: it was found that the hyperfine level splitting of CoI nuclei does not contain contributions from the direct or indirect exchange interaction with CoII ions. This was interpreted by the authors as evidence that CoI ions are not involved at all in the exchange interaction along chains. It should be noted that this conclusion was made by comparing experimental and calculated magnetic field strengths on the nucleus of the CoI ion. A certain error in calculations could appear, inter alia, because the magnetic moment was assumed to be located on CoII ions, and the weak magnetic moments of oxygen ions appearing due to their hybridization with CoII were ignored.

Weak interactions between CoII ions in adjacent chains occur via Co-O-O-Co oxygen bridges [42, 46]. There are two types of such bonds, which are illustrated in Fig. 1b. Note that in the case of bonds shown by dashed straight lines, the distance between oxygen ions is much greater than that for bonds depicted by solid straight lines, and these bonds are often neglected. The interchain bonds form a complex topology with helicoidal paths over the lattice, which will be discussed in Sections 2.3 and 3.3.

2.3 Ca₃Co₂O₆: the magnetic structure and phase diagram

The most interesting experimental results for $Ca_3Co_2O_6$ were obtained in the study of magnetization curves in a magnetic ordered phase [27, 30, 37-39, 51-53]. Below the transition temperature $T_{C1} = 24$ K, curves with a pronounced plateau at a level of 1/3 of the saturation magnetization were observed. This fact cannot be called unusual for triangular lattice AFM systems [54-56]. Such plateaus appear not only in Ising but also in Heisenberg systems [54, 56]. This is explained by the fact that a triangular lattice can be divided into three identical triangular sublattices embedded into each other. Then, the ferromagnetic interaction between next-tonearest neighbors in some or even zero magnetic field can produce a ferrimagnetic structure in which two sublattices are aligned in the same direction, while the third lattice is oriented in the opposite direction (Fig. 3a). It is this structure that possesses magnetization corresponding to the plateau at a height of 1/3. Curves with the plateau were observed only when the magnetic field was changed slowly enough, which can also be readily explained because we are dealing with a distinct Ising system. Notice also that a step in the zero magnetic field is related to the so-called AFM (PDA) or cell structure, which is displayed in Fig. 3b. The PDA ordering was discussed for the first time in papers [57, 58].

As temperature is further decreased (below $T_{C2} = 12$ K), two new steps appear in magnetization curves (Fig. 4a) [37, 38], which are located equidistantly over the magnetic field



Figure 3. Types of periodic structures entering the ground state of the 2D AFM Ising model on a trigonal lattice: (a) ferrimagnetic, (b) PDA, and (c) AFM stripe structures. The arrows indicate nearest-neighbor (solid arrow) and next-to-nearest-neighbor (dashed arrow) interactions, and numbers show a division into three sublattices. Grey circles are attributed to the sites of a trigonal lattice in which the spin direction is arbitrary: either 'spin up' (dark circles) or 'spin down' (white circles).

with a spacing of 1.2 T. Such a shape of the magnetization curve is quite unusual for a bulk long-range-order system. The specific feature at 12 K is also manifested in some other experiments. On the one hand, the spin–lattice and spin–spin relaxation times drastically changed in NMR experiments [33], which led the authors of this paper to the assumption about a possible phase transition in this region. On the other hand, careful measurements of the heat capacity revealed no traces of phase transitions in the T_{C2} region [49] (Fig. 5).

The magnetization curve exhibits at 2 K four magnetization steps and a broad hysteresis (Fig. 6) [37]. Moreover, the weak traces of three other steps are observed in magnetic fields above 3.6 T. These steps are separated by the same spacing of 1.2 T, as shown in the inset to Fig. 6. This result is absolutely unique; however, it does not exhaust all the unusual features of the Ca₃Co₂O₆ magnetic behavior. At temperatures below T_{C2} , the shape of a magnetization curve depends on the magnetic field variation rate (Fig. 4b). When this rate is 'high' (~ 1 T min⁻¹ for Ca₃Co₂O₆), the magnetization curve exhibits four steps. As the magnetic field variation rate is decreased to 0.01 T min⁻¹, two additional steps on the 1/3 plateau gradually decrease and almost disappear, and the



Figure 4. Change in the magnetization curve shape in $Ca_3Co_2O_6$: (a) with increasing temperature (2, 3, 4, 5, 10 K; the arrows show the order of curves) at a constant field growth rate of 0.1 T min⁻¹, and (b) at a constant temperature of 4 K and changing field growth rate [1 T min⁻¹ (solid curve), 0.1 T min⁻¹ (dashed curve), 0.01 T min⁻¹ (dotted curve) [38]; f.u.: formula unit.



Figure 5. Magnetic component of the heat capacity of $Ca_3Co_2O_6$ in magnetic fields of 0 T (circles), 2 T (squares), and 5 T (rhombs) oriented along the crystallographic *c*-axis [49]; the inset shows a magnified portion of the plots.

curve takes the shape typical of the high-temperature magnetic phase $(T_{C2} < T < T_{C1})$.

The dependence of the magnetization curve on the magnetic field growth rate indicates the occurrence of slow dynamic processes in the magnetic structure. For this reason, the frequency dependence of the dynamic magnetic susceptibility was carefully studied in Ref. [59]. The imaginary part of



Figure 6. Magnetization curves of $Ca_3Co_2O_6$ at T = 2 K and a magnetic field growth rate of 0.1 T min⁻¹ (f.u.: formula unit). The inset shows the magnetization derivative over the magnetic field strength, the arrows indicate the traces of steps in strong magnetic fields (see text) [38].



Figure 7. Imaginary part of the dynamic magnetic susceptibility of $Ca_3Co_2O_6$ (in electromagnetic units per mol) as a function of (a) temperature at frequencies of 0.01 Hz (squares), 0.1 Hz (circles), 1 Hz (triangles), 10 Hz (inverted triangles), 100 Hz (rhombs), 1000 Hz (asterisks), and (b) frequency at temperatures of 2.25 K (squares), 3.5 K (circles), 6 K (triangles), 8 K (inverted triangles), 10 K (rhombs), 11.5 K (asterisks), and 13 K (triangles pointing to the right) [59].

the susceptibility exhibits a broad peak, which resembles the response of an isolated chain, discussed in Section 2.1.

Some results of paper [59] are presented in Fig. 7. One can see, in particular, that, as temperature is lowered, the peak rapidly shifts to the red. The authors of Ref. [59] also pointed out the interesting fact that the peak height and position at



Figure 8. $Ca_3Co_2O_6$ magnetization relaxation in a permanent magnetic field at T = 4 K: (a) in different magnetic fields in the ascending magnetization curve, and (b) for 2.0, 2.3, and 2.7 T in the ascending (inverted triangles, rhombs, asterisks) and for 2.0 and 2.3 T (triangles, circles) in descending branches [38].

10 K depend on the hold time of a sample at the given temperature: the peak height noticeably increases and it shifts to the red after sample holding at 10 K for a few hours. The measurements of the dynamic susceptibility were interpreted using a model with two characteristic relaxation times, τ_1 and τ_2 . For T > 10 K, these times coincided, $\tau_1 = \tau_2 = \tau$, with $\ln \tau$ being proportional to the inverse temperature T^{-1} . As temperature was decreased below 10 K, one of the relaxation times continued to linearly increase as $\ln \tau \propto T^{-1}$, while another one saturated, reaching ~ 0.4 s.

The magnetization dynamics was analyzed in more detail by studying relaxation processes on very long time intervals (up to 10^4 s) in a permanent magnetic field [38, 60]. For this purpose, the external magnetic field on a sample was rapidly changed to the required value, and then the magnetization of the sample was measured after long sitting in a permanent magnetic field. At temperatures above 10 K, relaxation proceeded rapidly (for a few seconds). At low temperatures (4 K), the slow magnetization dynamics was quite complicated: the relaxation sign changed upon increasing the magnetic field above 2.3 T, as demonstrated in Fig. 8a. One can see from these plots that there are at least two slow relaxation mechanisms with different directions and various time constants.

The magnetic structure was studied by using neutron diffraction [27, 29, 61, 62]. It was pointed out in both old [27, 29] and later [61, 62] papers that the AFM peak intensity decreased when lowering the temperature below

 T_{C2} . Thus, the low-temperature magnetic phase of Ca₃Co₂O₆ should be more disordered than the hightemperature phase. The ratio of peak intensities observed near T = 0 K during cooling in a magnetic field (FC) and in its absence (ZFC) is 1.7, which is much greater than the expected value (1.3) for the PDA structure. From this follows the important conclusion that the magnetic structure of the low-temperature phase differs from the PDA order observed for $T_{C2} < T < T_{C1}$. Changes in the intensities of AFM and FM peaks in large single crystals in a magnetic field at T = 2 K were recently studied in detail by Fleck et al. [62]. All four magnetization steps were distinctly observed by changes in the intensity of these peaks. Note also that a weak peculiarity was also observed here at ~ 4.8 T, which should correspond to the fifth step.

The spin relaxation of muons (μ SR) in Ca₃Co₂O₆ was studied by Takeshita et al. [52, 53]. At temperatures below T_{C2} , a long 'tail' was revealed in the time dependence of the muon decay asymmetry function, while the asymmetry on the microsecond time scale was virtually absent for temperatures $T_{C2} < T < T_{C1}$. Most likely, this means that, in the first case, the decay occurred in stationary magnetic fields, whereas rapidly fluctuating microscopic magnetic fields existed in the second case, resulting in the fluctuation of magnetic moments. The characteristic time of magnetic fluctuations was estimated as 21 ns. Recent NMR measurements have revealed a broad fluctuation region above the temperature of transition to the ordered state, where the short-range order probably exists [63].

By partially replacing cobalt ions in Ca₃Co₂O₆, we can obtain a family of stoichiometric Ca₃CoBO₆ compounds, where B = Ni, Ru, Ir, Rh, and Mn [31, 61, 64–69]. The octahedral CoI sites in Ca₃CoRhO₆ and Ca₃CoIrO₆ compounds are occupied by rhodium and iridium ions, while CoII sites are occupied by cobalt ions as before. The charge and spin states of cobalt, rhodium, and iridium ions in these compounds were discussed in papers [64, 65, 67–69]. It has been established that Co²⁺ ions reside in the high-spin (S = 3/2) state, while Rh⁴⁺ and Ir⁴⁺ ions in the low-spin (S = 1/2) state, with both types of ions being ferromagnetically ordered in chains [31, 67, 68].

