Reactivity of metal-containing monomers 70.* Preparation and magnetic properties of metal-containing nanocomposites

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Nanocomposites containing magnetically active nanoparticles stabilized by the carboncontaining matrix formed in parallel were obtained by the polymerization—destruction synthesis. The composition, structure, and magnetic properties of nanocomposites synthesized by the thermal decomposition of unsaturated metal carboxylates and transition metal (Co^{II}, Ni^{II}, Fe^{III}) acrylamide complexes were studied by powder X-ray diffraction, scanning and transmission electron microscopy, and Mössbauer spectroscopy. The key macro stages and kinetic features of thermolysis of the metal-containing monomers were identified. The variation of the conditions of thermal transformations allows one to control the magnetic properties of nanocomposites from ferromagnetic to superparamagnetic behavior.

Key words: metal nanoparticles, magnetic properties, metal-containing nanocomposites, exchange anisotropy.

Magnetic and semiconductor nanoparticles are attractive investigation objects because the major contribution to the formation of their physicochemical characteristics is made the quantum-size effect. The considerable interest in the d-element nanoparticles is caused by their specific magnetic properties² and the possible design of high density magnetic recording media.³ Magnetic particles are widely used in biomedicine, 4-6 and the role of iron (magnetite and maghemite) having high biocompatibility is especially important. Iron- and cobalt-containing particles have high coercive force and magnetic susceptibility values; for example, saturation magnetization (σ_s , M_s) of the magnetite Fe₃O₄ is 92 emu g⁻¹ and that of γ -Fe₂O₃ is 74 emu g⁻¹,⁷ and the coercive force for the anisotropic nanoparticles of the latter varies from 200 to 400 Oe.8 However, a considerable drawback is the tendency of nanoparticles for aggregation and oxidation, which changes their magnetic properties. Therefore, development of efficient methods for stabilization of magnetic nanoparticles and approaches to control of their composition and structure depending on the nature of the metal-containing monomer is a topical task, and this is the subject of the present study.

Experimental

Unsaturated metal carboxylates and acrylamide complexes of Co^{II}, Ni^{II}, and Fe^{III} nitrates were synthesized and characterized as described previously.^{9,10} All of the obtained metal-containing monomers were solid powders.

Cobalt(11) acrylate. Found (%): C, 32.6; H, 3.7; Co, 27.5. $(CH_2=CHOCO)_2Co \cdot H_2O$. Calculated (%): C, 32.9; H, 3.6; Co, 26.9. IR (KBr pellet), v/cm⁻¹: 1640 (C=C); 1065 (=CH-C); 1360, 1560 (COO); 280 (M-O).

Nickel(n) acrylate. Found (%): C, 32.40; H, 3.7; Ni, 26.7. (CH₂=CHOCO)₂Ni · H₂O. Calculated (%): C, 32.9; H, 3.6; Ni, 26.9. IR (KBr pellet), v/cm^{-1} : 1640 (C=C); 1065 (=CH-C); 1360, 1560 (COO); 290 (M-O).

Iron(III) acrylate. Found (%): C, 31.7; H, 3.7; Fe, 24.6. [Fe₃O(CH₂=CHOCO)₆ \cdot 3H₂O]OH. Calculated (%): C, 31.9; H, 3.1; Fe, 24.5. IR (KBr pellet), v/cm⁻¹: 1635 (C=C); 1370, 1575 (COO); 525 (M-O).

Cobalt maleate(II). Found (%): C, 21.5; H, 2.2; Co, 28.5. $(OCOCH=CHOCO)_2Co \cdot 2H_2O$. Calculated (%): C, 23.0; H, 2.9; Co, 28.2. IR (KBr pellet), v/cm⁻¹: 1638 (C=C); 1366, 1435 (COO); 280 (M-O).

Iron(III) nitrate acrylamide complex. Found (%): C, 27.4; H, 3.7; Fe, 10.6; N, 18.6. $Fe(NO_3)_3(CH_2=CHCONH_2)_4$. Calculated (%): C, 27.0; H, 4.7; N, 16.5; Fe, 10.9. IR (KBr pellet), v/cm⁻¹: 3190, 3320 (NH); 1660 (CO); 1385 (NO_3); 280 (M-O).

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Cobalt(11) nitrate acrylamide complex. Found (%): C, 29.5; H, 4.9; Co, 11.8; N, 15.6. $Co(NO_3)_2(CH_2=CHCONH_2)_4$ ·2H₂O. Calculated (%): C, 28.6; H, 5.0; Co, 11.7, N, 16.7. IR (KBr pellet), v/cm⁻¹: 3190, 3290 (NH); 1665 (CO); 1385 (NO₃); 354 (M-O).

Nickel(II) nitrate acrylamide complex. Found (%): C, 29.7; H, 5.2; N, 15.2; Ni, 11.1. Ni(NO₃)₂(CH₂=CHCONH₂)₄· ·2H₂O. Calculated (%): C, 28.6; H, 5.0; N, 16.7; Ni, 11.7. IR (KBr pellet), v/cm⁻¹: 3195, 3290 (NH); 1665 (CO); 1385 (NO₃); 354 (M-O).

Nanocomposites were prepared by controlled thermolysis of metal-containing monomers in the isothermal mode at 643-1073 K in a self-generated atmosphere by a reported procedure.¹¹ The thermolysis gave finely dispersed dark-brown or black powders with the specific surface area (the thermolysis temperature, K, is in parentheses) $S_{sp} = 36.7$ (653), 29.5 (633), 15 (643), and 30.0 m² g⁻¹ (643) for the Co^{II}, Ni^{II}, and Fe^{III} acrylates and Co^{II} maleate, respectively. According to elemental analysis data, for example, the product of thermolysis of the acrylamide complex of Co^{II} nitrate at 673 K has the following composition (wt %): C, 37.0; H, 2.6; N, 8.7; the residue is 48.8 (in relation to Co 38.4%), the matrix after removal of the metal: C, 58.6; H, 3.2; N, 12.5. According to the gravimetric analysis, the metal-containing component accounts for 39.6 wt %, while the matrix is 60.4 wt. %. The kinetics of the isothermal transformations of metal-containing monomers (MCM) was studied based on gas evolution using a membrane zero manometer. Thermolysis was carried out under static isothermal conditions at temperatures T_{exp} in self-generated atmosphere (the samples were pre-evacuated at room temperature for 30 min) under dynamic vacuum conditions and under argon. The gaseous and condensed products of the thermal transformation were studied by IR spectroscopy in the 400–4000 cm⁻¹ range (Specord 75 IR spectrophotometer) and analyzed by mass spectrometry using an MS-3701 quadrupole mass spectrometer.

Powder X-ray diffraction analysis was carried out on DRON UM-2 and Philips PW 1050 diffractometers using Cu-Ka radiation ($\lambda = 1.5418$ Å). Magnetic measurements of metal—polymer nanocomposites were performed by means of an Oxford Instruments Vibrating Sample Magnetometer (VSM). The hysteresis loops were recorded in the temperature range of 5-300 K. The temperature dependences of the magnetization were measured in the same temperature range in low fields $(2 \cdot 10^{-3} \text{ T})$ using field cooling (FC) and zero-field cooling (ZFC) modes and at 0.6 T and 5–300 K. The electron microscopic examinations of metal-containing nanocomposites were performed using a Hitachi 3500 scanning electron microscope (15 kV), a JEOL transmission electron microscope with accelerating voltage of 100 kV, and JEM 3010 high-resolution electron microscope (300 kV). The particle geometric size distribution was determined from a sample of 50-100 measurements using photomicrographs.