XMCD measurements are indicative of the important role of the spin–orbit splitting and the anomalously large orbital contribution to Co^{2+} , similarly to CoII ions in $Ca_3Co_2O_6$. This model of the magnetic structure is consistent with observed total magnetic moments [65, 68]. Critical temperatures were considerably higher than in $Ca_3Co_2O_6$: $T_{C1} = 90$ K (Ca_3CoRhO_6) [66, 67, 69] and $T_{C1} = 30$ K (Ca_3CoIrO_6) [68]. At $T_{C2} = 30$ K, the transformation from the PDA structure to the low-temperature phase was observed in Ca_3CoRhO_6 [70], while $T_{C2} \approx T_{C1}$ tentatively in Ca_3CoIrO_6 , i.e., the PDA phase is absent [68], in accordance with μ SR results [71]. This feature of Ca_3CoIrO_6 was interpreted [68] as the result of a noticeable elongation of a unit cell along the *c*-axis in this compound, which violates the relationship between intra- and interchain magnetic interactions.

The magnetic behavior of both compounds has many common features with $Ca_3Co_2O_6$, such as a plateau at a level of 1/3 of the saturation magnetization, a step in the zero magnetic field, and a very slow magnetization relaxation [65, 67, 68]. The main difference consists in the absence of two additional steps in the 1/3 plateau. Quite recently, the $Sr_3Co_2O_6$ compound was synthesized, which also exhibits a behavior similar to $Ca_3Co_2O_6$ [72].

By further replacing cobalt ions and calcium, new compounds with the $A_3BB'O_6$ structure can be synthesized. In particular, the Sr₃NiRhO₆ compound was synthesized in this way [64, 73]. The Ni²⁺ (3d⁸) ions are located in CoII sites in the high-spin (HS) state (S = 1), while Rh⁴⁺ ions remain in octahedral CoI sites in the low-spin (LS) state (S = 1/2). In an individual chain, unlike examples considered above, a ferrimagnetic state is realized, in which the nickel and rhodium sublattices are oriented in opposite directions [73]. The temperature T_{C1} approximately equals 45 K. Above this temperature, as in Ca₃CoRhO₆, a broad short-range-order fluctuation region is observed. In Sr₃NiRhO₆, a step in the zero magnetic field and the 1/3 plateau were also revealed [73].

In various nonstoichiometric solid $Ca_3Co_{2-x}M_xO_6$ substitution solutions, where M = Fe, Cr [74–76], or $Ca_{3-x}R_xCo_2O_6$, where *R* is the strontium or rare-earth ion [77, 78], steps in the magnetization curve are blurred. In this case, the step height and position can change. As found for the $Ca_3Co_{2-x}Fe_xO_6$ compound, substitution may change the type of magnetic ordering [75].

Of special interest are $Ca_3Co_{2-x}Mn_xO_6$ substitution solutions ($x \approx 0.96$ [12, 79, 82]). These compounds belong to multiferroics combining magnetic and ferroelectric orderings. In chains, Mn^{4+} (S = 3/2) ions occupy CoI sites, while Co²⁺ ions occupy CoII sites. As the temperature is lowered, a crossover occurs from the high-spin (S = 3/2) state of Co²⁺ to the low-spin (S = 1/2) state [81]. Manganese ions are displaced along the *c*-axis to one of the neighboring cobalt ions, which breaks the symmetry with respect to inversion. The magnetic ordering along chains takes the form $\uparrow\uparrow\downarrow\downarrow\downarrow$, i.e., each Co-Mn block is oriented ferromagnetically, and blocks are antiferromagnetically ordered. At low temperatures, magnetization curves exhibit a plateau at a level of 3/4 of the saturation magnetization [80]. In $Ca_3Co_{2-x}Mn_xO_6$, the magnetoelectric effect is observed, i.e., the dependence of the electric polarization on the magnetic field, and this is one of the very rare examples of such a type in collinear magnetic systems. Unfortunately, a detailed discussion of the physics of magnetoelectricity in the $Ca_3Co_{2-x}Mn_xO_6$ compound is far beyond the scope of this review. Note only that magnetodielectric properties [83], i.e., the relationship between the magnetic field and dielectric constant, were also studied in $Ca_3Co_2O_6$, as well as the widely discussed interrelation between magnetoelectricity and frustration in various systems [84].

A heated dispute, which continues at present, was initiated by reports that chains in Ca₃Co₂O₆ are actually not ordered ferromagnetically, as assumed above, but contain a long-wavelength longitudinal spin density wave (SDW) propagating along the chain [60, 85–90]. It seems that the wavelength is incommensurable with the lattice period. In resonance X-ray scattering (RXS) and neutron diffraction spectra, an SDW is manifested in the form of peaks corresponding to magnetic scattering and centered at incommensurable wave vectors [85, 86]. Together with the geometrical frustration in a triangular chain lattice, the SDW should give rise to a complex incommensurable partially disordered AMF structure, which is now designated by iPDA. The basic characteristics of the iPDA have been established [87-89]. The SDW length is on the order of 200 lattice periods $(\sim 1000 \text{ Å})$, and the SDW has the form schematically presented in Fig. 9. In this case, the correlation length in the ab plane proves to be considerably smaller, about 180 Å. At



Figure 9. Schematic view of a spin density wave propagating along Co_2O_6 chains (only ions in CoII sites are shown).

temperatures above 12 K, the fraction of the SDW phase is virtually 100% [89]. As temperature is lowered, this fraction gradually decreases to 75% at 8 K. In the range from 8 to 12 K, the SDW depends on the hold time and gradually decays, which, in the opinion of the authors of Ref. [89], means that the SDW state is metastable. It has also been established that the SDW is rapidly suppressed in a magnetic field [87].

Nanostructured Ca₃Co₂O₆ was studied for samples of two types. Thin films were deposited by the laser-induced evaporation method [8, 91, 92]. In work [8], Ca₃Co₂O₆ films were deposited onto a single-crystalline Si(100) substrate. Films were produced in the form of closely packed singlecrystal nanorods 300 nm in length and 40 nm in diameter. Magnetization curves exhibited two magnetization steps and a 1/3 plateau at T = 10 K, which were similar to those in bulk material at this temperature. Samples of the second type were obtained by growing 50-300-nm thick epitaxial films with a small roughness on an SrTiO₃(001) substrate [91]. Notice that the epitaxy conditions were chosen so that the crystallographic *c*-axis of the film was directed along the substrate surface. Despite the high quality of films, no steps in magnetization curves were detected, and only a broad hysteresis revealed itself.

Nanocrystalline Ca₃Co₂O₆ particles a few hundred nanometers in length and about 50 nm in diameter were obtained by grinding a bulk sample in a planetary ball mill [93]. These particles were shown to be polycrystalline rather than amorphous, with the lattice parameters very close to the bulk parameters. At T = 15 K, two magnetization steps were observed, which are typical for the PDA structure. The steps were absent at low temperatures. It should be noted that the magnetic ordering temperature for both Ca₃Co₂O₆ films [8, 91] and nanoparticles [93] determined from the ZFC-FC magnetization curves ranged from 40 to 50 K, which is noticeably higher than the bulk value of T_{C1} .

2.4 CsCoCl₃, CsCoBr₃, and their related compounds

The structure of the CsCoCl₃ compound is formed by CoCl₃ chains oriented along the crystallographic *c*-axis and forming a regular triangular lattice in the *ab* plane (Fig. 10). Co²⁺ ions in the octahedral surrounding of Cl⁻ ions reside in the high-spin 'Ising' state, which is formed under the action of the spin–orbit interaction and triangular distortion of the octahedron [94]. Unlike Ca₃Co₂O₆, cobalt ions are packed into plane hexagonal layers. A strong AFM interaction between nearest cobalt ions occurs along CoCl₃ chains through the mediation of chlorine ions, with the intrachain exchange constant being estimated as 80 K (for a model with a hypothetical spin 1/2) [58]. Interchain interactions prove to be much weaker due to a large distance between chains. At temperature $T_{Cl} = 21$ K, the long-range magnetic order emerges in CsCoCl₃.



Figure 10. (See in color online). View of CoCl₃ chains in CsCoCl₃ along the crystallographic *c*-axis.

The magnetic structure in the ordered phase was studied by the neutron diffraction method [58]. It is convenient to analyze this structure by dividing the triangular lattice of one of the cobalt layers into three triangular sublattices embedded into each other, with magnetic moments M_1 , M_2 , and M_3 . At temperatures slightly below T_{C1} , a structure with $M_1 = -M_2$, $M_3 = 0$ was observed. Thus, the PDA phase was discovered, as already mentioned in Section 2.3 (Fig. 3b). The existence of the PDA structure had somewhat earlier been theoretically predicted and studied by Mekata [57]. Below 13.5 K, the PDA structure continuously transforms into a three-sublattice ferrimagnetic structure¹ [58], and the pure phase is observed $(M_1 = M_2 = -M_3)$ below 5 K. This transformation is well described in the mean field model [57, 58] and numerical models [96] assuming the existence of the two types of interchain interactions: the AFM interaction for nearest neighbors (J_1) , and the FM interaction for next-to-nearest neighbors (J_2) , with the ratio of interaction constants equal to $|J_2/J_1| = 0.4$.

Later on, CsCoCl₃ attracted great interest as a model system for studying spin excitations in Ising spin-1/2 chains [94, 97–99]. These excitations comprise solitons (or domain walls) in a one-dimensional system. Their nature was studied in detail by the neutron diffraction [100], NMR [101], and Raman scattering [102] methods.

One can easily see that, despite the AFM ordering of chains in CsCoCl₃, the magnetic ordering structure in the zero external magnetic field should be completely equivalent to a model for FM chains on a triangular lattice accurate to a change in the direction of magnetization in odd layers. On the other hand, its behavior in an external magnetic field becomes radically different. The total magnetic moment of each chain is zero, and therefore the magnetization remains close to zero in weak magnetic fields. In strong magnetic fields, two magnetization steps are observed at $H_{C1} = 33$ T and $H_{C2} = 43.9$ T, which correspond to the flip of part of the cobalt ion magnetic moments [103]. As a whole, the result is described by the mean field theory. Nevertheless, as pointed out by Amaya et al. [103], a few facts remain unexplained so far. First, yet another small step is observed at a low temperature in a magnetic field slightly lower than H_{C1} ,

which is preserved at different temperatures below 4.2 K and in studies performed in different strong pulsed magnetic fields. Second, a continuous increase in the magnetic moment is observed between transitions, as should be expected for the angular phase. However, such an explanation seems unlikely for a strong CsCoCl₃ Ising system. Finally, peaks in the time dependence of the differential magnetic susceptibility corresponding to these steps prove to be strongly asymmetric.

There is an alternative approach to the explanation of the nature of the phase transition in CsCoCl₃ in a strong magnetic field [103, 104], which considers the phase transition as the magnetization of an almost isolated strongly anisotropic Heisenberg chain.

Similar results were basically obtained for related CsCoBr₃ and RbCoCl₃ compounds [58]. Of interest for us are other compounds belonging to this class, RbCoBr₃ and TlCoCl₃ [95, 105–107], in which the structural phase transition causes the relative displacements of chains along the caxis. An important result of these displacements is the structuring of interactions even between nearest chains, which in turn leads to the formation of a complex magnetic ordering. The structural transition in TlCoCl₃ occurs at $T_{\rm S} = 68$ K², while the temperature of transition to the magnetic ordered state is $T_{C1} = 29.5$ K [106, 107]. It was assumed earlier that both transitions in RbCoBr3 occur simultaneously at $T_{\rm S} = T_{\rm C1} = 37$ K [105]. Later on, careful measurements revealed [108] that, in reality, yet another transition takes place, in which both the structure of chain displacements along the *c*-axis and magnetic structure change at $T_{S2} = T_{C2} = 31$ K. In addition, the low-temperature RbCoBr₃ phase and the phase above T_S in TlCoCl₃ prove to be ferroelectric [106].

The TlCoCl₃ compound does not contain the PDA phase. It was recently found that the PDA phase exists in RbCoBr₃ in a narrow temperature range between T_{C1} and T_{C2} [108, 109]. The low-temperature RbCoBr₃ phase is formed by a three-sublattice ferrimagnetic structure similar to CsCoCl₃. In TlCoCl₃, $\uparrow\uparrow\downarrow\downarrow$ type magnetic ordering is realized everywhere over the region below T_{C1} , where the arrows show the alternating of the magnetic moment directions of cobalt ions in a plane along the *a*-axis [107].

2.5 Magnetic structure of Sr₅Rh₄O₁₂

Consider now a new Sr₅Rh₄O₁₂ compound with a triangular lattice [110–112]. Among its features, we point out first of all that a magnetic system is formed in it by rhodium 4d ions rather than by 3d ions, as in the compounds considered above. This compound exhibits a pronounced Ising anisotropy. The $Sr_5Rh_4O_{12}$ structure is extremely complex. It is sufficient to say that rhodium ions are located in twelve nonequivalent crystallographic [110] sites. In addition, rhodium in this compound has the variable valence Rh³⁺-Rh⁴⁺ and, depending on the oxygen environment (the O octahedron and the triangular P prism), it can reside both in the HS state and in the LS state. The spin moments of rhodium ions along each of the chains alternate as follows [110]: S = 0 (Rh³⁺, 4d⁶, O, LS), S = 2 (Rh³⁺, 4d⁶, P, HS), S = 1/2 (Rh⁴⁺, 4d⁵, O, LS), and S = 1/2 (Rh⁴⁺, 4d⁵, O, LS). In this case, each unit cell contains six chains.

According to Ref. [113], we will assume that a chain is divided by nonmagnetic ions $(S = 0, \text{ Rh}^{3+})$ into blocks,

¹ As shown in paper [57], two types of the three-sublattice ferrimagnetic structure can be realized: $M_1 \neq M_2 \neq M_3 \neq 0$, and $M_1 = M_2 > 0$, $M_3 < 0$. In some papers (see, for example, Ref. [95]), they are denoted by 3FI and 2FI; however, in our opinion, this notation is not appropriate.

² In reality, a series of structural phase transitions occur in TlCoCl₃ [106, 107]. We are speaking here about the lowest-temperature transition.



Figure 11. (See in color online). Magnetization curves (ascending branch) of $Sr_5Rh_4O_{12}$ at different temperatures [110]. The arrows indicate the sequence order of curves for increasing temperature.

which are treated as elements of the Ising chain. Chains are separated from each other by the same distance (560 pm), and interchain Rh-O-Sr-O-Rh bonds are probably weak. Thus, the $Sr_5Rh_4O_{12}$ magnetic subsystem can be treated as a triangular lattice of weakly coupled ferromagnetic chains, similar to Co_2O_6 chains in $Ca_3Co_2O_6$.

The magnetization curves for Sr₅Rh₄O₁₂ are presented in Fig. 11. The saturation magnetization of $5.3 \mu_B$ proves to be slightly lower than the theoretical estimate $(6 \mu_{\rm B})$ for the spin sequence in the chain S = 0, 2, 1/2, 1/2 for the g factor equal to 2. One can see from the plots in Fig. 11 that two types of curves exist in reality. At a high temperature, we observe a typical PDA structure with two steps and a plateau at a level of $\sim 1/3$ of the saturation magnetization. However, unlike compounds with cobalt chain triangular lattices, the plateau slope in Sr₅Rh₄O₁₂ proves to be considerable. The lowtemperature behavior differs from that for all systems considered above: beginning from the zero magnetic field, an interval with a very weak magnetic moment exists. Then, the curve returns to the 1/3 plateau. Thus, we can assume that a special low-temperature phase is realized in the Sr₅Rh₄O₁₂ compound.

2.6 General peculiarities

In the conclusion of this section, we indicate the basic characteristics observed in experiments with triangular Ising chain lattices. As a rule, these compounds possess low- and high-temperature magnetic ordered phases. The high-temperature phase is universal, being the PDA structure, while low-temperature phases are quite diverse in their structure. The exception is only strongly distorted triangular lattices in RbCoBr₃ and TlCoCl₃, where the low-temperature phase is realized at once, and in Ca₃CoIrO₆, where the PDA phase is also probably absent. The complex slow magnetization dynamics is manifested in Ca₃Co₂O₆ and its related compounds.

3. Magnetic structure and phase diagram

3.1 Model of rigid chains

In all the compounds discussed above, the strongest magnetic interactions occur along chains, which allows one to treat them as elements of the magnetic structure. Chains can then be considered completely ordered at zero temperature, i.e., they can be treated as individual Ising superspins with two possible states in which the magnetization is oriented along the *c*-axis in two opposite directions. Taking into account weak interaction between adjacent chains, we arrive at the two-dimensional (2D) AFM Ising model (spin 1/2) on a triangular lattice with the Hamiltonian

$$\hat{H} = J \sum_{\langle ij \rangle} \sigma_i \sigma_j - B \sum_i \sigma_i \,, \tag{1}$$

where $\sigma_i = \pm 1$ is the spin projection for the *i*th chain onto the *c*-axis, $\langle ... \rangle$ means summation over the nearest neighbors in the triangular lattice, and *B* is the external magnetic field oriented along the *c*-axis. It should be noted that, because here J > 0 is the coupling constant between chains rather than between individual ions, the effective temperature always proves to be very low (with respect to *J*).

Model (1) was carefully studied by Wannier [114] in a zero magnetic field. He showed that the ground state of the model is strongly degenerate and formed by configurations of several types: stripe structures formed by alternating 'spinup' and 'spin-down' stripes, the PDA structure mentioned above (Fig. 3b), the special class of configurations called tripods by Wannier (Fig. 12a), and more complex structures. The appearance of tripods can be illustrated in the following way. Assume that the three adjacent spins of a PDA structure in a disordered sublattice are oriented downward (white circles in Fig. 12a). Then, a spin located in the middle of a triangle formed by them can flip, i.e., an additional state appears. Thus, tripods increase the entropy.

Wannier has failed to represent the ground-state structure in the explicit form; however, he managed to calculate the entropy density in the ground state (per site of the triangular lattice) [114]:

$$S_0 = \frac{2}{\pi} \int_0^{\pi/3} \ln(2\cos\omega) \,d\omega \approx 0.323\,.$$
 (2)

Notice that statistical weights of different ground-state configurations are considerably different. For example, the



Figure 12. Types of configurations: (a) isolated tripod, and (b) three starconnected tripods.

stripe structure has zero entropy, which means an exponentially small statistical weight. In other words, we can neglect these configurations because the probability of their appearance tends to zero. The entropy of the PDA structure can be readily calculated: each third spin can take any of the two possible states: $S_{PDA} = (1/3) \ln 2 \approx 0.231$. One can see that this state can be treated as the first approximation to the ground state. Then, we calculate the entropy of the PDA structure with tripods: $S_{\rm T} = (5/12) \ln 2 \approx 0.289$. This includes both isolated tripods and their different combinations, for example, a triad of tripods connected in the form of a star (Fig. 12b). The entropy of 'isolated tripod' type configurations, etc., can be separately calculated [115]. The proximity of the entropy to its exact value (2) characterizes the quality of the approximate representation of the ground state.

Consider now the low-temperature behavior of Ca₃Co₂O₆ in the rigid chain model. We already pointed out that the magnetization curves of this compound strongly depend on the rate of change of an external magnetic field. Taking into account the strong degeneracy of model (1), we assume that the system placed in a variable magnetic field resides in a metastable state, rather than in the ground state. The metastability condition can be formulated in the following way [115]:

$$\sigma_i h_i \ge 0 \,, \tag{3}$$

where

$$h_i = B - J \sum_{\langle ij \rangle} \sigma_j \tag{4}$$

means the effective field acting on the *i*th chain. Thus, if the magnetic moment of each chain is oriented along the effective field, the system is in a metastable state. In this case, the flip of the magnetization direction for any chain leads to an increase in energy.

We will study the evolution of the system upon varying the external magnetic field by using the single-flip technique which was earlier applied to describing nonequilibrium phenomena in the Ising model [116]. The probability of a magnetization flip in the *i*th chain is given by

$$W_i = \begin{cases} 0, & \text{if } \sigma_i h_i > 0, \\ 1, & \text{if } \sigma_i h_i \leqslant 0. \end{cases}$$

$$\tag{5}$$

From this it follows that the system placed in the variable magnetic field will be in the metastable state at each instant of time.

Now we should prepare the initial (ground) state of the system in a zero field. Let the PDA structure be utilized as the first approximation. As the magnetic field is increased, we will observe a magnetization jump in the zero field up to 1/3 of the saturation magnetization, because chains having an equal number of neighbors (shown by grey circles in Fig. 3b) are ordered along the external magnetic field direction at once after its appearance. As a result, we obtain a transformation to a three-sublattice ferrimagnetic structure in an arbitrarily weak magnetic field. This structure is preserved upon increasing the magnetic field up to B = 6J, at which a transformation to the ferromagnetic structure takes place. The magnetization curve with the initial PDA state exhibits two steps and a plateau at 1/3 of the saturation magnetization



Figure 13. Magnetization curves of Ca₃Co₂O₆ in the rigid chain model [115]: PDA (dashed line) taking into account single tripods (dot-and-dash line), and also single and pair tripods and star-like structures (solid line). Shown are nearest-neighbor configurations corresponding to steps in the curve.

(dashed straight line in Fig. 13). This line corresponds to the high-temperature magnetization curve of Ca₃Co₂O₆, and therefore we can assume that we are on the right road.