Results and Discussion

Preparation, composition, and microstructure of magnetically active nanocomposites. A study of the kinetics and mechanisms of thermal transformations of MCM showed that their thermolysis is a multistage process that includes three key macro stages: dehydration, polymerization of the dehydrated monomer, and decarboxylation of the metal-containing groups of the resulting polymer to give a metal-containing phase.^{12,13} According to thermal analysis data, dehydration of the monomeric crystal hydrates, for example, acrylic acid salts, occurs at $T_{exp} =$ = 353-487 K ([Fe₃O(CH₂=CHOCO)₆·3H₂O]OH, Fe₃OAcr₆), 413–453 K (Co(CH₂=CHOCO)₂·H₂O, $CoAcr_2$), 373–473 K (Ni(CH₂=CHOCO)₂·H₂O, NiAcr₂), that of the acrylamide and complex [Co(CH₂=CHCONH₂)₄(H₂O)₂](NO₃)₂ (CoAAm) occurs at 328-362 K. The increase in the temperature of the dehydrated monomer to $T_{exp} = 473 - 573$ K induces solidphase polymerization. In this temperature region, in addition to the insignificant weight loss by the sample (<10 wt. %), slight gas evolution occurs. In the case of metal acrylates, the major gas components are CO2 and H2C=CHCOOH and HOOCCH=CHCOOH vapors, which condense at room temperature on the reactor walls. Characteristic temperatures of polymerization are ~543 K (CoAcr₂), ~563 K (NiAcr₂), ~518 K (Fe₃OAcr₆), and 488–518 K (Co[OOCCH=CHCOO] · 2H₂O, CoMal). The polymerization is accompanied by changes in the IR absorption spectra of the dehydrated monomer, in particular, a decrease in the intensity of the C=C stretching band and convergence of the C=O stretching frequencies, giving rise to one broadened absorption band at 1540-1560 cm⁻¹. When $T_{exp} > 523$ K, thermally polymerized samples undergo intense gas evolution. The gas evolution rate $W = d\eta/dt$ decreases monotonically with an increase of the degree of conversion $\eta = \Delta \alpha_{\Sigma,t} / \Delta \alpha_{\Sigma,f}$, where $\Delta \alpha_{\Sigma,t} = \alpha_{\Sigma,t} - \alpha_{\Sigma,0}$, $\Delta \alpha_{\Sigma,f} = \alpha_{\Sigma,f} - \alpha_{\Sigma,0}, \alpha_{\Sigma,f}, \alpha_{\Sigma,t}, \text{ and } \alpha_{\Sigma,0} \text{ are the final, cur-}$ rent, and the initial numbers of moles of gas products, respectively, evolved per mole of the starting sample at room temperature. The gas evolution kinetics $\eta(\tau)$ is satisfactorily approximated in the general form (up to $\eta \le 0.95$) by the equation for two parallel reactions:⁹

$$\eta(\tau) = \eta_{1f} [1 - \exp(-k_1 \tau)] + (1 - \eta_{1f}) [1 - \exp(-k_2 \tau)], \quad (1)$$

where $\tau = t - t_0$ (t_0 is the sample heating time, $\eta_{1f} = \eta(\tau) \big|_{k_2 t \to 0, k_1 t \to \infty}$, k_1 and k_2 are the effective rate constants for the reactions. The parameters k_1 , k_2 , η_{1f} and $\Delta \alpha_{\Sigma,f}$ depend on the temperature of the thermolysis (T_{term}):

$$\eta_{1f}, \Delta \alpha_{\Sigma, f} = A \exp[-E_{a, \text{eff}}/(RT)], \qquad (2)$$

$$k_{\rm eff} = k_{0,\rm eff} \exp[-E_{a,\rm eff}/(RT)], \qquad (3)$$

where A and $k_{0,eff}$ are pre-exponential factors, $E_{a,eff}$ is the effective activation energy.

The initial gas evolution rate $W_{\tau=0} = W_0$ is

$$W_0 = \eta_{1t} k_1 + (1 - \eta_{1t}) k_2. \tag{4}$$

Equations (1) and (4) describe the gas evolution kinetics of NiAcr₂ and co-crystallized FeCoAcr, Fe₂CoAcr, and Fe₂NiAcr (Table 1).