Let us now define more exactly the ground state of the system by including isolated tripods into our consideration. The probability of their appearance on the PDS structure can be readily calculated [115]. Tripods contain a new local nearest-neighbor configuration: four neighbors are located along the magnetic field, and two in the opposite direction. This, in turn, gives rise to a new small step in the magnetization curve, B = 2J. The inclusion of a pair of connected tripods into the consideration does not qualitatively change the shape of the curve, while configurations with three starconnected tripods (Fig. 12b) produce a new step at B = 4J. Note that the further refinement of the ground state cannot qualitatively change the picture, because all the possible nearest-neighbor configurations are exhausted. To determine the height of the steps, it is necessary to calculate the appearance probabilities of each of the configurations. The magnetization curve, obtained analytically in work [115], is depicted by the solid line in Fig. 13. It agrees well with the experimental low-temperature magnetization curve of Ca₃Co₂O₆.

The strong degeneracy of the 2D AFM Ising model has another important consequence. Very weak next-to-nearestneighbor interactions partially lift this degeneracy and select a certain type of configuration for the ground state. We will expand model (1) by including such interactions:

$$\hat{H} = J \sum_{\langle ij \rangle} \sigma_i \sigma_j + J' \sum_{\langle \langle ij \rangle \rangle} \sigma_i \sigma_j - B \sum_i \sigma_i , \qquad (6)$$

where $\langle \langle \ldots \rangle \rangle$ denotes summation over next-to-nearest neighbor pairs, as shown in Fig. 3a. In the case of the FM interaction (J' < 0), the three-sublattice ferrimagnetic system becomes the ground state, as in the case of CsCoCl₃ and its related compounds. For J' > 0, the ground state is a twosublattice stripe structure (Fig. 3c). In weak magnetic fields, the magnetic moment of such a structure is close to zero (a two-sublattice Ising antiferromagnet), as observed in $Sr_5Rh_4O_{12}$ [110, 111]. Therefore, weak AFM next-to-nearest-neighbor interactions can produce a special low-temperature phase in this compound [113].

The degeneracy of the 2D AFM Ising model (1) can also be partially lifted by a reduction of symmetry. In this case, the nearest-neighbor interaction constants are different. The displacements of chains along the *c*-axis in RbCoBr₃ and TlCoCl₃ produce exactly such a situation and lead to the appearance of a new ground state which is determined by the form of distortions: a stripe structure in TlCoCl₃ [107], and a three-sublattice ferrimagnetic structure in RbCoBr₃ [108, 109].³ In Sr₅Rh₄O₁₂, chains are not, strictly speaking, equivalent to each other, and weak differences between nearest-neighbor interaction constants is the second possible scenario of the appearance of the low-temperature phase in Sr₅Rh₄O₁₂.

Thus, weak next-to-nearest-neighbor interactions or structural distortions partially lift the degeneracy, thereby producing different types of ground states.

3.2 Effective field models

It is useful to begin the discussion of the properties of a triangular Ising chain lattice at nonzero temperature with effective field models. Two types of models have been proposed. The models of the first type are purely two-dimensional. The 2D effective field model was first developed by Mekata [57] to describe the CsCoCl₃ phase diagram. Chains are still assumed rigid, i.e., completely ordered with two possible states.

Consider Hamiltonian (6) with the AFM nearest-neighbor interaction (J > 0) and the FM next-to-nearest-neighbor interaction (J' < 0). We divide the entire triangular lattice into three sublattices, as illustrated in Fig. 3b. Then, we can write down the Hamiltonian of the *l*th sublattice in the molecular field approximation as [57]

$$\hat{H}_{l} = 3J(\langle \sigma \rangle_{m} + \langle \sigma \rangle_{n}) \sum_{i} \sigma_{i}^{l} + 6J' \langle \sigma \rangle_{l} \sum_{\langle \langle ij \rangle \rangle} \sigma_{i}^{l} - B \sum_{i} \sigma_{i}^{l} .$$
(7)

Here, the respective *l*, *m*, and *n* superscript and subscripts denote three sublattices, and the subscript *i* is the number of a unit cell, each one of which containing three sites of the 2D lattice. Expression (7) comprises $\langle S \rangle_l$ magnetizations averaged over the *l*th sublattice, which are determined from the equation [57]

$$\langle \sigma \rangle_{l} = \tanh \left\{ \beta \left(\alpha \langle \sigma \rangle_{l} + \langle \sigma \rangle_{m} + \langle \sigma \rangle_{n} + \gamma \right) \right\},\tag{8}$$

where coefficients are $\alpha = 2J'/J$, $\beta = -3J/(k_BT)$, and $\gamma = -B/(3J)$, k_B is the Boltzmann constant, and *T* is temperature.

Three equations (8) for sublattices form a set determining the magnetization of sublattices at a given temperature. In particular, the expansion of the right-hand part near the point $\langle \sigma \rangle_l = \langle \sigma \rangle_m = \langle \sigma \rangle_n = 0$ at $\gamma = 0$ allows one to determine the magnetic ordering temperature in the given system:

$$T_{\rm C1} = \frac{3}{k_{\rm B}} (J - 2J') \,. \tag{9}$$

³ In RbCoBr₃, a strong coupling takes place between the magnetic ordering and lattice deformation, and therefore its phase diagram is described by the complex spin–lattice Hamiltonian [108, 109].

By using Hamiltonian (7) and equations (8), we can calculate the free energy of the system and all basic thermodynamic characteristics [57].

The most important result obtained by using the 2D effective field model is the discovery of the second-order phase transition from the high-temperature PDA phase to the low-temperature ferrimagnetic phase in the absence of a magnetic field at temperature T_{C2} [57], which corresponds to the observed phase diagram of CsCoCl₃. The nature of this transition is related to the above-mentioned peculiarity of the ground state for the 2D AFM Ising model, namely, its strong degeneracy. The PDA structure, unlike the ferrimagnetic one, has nonzero entropy S. At high temperatures, this produces a gain in the free energy: F = E - TS. At very low temperatures, the next-to-nearest-neighbor interactions partially lift the degeneracy, while the energy of the ferrimagnetic structure slightly decreases compared to the PDA phase. Notice also that, depending on the phase diagram region, two types of ferrimagnetic structures can appear.⁴

The two-dimensional model considered above has two disadvantages. First, it assumes the division of the lattice into sublattices. We saw in Section 3.1 that such a division is not always justified. The second disadvantage is related to the rigid chain approximation. To estimate restrictions imposed by this approximation, note first of all that chains in real materials have a finite length.

The chain length in $Ca_3Co_2O_6$ was estimated in Ref. [117] from simple considerations as a magnitude on the order of 100 lattice periods (or 100 magnetic ions). We will see below that the exact magnitude of the chain length is not important. Notice that this estimate is consistent with the distance between two SDW nodes (see Section 2.3). The value of the spin–spin correlation function for an Ising chain with a finite length *L* in the zero magnetic field is well known [118]:

$$\Gamma(r) = \langle \sigma_i \sigma_{i+r} \rangle = \tanh^r(K), \qquad (10)$$

where $K = |J_0/k_B T|$, J_0 is the magnitude of the nearestneighbor exchange interaction in the chain, and r is the distance in the units of the chain period. We assume that $J_0 < 0$. Note that the result obtained below is valid both for FM and AFM chains. If $\Gamma(L) \approx 1$, the chain can be considered completely ordered. When $\Gamma(L) \rightarrow 0$, the chain is, on the contrary, completely disordered. The characteristic order–disorder transition temperature estimated from formula (10) is [117]

$$K \approx \frac{1}{2} \ln L \,. \tag{11}$$

One can see from expression (11) that this temperature weakly depends on the chain length, and the approximate estimate is sufficient. On the other hand, the correlation function exponentially depends on temperature, as is seen from formula (10). Because of this, the transition of the chain from the ordered state to the disordered state occurs in a narrow temperature range. Finally, assuming that $J_0 \approx 20$ K for Ca₃Co₂O₆, we estimate the transition temperature as approaching 11 K [117], which almost exactly corresponds to the value of T_{C2} for this compound.

Our consideration leads to two conclusions. First, the rigid chain model cannot, strictly speaking, be applied to the high-temperature phase because, for example, chains in the

⁴ See footnote 1.

zero effective field in a PDA structure (grey circles in Fig. 3b) will be disordered. Second, the transition from the low-temperature phase to the high-temperature one in $Ca_3Co_2O_6$ can be caused by the disordering of part of the chains.

To go beyond the scope of a purely two-dimensional model, the mean field model for $Ca_3Co_2O_6$ was formulated in Ref. [117], which assumes that each of the chains is located in the effective field defined by an expression analogous to formula (4):

$$\tilde{h}_i = B - J \sum_{\langle ij \rangle} \langle \sigma \rangle_j \,.$$

Here, $\langle \sigma \rangle_j$ under the sum sign is the mean magnetization of the *j*th chain, and summation is again performed over nearest neighbors. We can now write down the Hamiltonian for the *i*th chain in the effective field as

$$\hat{H}_{i} = J_{0} \sum_{\langle \lambda \mu \rangle} \sigma_{i\lambda} \sigma_{i\mu} - \tilde{h}_{i} \sum_{\lambda} \sigma_{i\lambda} , \qquad (12)$$

where subscripts λ and μ denote the number of a magnetic ion in the *i*th chain. Next, we can easily calculate the mean magnetization $\langle \sigma \rangle_j$ for each of the chains, which, in turn enters into the expression for the effective field. In paper [117], the known analytical solution for a chain in a magnetic field with periodic boundary conditions was used, which was obtained by the transfer-matrix method [118].

As we saw in the previous section, the magnetic structure in $Ca_3Co_2O_6$ is obviously nonperiodic, at least in the zero magnetic field. Therefore, the division into sublattices in this case is impossible. As for the rigid chain model, we should calculate the appearance probabilities of various configurations, taking a finite temperature into account, which allows us to determine the total magnetization [117]. The results obtained are presented in Fig. 14. The plots demonstrate well the transition from the low-temperature phase to the hightemperature one. The high-temperature phase proves to be a PDA one.

The explanation of the nature of this transition somewhat differs from that presented above for CsCoCl₃. At a low temperature, as was established in the rigid chain model, the total entropy of the system corresponds to the 2D AFM Ising



Figure 14. Magnetization curves of $Ca_3Co_2O_6$ in the effective field model at T = 2 K (*I*), 120 K (*2*), and 16 K (*3*) [117].

model on a triangular lattice. At high temperatures in a zero magnetic field, some chains can be found in a zero effective field (for example, chains shown by grey circles for the PDA phase in Fig. 3b). It can be easily verified that they become disordered at the lowest temperature. The disordered chains make a very large contribution to the total entropy. Thus, the greater the number of chains in the zero effective field, the greater is the gain in the free energy of the system [117]. Among all the configurations contained in the ground state of the 2D AFM Ising model on a triangular lattice, the maximum number of disordered chains can be found in the PDA phase. Therefore, this phase should be the universal high-temperature phase.