Sample	Element analysis data of			$W_0 = k_{0,\text{eff}} \exp[-E_{a,\text{eff}}/(RT_{\text{term}})]$		
	the th	ermolysis j	products, wt. %	$k_{0,\text{eff}}/\text{s}^{-1}$	E _{a,eff} ∕kJ mol ^{−1}	
	С	Н	Metal-containing component			
CoAcr ₂	26.6	1.1	86.8	$3.0 \cdot 10^{14}$	238.3	
Fe ₃ OAcr ₆ (473–573 K)	29.6	1.9	67.1	$4.2 \cdot 10^{21}$	246.5	
Fe ₃ OAcr ₆ (573–643 K)	29.6	1.9	67.1	$1.3 \cdot 10^{6}$	127.5	
NiAcr ₂	27.6	1.1	83.7	$4.4 \cdot 10^{17}$	247.0	
FeCoAcr	_	_	_	$1.3 \cdot 10^{12}$	207.0	
Fe ₂ CoAcr	33.4	3.3	_	$1.1 \cdot 10^{12}$	205.0	
Fe ₂ NiAcr	_	_	_	$2.7 \cdot 10^{14}$	205.0	
CoMal	—	—	—	$1.1 \cdot 10^{6}$	125.4	

Table 1. Kinetic parameters of gas evolution during thermolysis of unsaturated metal carboxylates

When
$$k_2 \approx 0$$
, $\eta_{1f} \rightarrow 1$

 $\eta(\tau) \approx 1 - \exp(-k_1 \tau), \tag{5}$

 $W_0 \approx k_1. \tag{6}$

Equations (5) and (6) describe the gas evolution kinetics during thermal transformations of Co^{II} acrylate and maleate (Fig. 1).

Composition of gaseous and solid products of thermolysis of MCM. The major gaseous product formed in the transformations of the metal acrylates and maleates and their co-crystallizates is CO_2 . This was confirmed by IR spectroscopy and mass spectrometry. Carbon monoxide, hydrogen, and H_2O , $H_2C=CHCOOH$, and HOCOCH=CHCOOH vapors, which condense at room temperature, are formed in much smaller amount. Apart



Fig. 1. Gas evolution kinetics $\eta(t)$ (*a*) and semilogarithmic lines $(\log(1 - \eta) vs. t)$ (*b*) for the thermolysis of Co^{II} maleate (CoMal) in self-generated atmosphere at 653 (*1*), 643 (*2*), 633 (*3*), 623 (*4*), and 613 K (5).

from the above-listed gaseous products, CH4 was found in the case of CoAcr₂ (trace amount) and NiAcr₂ (amount comparable with CO₂). Electron microscopic examination of the final products of MCM thermolysis showed morphologically similar images, namely, electron-dense particles distributed in a less electron-dense matrix. The particles are nearly spherical, they have a narrow size distribution, and occur as both single structures and aggregates (Fig. 2). According to transmission electron microscopy data for the nanocomposite based on Fe^{III} acrylate obtained at 663 K (degree of conversion of 55.5%), two fractions of particles with average sizes of 12.3 and 22.1 nm are present. The average size of nanocrystallites calculated by the Scherrer equation is 13.5 nm. According to X-ray diffraction data for the thermolysis product of Co^{II} acrylate, the average particle size is 7 nm. The fraction of particles of 6.7 nm size is ~50%, the fractions of 12 and 21 nm particles correspond to 27 and 14 %, respectively, and the fraction of other particles is 8.4%. The major nanocrystalline phase of the product is CoO, which is formed at 643 K for a degree of conversion of 48.6%. Cobalt oxides or carbides of non-stoichiometric compositions are also formed in minor amounts. It is noteworthy that the average size of particles formed upon thermal transformations of unsaturated metal carboxylates is below that observed for the products of thermal transformations of saturated metal carboxylates (see Fig. 2, e). Nano-sized particles are located in the matrix rather uniformly, the average distance between the particle centers being 8–10 nm. The X-ray diffraction patterns of some obtained nanocomposites are presented in Fig. 3.

Magnetic properties of cobalt-containing nanocomposites. The magnetic characteristics of cobalt nanoparticles are known to be tightly connected with their structure, especially in core—shell structures.¹⁴ As shown previously,¹⁵ the nature of the unsaturated MCM ligand can con-



Fig. 2. Microstructure of the products of thermolysis (T = 773 K) of acrylamide Co^{II} (a,a') and Fe^{III} (b,b') complexes, Co^{II} acrylate (643 K) (c) and size distribution of the metal-containing particles in the nanocomposites based on them: (d) Co^{II} acrylate; (e) Fe^{III} acrylate (I), Fe(HCOO)₂·2H₂O (2), Co^{II} maleate (3).

siderably affect the phase composition and the structure of the thermolysis products being formed. Therefore, it was of interest to compare the magnetic properties of the products of thermolysis of various monomeric precursors, the Co^{II} acrylate (CoAcr₂) and acrylamide (CoAAm) complexes.