3.3 Model of incommensurate magnetic ordering in $Ca_3Co_2O_6$

In Ref. [88], a model was developed for describing the incommensurate iPDA structure discussed in Section 2.3. The key moment is the fact that, in reality, two types of interactions exist between adjacent chains in $Ca_3Co_2O_6$ through Co-O-O-Co oxygen bridges, which are shown by solid and dashed straight lines in Fig. 1b. In the case of interactions shown by dashed straight lines, oxygen ions are separated from each other by a noticeably longer distance and, as a rule, neglected. Nevertheless, estimates show [88] that interaction constants can be commensurate. Both types of interchain bonds form helicoidal paths with different topologies, which can lead to the competition of these interactions if, for example, they have the AFM nature.

A primitive rhombohedral cell of $Ca_3Co_2O_6$ contains two magnetic CoII ions with coordinates (1/4, 1/4, 1/4) and (3/4, 3/4, 3/4). Note that chains in this cell are oriented along the [111] direction (the *c*-axis of the hexagonal cell considered above). Then, the lattice contains two types of magnetic ions with magnetic moments M_1 and M_2 . Grouptheoretic analysis shows that experimental RXS and neutron diffraction data [85–87, 89] correspond to the following magnetic structure (see Fig. 9):

$$\mathbf{M}_{1}(\mathbf{R}) = \mathbf{M}\cos\left(\mathbf{kR}\right),$$

$$\mathbf{M}_{2}(\mathbf{R}) = -\mathbf{M}\cos\left(\mathbf{kR} + \pi\Delta\right),$$
(13)

 \mathbf{M} is a vector prior to a large the [111] dim

where **M** is a vector oriented along the [111] direction, and **R** is the vector of cell translation with respect to the initial cell. Here, $\mathbf{k} = 2\pi(\Delta/3, \Delta/3, \Delta/3)$ is the wave vector of the SDW. If the parameter Δ slightly differs from 1, the SDW appears.

Further analysis was performed in Ref. [88] in the framework of the Heisenberg model with three types of interactions: one along the chain, and two others between the nearest chains. The model also included the uniaxial single-ion anisotropy. As a result, it was shown that there is a set of parameters corresponding to the value of $\Delta = 1.01$ observed in experiments.

It should be noted that the model considered above was initially based on a very narrow class of solutions (13), and therefore it cannot answer, for example, the question about the stability of the SDW obtained. In work [90], the Heisenberg model was studied by the renormalization group method for the density matrix on the same lattice as in paper [88]. Solutions corresponding to the iPDA structure were also obtained in work [90]. However, the enhancement of the uniaxial anisotropy completely suppressed the SDW and led to the commensurate magnetic structure. Thus, the issue of the nature of the iPDA state remains open.

4. Glauber dynamics in Ising systems

4.1 Dynamics of an isolated chain

As already mentioned, the Ising model constitutes a statical model, i.e., it does not involve the dynamics of the system under study. For a one-dimensional Ising spin chain, Glauber proposed a stochastic model in which the interaction of the chain with a heat reservoir is assumed [6]. In this section, we will discuss the basic ideas of the Glauber dynamics.

Consider the spins of N fixed particles in a chain as stochastic functions of time $\sigma_i(t)$ taking two values, ± 1 . The spin flip occurs due to interaction with an external agent: a heat reservoir. However, it is obvious that the spin flip probability should depend on the instantaneous values of adjacent spins.

The number of states of a system comprising *N* spins is 2^N . Each spin configuration has the probability $p(\sigma_1, \ldots, \sigma_N, t)$, which obeys the master kinetic equation

$$\frac{\mathrm{d}}{\mathrm{d}t} p(\sigma_1, \dots, \sigma_N, t) = -\left[\sum_i w_i(\sigma_i)\right] p(\sigma_1, \dots, \sigma_N, t) + \sum_i w_i(-\sigma_i) p(\sigma_1, \dots, -\sigma_i \dots, \sigma_N, t), \qquad (14)$$

where $w_i(\sigma_i)$ is the spin flip probability for the *i*th spin per unit time, provided all other spins remain fixed. One can see from the right-hand side of formula (14) that the emergence probability of the state $\{\sigma_1, \ldots, \sigma_N\}$ decreases due to the flip of any of the spins composing the given configuration and increases due to the flip of the spin in the configuration that differs from the specified configuration only by the value of this spin. In the case of a contact with a thermostat, the master kinetic equation should lead the system to the Gibbs distribution [119].

The most interesting quantities that can be obtained from the system of equations (14) are local mean magnetic moments

$$q_i(t) = \langle \sigma_i(t) \rangle = \sum_{\{\sigma\}} \sigma_i p(\sigma_1, \dots, \sigma_N, t),$$

and correlation functions

$$r_{ik}(t) = \langle \sigma_i(t) \sigma_k(t) \rangle = \sum_{\{\sigma\}} \sigma_i \sigma_k p(\sigma_1, \dots, \sigma_N, t).$$

Here, the sum over $\{\sigma\}$ means summation over 2^N spin configurations. From the system of equations (14), the following equations for local mean magnetic moments and correlation functions can be obtained [6]:

$$\frac{\mathrm{d}}{\mathrm{d}t} q_k(t) = -2 \langle \sigma_k(t) w_k [\sigma_k(t)] \rangle, \qquad (15)$$

$$\frac{\mathrm{d}}{\mathrm{d}t}r_{ik}(t) = -2\langle\sigma_i(t)\,\sigma_k(t)\big\{w_i\big[\sigma_i(t)\big] + w_k\big[\sigma_k(t)\big]\big\}\big\rangle.$$
 (16)

Thus, the time evolution of the quantities of interest to us is completely determined by the choice of the spin flip probability $w_i(\sigma_i)$, which, in turn, depends on the character of interaction with a heat reservoir and the mutual orientation of adjacent spins. Here, the following restrictions on the form of $w_i(\sigma_i)$ appear. First, the spin flip probability should reflect real tendencies taking place in the system, for example, to the FM or AFM ordering. Second, for an arbitrary system of spins connected with a heat reservoir and residing in the thermodynamic equilibrium, the principle of detailed balancing, namely

$$w_i(\sigma_i) p_i(\sigma_i) = w_i(-\sigma_i) p_i(-\sigma_i)$$
(17)

should be satisfied, where $p_i(\sigma_i)$ is the probability that the *i*th particle has the spin σ_i for the fixed spins of other particles.

The spin flip probability for an FM Ising spin chain with the Hamiltonian $H = J \sum_{\langle ij \rangle} \sigma_i \sigma_j$ (J < 0) was proposed by Glauber in the form [6]

$$w_i(\sigma_i) = \frac{\alpha}{2} \left\{ 1 - \frac{1}{2} \gamma \sigma_i(\sigma_{i-1} + \sigma_{i+1}) \right\}.$$
 (18)

Expression (18) contains two parameters. The parameter α specifies the time scale of the spin flip and is free in this theory, because the mechanism of interaction of the Ising system with a heat reservoir remains uncertain. The parameter γ is determined from the principle of detailed balancing [6]: $\gamma = \tanh(-2J/k_{\rm B}T)$.

So far, we have said nothing about boundary conditions: expression (18) makes sense only for internal spins of a chain with opened ends or for a ring (periodic boundary conditions). For spins at the ends of a finite chain with length N, the absence of one of the neighbors should be taken into account [120]:

$$w_i(\sigma_i) = \frac{\alpha}{2} \left[1 - \beta \sigma_i \sigma_{i\pm 1} \right], \tag{19}$$

where the quantity $\beta = \tanh(-J/k_BT)$ is also determined from the detailed balance principle. The '+' sign in the subscript in formula(19) is used for i = 1, and '-' for i = N.

Mathematical approaches to the solution of a system of equations for mean local moments (and correlation functions as well) for open and closed spin chains are different. Thus, the system of recurrent equations

$$\frac{\mathrm{d}}{\mathrm{d}(\alpha t)} q_k(t) = -q_k(t) + \frac{1}{2} \gamma \big[q_{k-1}(t) + q_{k+1}(t) \big], \qquad (20)$$

$$\frac{\mathrm{d}}{\mathrm{d}(\alpha t)} r_{ik}(t) = -2r_{ik}(t) + \frac{1}{2} \gamma [r_{ik-1}(t) + r_{ik+1}(t) + r_{i-1k}(t) + r_{i+1k}(t)]$$
(21)

is obtained for a ring.

One can see from expressions (20) and (21) that it is convenient to combine the constant α with a time variable and to set it equal to unity. Notice also that Glauber [6] proposed an elegant image method for calculating correlation functions both for a ring [6] and for a finite chain [121].

The evolution of the mean moments of a finite chain with open ends can be described in the matrix form. For the column vector $\mathbf{q} = \{q_1, \ldots, q_N\}$, equations similar to equation (20) can be written in the form [120]

$$\dot{\mathbf{q}} = \mathbf{M}\mathbf{q}\,,\tag{22}$$

where

$$\mathbf{M} = \begin{pmatrix} -1 & \beta & 0 & \cdots & 0 & 0 \\ \gamma/2 & -1 & \gamma/2 & \cdots & 0 & 0 \\ 0 & \gamma/2 & -1 & \cdots & 0 & 0 \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ 0 & 0 & 0 & \cdots & -1 & \gamma/2 \\ 0 & 0 & 0 & \cdots & \beta & -1 \end{pmatrix}.$$

Spatial correlation functions r_{ik} of a chain form the symmetric matrix **r**. The time evolution equation of this matrix has the form [121]

$$\dot{\mathbf{r}} = \mathbf{M}\mathbf{r} + \mathbf{r}\mathbf{M}^{T}.$$
(23)

Two characteristic times can be singled out in the Glauber dynamics of an Ising chain [121]. The first, τ_1 , is the relaxation time of the mean magnetic moment $q = 1/N\sum_i q_i$. This time for an Ising ring or an infinite chain was found by Glauber [6]:

$$\tau_1 = \frac{1}{\alpha(1-\gamma)} \,. \tag{24}$$

The expression for the relaxation time of the mean magnetic moment for an open chain is more complicated [120, 121] and is determined by the system size. It is also interesting to note that the critical dynamics of a chain $(T \rightarrow 0)$ with an arbitrary length differs from the ring dynamics and is anomalous [120].

At low temperatures, the probability distribution of the chain states as a function of the chain magnetic moment exhibits two pronounced peaks corresponding to the two magnetization states of the chain as a whole. Thus, the Ising chain is an example of a bistable stochastic system [122]. Inter alia, it is possible to talk about a stochastic resonance in the chain [123].

The description of the magnetization dynamics in a system with two almost stable states in terms of the mean moment is incomplete. Strictly speaking, it is valid for an ensemble of noninteracting chains. It is then useful to introduce the second relaxation time, τ_2 , describing the transition from the completely disordered state of the chain to one of the almost ordered states, i.e., the dynamic spontaneous breaking of the symmetry [121]. Obviously, this process does not affect the mean moment of an atom in any way. At low temperatures, one has $\tau_1 \ge \tau_2$. In the time interval $\tau_2 \ll t \ll \tau_1$, the chain is completely ordered and can be utilized as a memory element. Notice also that the temperature dependence of τ_1 obtained in the Glauber theory well describes the experimental results obtained for the above-mentioned CoPhOMe SCM compound [124].

We have already said that α is a free parameter (constant). However, a more detailed study reveals that the coefficient α should depend on temperature [21]. This fact is described in the Heisenberg model with a strong uniaxial anisotropy. The temperature dependence of the characteristic spin-flip time in the absence of the local field of neighbors is determined by the anisotropy parameter and has an activation nature [21]:

$$\tau_0 = \alpha^{-1} = \tau_i \exp\left(\frac{\Delta_a}{k_B T}\right),\tag{25}$$

where τ_i describes the inner spin dynamics in contact with a heat reservoir in the absence of the energy barrier. Recall that Δ_a is the anisotropy parameter (see Section 2.1).

The process of simultaneous flip of several spins can also be included into consideration [125]. Alternative models for describing the stochastic dynamics of the Ising chain also exist [126, 127]. For example, the Kawasaki model [126] considers the stochastic simultaneous flip of a pair of opposite adjacent spins. In this case, the magnetization remains invariable. Note also that because the Glauber model is one of the few exactly solvable models of nonequilibrium dynamics, many theoretical papers have been devoted to studying its various aspects (see, for example, papers [128–130]).

The involvement of a magnetic field in the system changes the spin-flip probability. For example, for a closed Ising chain placed in an external magnetic field and possessing the Hamiltonian

$$\hat{H} = J_0 \sum_{\langle ij \rangle} \sigma_i \sigma_j - B \sum_i \sigma_i \,, \tag{26}$$

Glauber derived the expression

$$w_i'(\sigma_i) = w_i(\sigma_i) \left[1 - \sigma_i \tanh\left(\frac{B}{k_{\rm B}T}\right) \right]$$
 (27)

for the spin-flip probability in the magnetic field, which also satisfies the principle of detailed balancing. Here, $w_i(\sigma_i)$ is the spin-flip probability in the absence of the magnetic field, and $\gamma = \tanh(-2J_0/k_BT)$. Formula (27) is not the only possible one, as shown in the next section.

4.2 Spin-flip probability in the Glauber dynamics

The question about the expression for the spin-flip probability in the Glauber dynamics becomes most important during its generalization to lattices of different dimensionalities. Thus, the linearized spin-flip probability generalized to a system with an arbitrary dimensionality was reported in the form [131]

$$w_i(\sigma) = 1 - \frac{\lambda}{2d} \,\sigma_i \sum_{\langle ij \rangle} \sigma_j \,, \tag{28}$$

where λ is an arbitrary parameter varying from 0 to 1, *d* is the system dimensionality, and summation is performed over 2*d* nearest neighbors in a hypercubic lattice. This expression for the transition probability proved to satisfy the principle of detailed balancing only in the case of the one-dimensional model. If $d \ge 2$, this form of the transition probability does not satisfy the principle of detailed balancing and cannot lead the system to the Gibbs distribution.

From the point of view of the Glauber approach, the choice of the spin-flip probability is ambiguous. Indeed, let us consider the requirement of detailed balancing (17) in more detail. Under the conditions of the statistical equilibrium, the probability that the *i*th spin will take the value σ_i is proportional to the Boltzmann factor exp $(-E_i/k_BT)$. For a type (1) Hamiltonian with any dimensionality and an arbitrary number of nearest neighbors, we obtain

$$\frac{w_i(\sigma_i)}{w_i(-\sigma_i)} = \frac{\exp\left[-\sigma_i/(k_{\rm B}T)\left(J\sum_{\langle ij\rangle}\sigma_j - B\right)\right]}{\exp\left[\sigma_i/(k_{\rm B}T)\left(J\sum_{\langle ij\rangle}\sigma_j - B\right)\right]}$$
(29)

for the *i*th spin. Because the subscript *i* is fixed, summation in formula (29) is performed over its nearest neighbors.

It follows from the last formula that functions $w_i(\sigma_i)$ are defined accurate to the ratio $w_i(\sigma_i)/w_i(-\sigma_i)$, which is the reason for their ambiguity. After some algebraic transformations, we arrive at the expression for the spin-flip probability

$$w_i(\sigma_i) = \frac{\alpha}{2} \left\{ 1 - \sigma_i \tanh\left[\frac{1}{k_{\rm B}T} \left(-J\sum_{\langle ij\rangle} \sigma_j + B\right)\right] \right\}.$$
 (30)

It should be noted that the numerator and denominator in expression (29) can be factorized, and similar transformations can be taken on individual factors. This gives a new



Figure 15. Magnetic structure on a 96 \times 96 rhombic supercell during relaxation at 5 K in a magnetic field of 1.2 T (a, b) and 2.4 T (c, d) for times 125 s (a, b) and 1250 s (b, d), respectively [134].

expression

$$w_i(\sigma_i) = \frac{\alpha}{2} \left(1 - \sigma_i \tanh \frac{B}{k_{\rm B}T} \right) \prod_{\langle ij \rangle} \left[1 - \sigma_i \sigma_j \tanh \left(-\frac{J}{k_{\rm B}T} \right) \right],$$
(31)

satisfying formula (29).

The stochastic dynamics of Ising systems is simulated using both forms of the function $w_i(\sigma_i)$. They correspond to the so-called hard (30) and soft (31) dynamics [132, 133]. Original Glauber expression (27) describes the soft dynamics of the chain. Possible variants are not exhausted by expressions (30) and (31). If strong interactions J_0 exist in the system, as for example, along Co₂O₆ chains in Ca₃Co₂O₆, as do weak ones, for example, interchain interactions J_1 , they can also be factorized in exponents of expression (29) to obtain

$$w_{i}(\sigma_{i}) = \frac{\alpha}{2} \left\{ 1 - \sigma_{i} \tanh\left[\frac{1}{k_{B}T}\left(-J_{1}\sum_{\langle ij \rangle}\sigma_{j} + B\right)\right] \right\}$$
$$\times \prod_{\langle \langle ij \rangle \rangle} \left[1 - \sigma_{i}\sigma_{j} \tanh\left(-\frac{J_{0}}{k_{B}T}\right)\right]. \tag{32}$$

Here, $\langle \rangle$ and $\langle \langle \rangle \rangle$ denote summation over nearest-neighbor pairs with weak and strong interactions, respectively.

All the above expressions for the spin-flip probability lead the nonequilibrium Ising system in the process of evolution to the Gibbs distribution, but only expression (30) has a clear physical meaning. This expression describes the stochastic dynamics of an isolated spin in the effective field $-J\sum_{\langle ij \rangle} \sigma_j + B$. For this reason, we used below in all numerical calculations the hard stochastic dynamics described by expression (30). The discussion of the influence of the form of the function $w_i(\sigma_i)$ on the results of simulating the dynamics is presented in Refs [132, 133].

4.3 Two-dimensional simulation in a rigid chain model

The analytical model of rigid chains presented in Section 3.1 does not contain the spin dynamics in the explicit form: according to condition (5), the change in the sign of the effective field causes an instantaneous spin flip. At the same time, as discussed above, the $Ca_3Co_2O_6$ magnetization curves demonstrate a strong dependence on the rate of magnetic field change. The Glauber theory opens up the possibility of studying the stochastic dynamics of an Ising system.

The 2D Glauber dynamics calculations were performed numerically on rhombic $n \times n$ supercells (Fig. 15) with periodic boundary conditions [134, 135]. Chains were assumed rigid, i.e., they had two possible magnetization states [Hamiltonian (1) on a triangular lattice]. The spin-flip probability in a chain was calculated by the hard dynamics expression (30). Test calculations with 18×18 , 36×36 , 48×48 , 96×96 , and 192×192 cells demonstrated that n = 96 provides a good convergence, repeatability of calculations, and low noise of the total magnetization. Therefore, the 96×96 cell was used in all 2D calculations presented below. We emphasize that it is desirable to select the cell size to be at least a multiple of six to eliminate the influence of boundary conditions on ordered structures with a period equal to two (stripe phase) or three (PDA phase) intersite distances.

The rhombic supercell (see Fig. 15) is mapped onto a square C'_{ij} matrix with elements equal to ± 1 . Thus, this matrix determines the state of the supercell at each instant of time. Summation over interacting nearest neighbors of an element in expression (30) can be performed either directly or by applying the known standard convolution of the C matrix with the nearest-neighbor interaction matrix N:

$$A_{i,j} = \sum_{k,l=1}^{3} \mathbf{C}_{i+k-2,j+l-2} \,\mathbf{N}_{k,l} \,, \tag{33}$$

where i, j = 2...(n + 1), and *n* is the linear size of the supercell. To perform the convolution, the C' matrix should



Figure 16. Magnetization curves in a growing magnetic field: (a) at T = 4 K and different magnetic field growth rates, and (b) at different temperatures for the magnetic field growth rate equal to 0.1 T min⁻¹ [134].

be expanded to the $(n+2) \times (n+2)$ C matrix based on periodic boundary conditions.⁵ The interaction matrix for a triangular lattice has the form

$$\mathbf{N} = \begin{bmatrix} 0 & 1 & 1 \\ 1 & 0 & 1 \\ 1 & 1 & 0 \end{bmatrix},\tag{34}$$

where elements with which the interaction occurs correspond to 1.

Test calculations revealed that the calculation of the hyperbolic tangent [in expression (30)] takes up most of the time spent for calculating the dynamics. The number of such operations can be reduced. Altogether, 26 configurations of the given spin and nearest neighbors exist. Therefore, 26 possible values of the hyperbolic tangent can be calculated preliminarily and then selected from a table, depending on the configuration for the given site. This procedure accelerates the calculation on a 96 \times 96 cell no less than threefold times.

The PDA structure or a random spin distribution was taken as the initial structure for simulations. Then, the structure relaxation proceeded at the given temperature without a magnetic field. The typical number of calculation steps in time was about 2×10^6 .



Figure 17. Magnetization relaxation for 2D simulations in different magnetic fields at T = 5 K (a), and 8 K (b) [135].

Figure 16 depicts the $M(\mu_0 H)$ curves obtained at different temperatures for different growth rates of the magnetic field [134]. Good agreement between the calculated curves and experimental data [38] is achieved at $\alpha = 0.21 \text{ s}^{-1}$. It is readily seen that equidistant steps in the magnetization curve disappear both upon decreasing the magnetic field growth rate (Fig. 16a) and with increasing temperature (Fig. 16b). The calculated magnetization curves reproduce even rather fine details of experimental magnetization curves, such as the overlap of the ascending and descending branches [38, 134]. It is interesting that the 2D simulation describes even the transition from the low-temperature to the high-temperature (PDA) phase although, as shown in Section 3.2, this transition is related to the disordering of chains. The interpretation of the transition in terms of the 2D model is similar to that in the Mekata theory [57] and reduces to describing the increase in entropy during the disordering of one of the 2D sublattices in the PDA phase.