The dependences of the magnetization of the CoAcr₂ thermolysis product ($T_{exp} = 643$ K) on the magnetic field strength at 5 and 300 K at about ±1.1 T (916.6 kA m⁻¹) are shown in Fig. 4. As the temperature decreases, the hysteresis loop is broadened, and high-field magnetization increases. The coercive force is 0.08 and 0.03 T for temperatures of 5 and 300 K, respectively. The hysteresis loop at 300 K corresponds to the typical behavior of a material with preferable ferromagnetic order. At low temperature, the pattern of the magnetization curve considerably changes, and the susceptibility (d*M*/d*H*) in high fields increases almost 5-fold, indicating a considerable contribution of the antiferromagnetic CoO phase.

At room temperature, the product of CoAcr_2 thermolysis ($T_{\text{exp}} = 643$ K) has a saturation magnetization of

4.48 emu g⁻¹m while at 5 K, this value is 1.98 emu g⁻¹. Note that the latter value is much higher than that measured¹⁶ in the same fields for 560 nm CoO particles $(0.02 \text{ emu g}^{-1})$. Moreover, the M(T) curve shows no transition corresponding to the Neel temperature for CoO $(T_{\rm N} = 293 \text{ K})$, indicating additional ferri/ferromagnetic phases with a Curie point above the room temperature. The coercive force decreases from 0.0814 T at 5 K to 0.031 T at 300 K and has a characteristic maximum at ~25 K. The residual magnetization (M_r) is 2.325 (5 K) and 0.816 mT (300 K).

In ZFC measurements, a monotonic increase with temperature rise was observed, the broad gap between the FC and ZFC curves being indicative of the presence of fairly strong interactions between the particles; the negative ZFC-magnetization values are apparently caused by the effect of the diamagnetic organic matrix. Cobalt nanoparticles with a metal core and oxide CoO shell demonstrate so-called exchange anisotropy phenomenon,^{17,18} which is caused by exchange interaction at the boundary of two different ferro- and antiferromagnetically ordered systems. The exchange anisotropy is phenomenologically



Fig. 3. X-Ray diffraction patterns for the products of thermolysis of the acrylamide complexes formed at different thermolysis temperatures: CoAAm at 873 (*a*) at 1073 K (*b*), FeAAm at 773 (*c*) and 873 K (*d*), NiAAm at 773 (*e*) and 873 K (*f*).

manifested as the difference of the hysteresis curves obtained upon FC and ZFC measurements. As can be seen in Fig. 4, the ZFC hysteresis curve for the product of CoAcr₂ thermolysis is symmetric relative to the origin of coordinates, whereas the FC curve is non-symmetric (shifted to negative fields), *i.e.*, exchange interaction between the ferromagnetically ordered core spins and the antiferromagnetically ordered shell spins arises at the core/ shell interface. Note that the products of thermal transformations of unsaturated metal dicarboxylates (Co^{II} itaconate and acetylenedicarboxylate) show a ferromagnetic behavior at room temperature, and the hysteresis loops measured at 5 K in the FC mode with applied magnetic field strength of 5 T are also typical of systems with exchange anisotropy. For the products of thermolysis of Co^{II} acetylenedicarboxylate and itaconate, the exchange bias field $(H_{\rm eb})$ and the coercive force were $H_{\rm eb} = 1.8$ and 1.3 Oe, $H_{\rm c} = 2.5$ and = 2.0 kOe, respectively.