The results obtained indicate the existence of two characteristic times. The first, on the order of 1 s (α^{-1}) , is related to the chain flip process (a single spin in the 2D model). The second time is rather large, on the order of a few hours.

Yet another experimental result, which required a theoretical explanation, is the magnetization relaxation in $Ca_3Co_2O_6$ in a permanent magnetic field [38]. The results of 2D simulations of the relaxation process with the same parameters as for magnetization curves are presented in Fig. 17. One can see that the calculated curves reproduce the nonexponential relaxation of the magnetic moment and the

⁵ The copies of the first and last columns of the C' matrix become, respectively, the last and first columns of the C matrix. The first and last rows of the C' matrix are copied similarly.

change in the relaxation sign in a magnetic field above 2.4 T. In addition, the characteristic time scale on the order of 10^3 s appears again (at T = 5 K), which considerably exceeds α^{-1} .

The nature of two additional steps on the 1/3 plateau in magnetization curves and of the slow dynamics of the magnetic moment is illustrated by the evolution of the magnetic structure of the supercell in an alternating magnetic field [135] (see Fig. 15). After magnetic field switching, the initial state undergoes the transition to the ferrimagnetic state. Here, it is important that the ferrimagnetic state on a triangular lattice is triply degenerate (the open circles in Fig. 3a can belong to one of the three sublattices). Because a new phase emerges from a few nucleation centers, large-scale formations appear—domains of the ferrimagnetic phase, which are clearly seen in Fig. 15. Steps in magnetization curves are related namely to the domain structure, while the domainless ferrimagnetic state gives rise to the 1/3 plateau without additional steps.

The domain structure in the ferrimagnetic phase explains many phenomena observed in the Ca₃Co₂O₆ compound [134-137]. The slow relaxation with long characteristic times considerably exceeding α^{-1} is related to slow motion (creep) of domain walls [134, 135]. Domains grow with time, as shown in Fig. 15, which leads to a decrease in the total length of boundaries and to a decrease in the height of steps. Notice also that there are two types of domain walls corresponding to two additional steps in magnetization curves, with the first additional step reducing the magnetization value with respect to the 1/3 plateau, while the second step increases it. As a result, the relaxation of these two types of domain boundaries has different signs. In the limit of very long times or a very slowly varying magnetic field, the system passes to the single-domain state. Thus, the static magnetization curve should have only the 1/3 plateau without additional steps.

It also follows from this that the magnetization curves of nanostructured $Ca_3Co_2O_6$ samples should tend to the 1/3-plateau curve without additional steps, because a singledomain state should be rapidly established on a small cluster. This conclusion requires, however, additional verification, because cluster boundaries can strongly affect the magnetic structure.

The 2D simulation of a response to a variable magnetic field, performed in Ref. [136], revealed a significant disadvantage of the standard Glauber model—the absence of the temperature dependence of α . The experimental dependence of the complex susceptibility fits the appropriate theoretical dependence well upon introducing the exponential temperature dependence of α as in formula (25) [136]. Here, we should recall that the spin flip in the 2D model corresponds in reality to the chain remagnetization.

Assume that the effective field of the chain is defined as follows:

$$-J\sum_{\langle ij
angle}\sigma_j+B<0\,;$$

then the spin-flip probability is $w_i(\sigma_i) > \alpha/2$. Let the spin flip originates from the end element of the chain. The effective field for this element contains a term connected with a nearest neighbor along the chain, which produces a potential barrier for the spin flip on the end element and, hence, the entire chain as a whole. It follows from these considerations that, by introducing the temperature dependence of α into the 2D model, we should set $\Delta_a \approx |J_0|$ in formula (25), where J_0 is the nearest-neighbor interaction in the chain. Thus, the appearance of the dependence $\alpha(T)$ brings the 2D model beyond the scope of a purely two-dimensional model.

4.4 Three-dimensional simulation

The 2D model has two substantial disadvantages. First, although it correctly estimates the transition temperature to the high-temperature phase, this model cannot be used in the high-temperature region, where the disordering of chains is substantial. Second, the chain magnetization flip is considered an instantaneous process proceeding with some probability.

The generalization of a Glauber chain lattice to the real three-dimensional structure of CoII ions in $Ca_3Co_2O_6$ was performed in papers [135, 138]. Following the concept of the hard Glauber dynamics, the spin-flip probability for the *i*th spin in the chain per unit time can be written down as [138]

$$W(\sigma_i) = \frac{\alpha}{2} \left[1 - \sigma_i \tanh\left\{ -\frac{J_0}{k_{\rm B}T} \sum_{\langle ij \rangle} \sigma_j - \frac{J_1}{k_{\rm B}T} \sum_{\langle \langle ik \rangle \rangle} \sigma_k + \frac{B}{k_{\rm B}T} \right\} \right],\tag{35}$$

where $J_0 = -20$ K and $J_1 = 1.6$ K are parameters of the intraand interchain interactions, respectively, $\langle \rangle$ and $\langle \langle \rangle \rangle$ denote summation over lattice sites nearest the *i*th site along the chain and in adjacent chains (along solid straight lines in Fig. 1b), respectively, and $\alpha \approx 20 \text{ s}^{-1}$. The parameter J_0 of the intrachain FM interaction was obtained from theoretical and experimental estimates (see Section 2.2), while J_1 is determined by the step width in the magnetization curve ($\Delta B = 1.2$ T for Ca₃Co₂O₆).

Here, a number of difficulties appearing in 3D simulations should be pointed out. First, it is necessary to cover at least two time scales. On the one hand, the time step should be much shorter than the chain-flip time. On the other hand, the total calculation time should be longer than the characteristic slow relaxation times. This leads to an increase in the number of steps in time. Second, as pointed out above, the topology of the magnetic sublattice in $Ca_3Co_2O_6$ is extremely complex. In 3D Monte-Carlo simulations [138], the topology was simplified by reducing it to a stack of plane triangular layers. The mathematical description of interactions between the sites of the real $Ca_3Co_2O_6$ magnetic sublattice used in papers [135, 138] is presented in the Appendix.

3D simulations were performed by the example of a $24 \times 24 \times 36$ rhombic supercell. Boundary conditions in the *ab* plane were periodic, and chains had a finite length along the *c*-axis. Notice that the finite length of chains has a fundamental meaning. The free ends of chains were produced with the help of a layer filled with zero elements. Then, as in the 2D case, all possible values of the flip probability were preliminarily calculated and tabulated. The number of these values calculated from expression (35) in the 3D model taking the finite length of chains into account is 195. Later on, depending on the configuration of the central spin and its nearest neighbors, the value of the flip probability was selected from the table compiled.

The start state for the three-dimensional calculation was a random spin structure. Then, the relaxation of this structure proceeded at the given temperature without a magnetic field, similarly to the 2D model. The examples of initial structures (shown are averaged magnetizations over chains) at 5 K and 15 K and vertical cross sections of a cluster along the *c*-axis



Figure 18. (See in color online). Magnetic structure of a 3D $24 \times 24 \times 36$ supercell: magnetization averaged over chains at 5 K (a) and 15 K (b), and vertical cross sections of a cluster along the *c*-axis in the absence of a magnetic field [138].



Figure 19. Magnetization curves in the 3D model in the growing magnetic field (a) at T = 8 K and different magnetic field growth rates, and (b) at different temperatures and the magnetic field growth rate of 0.1 T min⁻¹ [138].

and over the middle line of a rhomb are presented in Fig. 18. Notice that at a low temperature (Fig. 18a), the magnetic structure virtually reproduces the results of 2D simulations [134, 135]. The vertical cross section of the cluster shows that all the chains are completely ordered. At a high temperature (Fig. 18b), a structure close to a PDA one appears, and chains become substantially disordered.

Figure 19 displays the M(B) dependences of the mean magnetization on the magnetic field intensity calculated at different temperatures for a magnetic field growth rate on the order of 0.1 T min⁻¹ (Fig. 19b) and for different rates at 8 K (Fig. 19a). It should be noted that the second and third steps in the magnetization curve disappear with increasing temperature or decreasing magnetic field growth rate. The form of the magnetization curve as a whole is consistent with the results of 2D simulations and experimental data. The



Figure 20. Magnetization relaxation in the 3D model in a $96 \times 96 \times 36$ supercell in Ca₃Co₂O₆ in different magnetic fields in the ascending magnetization curve at T = 8 K [135].

observed transition from the low-temperature to hightemperature phase in 3D simulations is related to the disordering of chains.

The magnetization relaxation in the 3D model demonstrates not only the change in sign, but also nonmonotonic relaxation at B = 2.4 T (Fig. 20), which is explained by the fact that the relaxation time of the two types of domain boundaries proves to be different. This effect was observed in experiments [38] and is not reproduced in the 2D model.

Additional materials on the numerical 2D and 3D simulations of the Glauber magnetization dynamics can be found at http://sarfti.ru/HMFLab/ssph.html.

5. Monte Carlo simulation

5.1 Metropolis and Wang–Landau algorithms

It is useful to begin the discussion of the results concerning simulation of the static (thermodynamic) magnetization curve with a brief comparison of two Monte Carlo computational algorithms. During integration over the phase space in the classical Monte Carlo method, it is necessary to take into account a great number of calculation points with small weight coefficients, which strongly increases the calculation time. To reduce the latter, the Metropolis algorithm was developed [139].

Mean values are successively calculated in the Metropolis algorithm in the following way: the state of a system is randomly changed and the energies of the system before and after the change are compared. If the given change reduces the system's energy, the new state is accepted. Otherwise, the new state is accepted with the probability equal to

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 $\exp\left(-\Delta E/k_{\rm B}T\right)$, namely

$$p(\text{old} \to \text{new}) = \min\left\{\exp\left(-\frac{\Delta E}{k_{\text{B}}T}\right), 1\right\}.$$
 (36)

If the new state is not accepted, we return to the previous state. The mean value of the characteristic of interest to us is found in this algorithm as the arithmetic mean of the values of the given characteristic obtained over the entire sequence of states:

$$F = \frac{1}{N} \sum_{j=1}^{N} F_j \,, \tag{37}$$

where F_j denotes this characteristic at the *j*th iteration. The mean value determined in such a way is also the mean taken over the equilibrium distribution [139].

It was found that the algorithm described above can lead to the 'sticking' of the system in a local minimum of the system. For this reason, the Wang-Landau algorithm was proposed for systems with many local minima (for example, frustrated magnetic systems) [140]. This algorithm is based on the following observation: if during a random walk in the energy space the probability of visiting an energy level is inversely proportional to the density of states at this energy, the visit histogram will be flat. For example, the degenerate ground state of Hamiltonian (1) on a triangular lattice gives an enormous density of states at the ground state energy. Then, the probability of visiting such states should be reduced proportionally to the density of states, which is not known beforehand. This is achieved by systematically modifying the initial density of states to obtain a flat histogram on the given energy interval. The density of states is changed at each random walk step.

The density of states of a magnetic system is the function g(E, M) of energy and magnetization. Before calculations, the energy region is divided into individual intervals [140]. At the very beginning of the random walk, the density of states is not known *a priori*, and therefore all the densities of states are assumed equal: g(E, M) = 1. Then, we start a random walk in the energy region, performing random spin flips and changing the state of the system as a whole. If E_1 and E_2 are the energies before and after a change of the system's state, respectively, then the probability of accepting the new state is given by the expression

$$p(E_1, M_1 \to E_2, M_2) = \min\left\{\frac{g(E_1, M_1)}{g(E_2, M_2)}, 1\right\}.$$
 (38)

Each time after visiting a certain state, the corresponding density of states is multiplied by a factor f > 1, i.e., $g(E, M) \rightarrow g(E, M) f$. If the new state is rejected, the preceding density of states is multiplied by the same factor f. In work [140], the initial factor $f = f_0 = e$ was used, which allows one to rapidly reach all the energy levels even for very large systems. Then, we continue the random walk in the energy space and change the densities of states until the visit histogram F(E, M) becomes 'flat'. At this stage, we can say that the density of states converged to its true value with an accuracy proportional to $\ln f$. Therefore, we reduce the factor $f_1 = \sqrt{f_0}$ by a certain rule (any function monotonically decreasing to 1 can be utilized) and set the histogram values equal to zero: F(E, M) = 0. We then start the following random walk cycle with a new factor $f = f_1$ until the histogram again becomes flat, and after that the factor is changed again: $f_{i+1} = \sqrt{f_i}$. The calculation is assumed converged if the modifying factor becomes smaller than a certain preliminarily specified value (for example, $f_{\text{fin}} =$ $\exp(10^{-8}) \approx 1.00000001$). Notice that an absolutely flat histogram cannot be obtained, and the term 'flat histogram' means that the values of F(E, M) for all possible *E* and *M* are no less than 80% of the mean value for the histogram.

After calculating the true value of the density of states, we can obtain the thermodynamic and magnetic quantities of the system at any temperatures in any magnetic fields. In the case of a magnetic system, the density of states g(E, M) is the function of energy and magnetization. Then, for example, the internal energy of the system has the form [140, 143]

$$U(T,H) = \frac{\sum_{E,M} \hat{H}g(E,M) \exp(-\hat{H}/k_{\rm B}T)}{\sum_{E,M} g(E,M) \exp(-\hat{H}/k_{\rm B}T)},$$
 (39)

and the magnetization as a function of temperature and magnetic field takes the form

$$M(T,H) = \frac{\sum_{E,M} M g(E,M) \exp(-\hat{H}/k_{\rm B}T)}{\sum_{E,M} g(E,M) \exp(-\hat{H}/k_{\rm B}T)} .$$
 (40)

5.2 Static magnetization curves

The first 2D and 3D Monte Carlo calculations of static magnetization curves for the $Ca_3Co_2O_6$ compound were performed using the Metropolis algorithm [141, 142]. Magnetization curves demonstrated the formation of domains which were similar to those discussed above, the 1/3 plateau, and two small additional steps. As the temperature increased, two additional steps disappeared and the 1/3 plateau typical for the PDA phase was observed, i.e., a transition from the low-temperature to high-temperature phase had occurred.

The introduction of a random scatter in the nearestneighbor interactions into Hamiltonian (1), for example, in the form $J \rightarrow J(1 + \Delta_r)$, where Δ_r is a small random number, increased the height of the steps. The random scatter in the nearest-neighbor interactions imitated the emergence of defects and disordering. The 2D simulation was performed in the rigid chain model on a rhombic cell, similar to that considered in Section 4.3. The 3D model contained a simplified description of the Ca₃Co₂O₆ magnetic sublattice: planar two-dimensional triangular layers without helicoidal paths.

In the 3D Monte Carlo calculations, as in the Glauber dynamics, the transition to the high-temperature phase was accompanied by the disordering of part of the chains. However, these results could not completely explain experimental magnetization curves, because, as pointed out above, the height of steps changes in experiments, depending on the rate of magnetization change in one and the same sample [38].

The Metropolis and Wang–Landau algorithms applied to the calculation of the static magnetization curve of Ca₃Co₂O₆ were carefully compared in Ref. [143]. Simulations were performed for a 2D 12 × 12 cluster with periodic boundary conditions. The results of simulations are presented in Fig. 21. The magnetization curves and dependences of the internal energy at high temperature (T = 10 K) coincided, whereas a qualitative difference was revealed at low temperature (T = 2 K). The Wang–Landau algorithm gives a flat 1/3 plateau corresponding to the single-domain state, unlike the



Figure 21. Dependences of (a, b) the relative magnetization and (c, d) the internal energy in the AFM Ising model on a triangular lattice on the magnetic field according to the Wang–Landau (solid lines) and Metropolis (circles) algorithms at different temperatures [137].

four steps obtained with the help of the Metropolis algorithm. A comparison of internal energies at low temperature shows that the Wang–Landau algorithm results in the lower-energy state.

Thus, two important conclusions follow from paper [143]: (i) The Monte Carlo simulation of the static state of a strongly frustrated magnetic system should be performed applying the Wang–Landau algorithm, and (ii) static magnetization curves of $Ca_3Co_2O_6$ have two steps and the 1/3 plateau both at high and at low temperatures. These conclusions are consistent with the simulated results of the Glauber dynamics.

To avoid qualitative errors, almost all papers on simulation of static magnetization curves were performed after the publication of paper [143] using the Wang–Landau algorithm [137, 144]. Notably, the influence of two types of disordering was investigated: vacancy formation [144], and random variations in the nearest-neighbor interactions [143]. It was shown that, in both cases, the four magnetization steps observed in experiments were not reproduced in model magnetization curves: when vacancies were introduced, a great number of small steps appeared, whereas in the case of random variations in the nearest-neighbor interactions, the magnetization curve became smeared without the formation of news steps. Thus, the fact that two additional steps are related to the dynamic effect is again confirmed.

6. Conclusions

We have shown that the diversity of low-temperature phases in frustrated Ising chain lattices is related to the partial removal of degeneracy due to very weak next-to-nearestneighbor interactions or a weak anisotropy of nearestneighbor interactions. The three groups of frustrated compounds discussed in the review represent the three most characteristic types of low-temperature magnetic structures on an undistorted triangular lattice: $Ca_3Co_2O_6$ (only AFM nearest-neighbor interactions), $CsCoCl_3$ and some others (FM next-to-nearest-neighbor interactions), and $Sr_5Rh_4O_{12}$ (AFM next-to-nearest-neighbor interactions). The transition to the high-temperature PDA phase is universal for a triangular lattice and is determined by the entropy of disordered chains.

In a more general case, the following rule is valid [117]: in a zero external magnetic field, of all the 2D configurations of the degenerate ground state at high temperatures, only those in which the number of chains with a zero effective field is maximal remain. It is these chains that are disordered first of all.

The stochastic Glauber dynamics well describes the nonequilibrium evolution of the $Ca_3Co_2O_6$ magnetization in a broad temperature range on different time scales. The static magnetization curve of this compound is described by the Wang–Landau algorithm and contains two steps with the 1/3 plateau. Two additional steps appear due to the nonequilibrium domain structure in the ferrimagnetic phase. The very slow magnetization dynamics occurs due to the slow motion of domain walls.

In conclusion, we would like to emphasize some unsolved problems concerning the $Ca_3Co_2O_6$ magnetic structure. It has been reliably established that an incommensurate longitudinal large-period spin density wave appears in Co_2O_6 chains. Nevertheless, in our opinion, the theoretical description of this phenomenon is still incomplete, which was discussed in Section 2.3.

Another interesting problem is the traces of magnetization steps in strong magnetic fields (4.8, 6.0, and 7.2 T), which are observed at very low temperatures. To date, even a qualitative explanation of this phenomenon is absent. It is possible that part of the CoI ions in some small regions of a sample, for example, near defects, reside in the magnetic state (S = 2). Then, the magnetic moment of the chain doubles, and a step in the magnetic field between magnetization steps should also be doubled.

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7. Appendix. Magnetic interactions in Ca₃Co₂O₆

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The spin state of CoII ions in a real Ca₃Co₂O₆ lattice is described by the three-dimensional $i \times j \times k$ array, where *i* and *j* indices describe coordinates of chains in a plane, similarly to the rhombic 2D cell, while the third index describes the coordinate along the crystallographic *c*-axis. Chains in three sublattices of Ca₃Co₂O₆ are displaced with respect to each other along the *c*-axis by 2/3 of the unit cell size. The real coordinates of magnetic ions in the lattice are determined by indices *i*, *j*, and *k* as $x_{ijk} = \cos(\pi/3) i + j$, $y_{ijk} = \sin(\pi/3) i$, and $z_{ijk} = 1/3 \mod_3 [2(i-j)] + k$, where mod₃ is the function of the residue of division by 3.

We can introduce the interaction matrix which determines the indices of sites in adjacent chains interacting with the given site along solid straight lines in Fig. 1b:

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$$\mathbf{N}' = \begin{vmatrix} 0 & -1 & 1 \\ 1 & 0 & 1 \\ -1 & 1 & 1 \\ 1 & -1 & -1 \\ 0 & 1 & -1 \\ -1 & 0 & -1 \end{vmatrix} .$$
(A.1)

Each row of the matrix is related to the nearest interacting neighbor; in the first column, Δi is the displacement inside a supercell over the index *i* with respect to the chosen site; in the second column, Δj is the similar displacement over the index *j*, and in the third column, *z* determines only the direction of displacement along the crystallographic *c*-axis, while the displacement is determined from the expression

$$h_0 = \frac{1}{3} \mod_3 \left[2(i-j) \right],$$
 (A.2)

where *i* and *j* are the moving indices of the chain under study. The interaction occurs with elements of other chains, which differ in height by 2/3 of the layer height. Therefore, the third index of the site with which the interaction occurs will be given by the expression

$$k' = \text{fix}\left[k + \frac{2}{3}z + h_0\right],$$
 (A.3)

where k is the third index of the element considered, z is a value from the N' matrix, and the function fix (x) determines the round-off of x towards the $-\infty$ side. Thus, interchain

bonds appear for $k - k' = 0, \pm 1$. The merit of this procedure is its universality for all sublattices. A model for competing bonds (dashed straight lines in Fig. 1b) can be constructed similarly. The interaction with nearest neighbors along the chain does not cause difficulties.

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