Unlike the products of thermolysis of carboxylate type MCM, nanocomposites based on acrylamide complexes



Fig. 4. Magnetization *vs.* magnetic field strength (*a*) and FC and ZFC hysteresis loops (*b*) measured at 5 K in a 1.1 T field for the CoAcr₂ thermolysis product.

contain highly dispersed metal phase or, at higher temperatures of thermolysis, metal carbide phase. For example, in the products of thermolysis of CoAAm at T_{exp} = = 673–873 K, the metal phase is β -Co with the lattice parameter $\alpha_1 = 3.54470$ Å and at 1073 K, this is CoC_x $(\alpha_2 = 3.61265 \text{ Å}).^{15}$ Therefore, it was of interest to track the magnetic properties of the products of thermal transformations of CoAAm obtained at temperatures of 673, 773, 873, and 1073 K. The hysteresis loops measured in the temperature range of 90-300 K attest to the ferromagnetic behavior of the thermolysis products (Fig. 5). However, the pattern of the curves, especially in the case of thermolysis product formed at 673 K, indicate the probable presence of a disordered interfacial layer with a skewed spin structure on the surface of magnetic particles. The sample does not show clear-cut superparamagnetic behavior at room temperature, although the average size of nanocrystallites is 7 nm, *i.e.*, they are smaller than the critical size needed for the superparamagnetism to be manifested.

The coercive force and the residual magnetization decrease as the temperature increases. For example, for the product of CoAAm thermolysis at 673 K, the H_c value changes from 0.068 T (68 kA m⁻¹) to 0.005 T (5 kA m⁻¹) and M_r varies from 13.6 to 2.2 emu g⁻¹ as the temperature is raised from 5 to 300 K. The saturation magnetization changes little with temperature. Similar trends are also characteristic of other products.

The magnetization in the FC measurements almost does not depend on the temperature; in the case of ZFC measurements, the magnetization increases with temperature rise; however, no maximum corresponding to the blocking temperature is present.

Comparative analysis of the magnetic characteristics of CoAAm nanocomposites obtained at different temper-

atures of thermolysis demonstrated that H_c , M_s , and M_r increase as the temperature of thermolysis increases. The highest H_c value is observed for the product of thermolysis at 1073 K with a nanocrystallite size of 10–18 nm. As the particle size increases, the effective anisotropy of nanocrystals is enhanced, resulting in a decrease in the role of thermal fluctuations.

Magnetic properties of iron-containing nanocomposites. According to powder X-ray diffraction, the solid product of transformation of Fe^{III} acrylate at the thermolysis temperature $T_{exp} = 663$ K is highly dispersed nanocrystalline magnetite with a 13 nm average size of particles homogeneously dispersed in the matrix. The magnetization curves of a sample of this product measured at 5 and 300 K in a ± 1.1 T range are shown in Fig. 6. The hysteresis loops are symmetric relative to the origin of coordinates and closed. The coercive forces are 0.008 T and 2.73 mT for temperatures of 5 and 300 K, respectively. As the temperature is raised from 5 to 300 K, the saturation magnetization varies from 25.66 to 21.82 emu g^{-1} . Note for comparison that the corresponding values for the "bulk" magnetite obtained in the same fields are 98 and 92 emu g^{-1} .¹⁹ The decrease in the magnetization is likely to be due to the antiferromagnetic spin structure of the surface atoms of the nanoparticles. The magnetization dependences on the temperature measured in the FC and ZFC modes in a 0.005 T field are shown in Fig. 7. As in the case of Co systems, the shape of the curves attests to strong interparticle interactions.

The hysteresis loops for the product of thermolysis of the acrylamide complex of Fe^{III} nitrate at 873 K were recorded at 5 and 300 K (Fig. 8). The shape and the pattern of the curves correspond to a ferromagnetic material. The saturation magnetization is 40 emu g⁻¹ at room temperature. The hysteresis loop at 300 K has a minor inflec-



Fig. 5. Magnetization vs. magnetic field in the temperature 90–300 K for the CoAAm thermolysis products formed at 673 (*a*), 773 (*b*), 873 (*c*), and 1073 K (*d*).

tion, indicating the presence of two phases with different coercive forces. This fact is consistent with the Mössbauer spectroscopy data and confirms that the product of ther-



Fig. 6. Magnetization *vs.* magnetic field at temperatures of 5 and 300 K for the Fe^{III} acrylate thermolysis product at ± 1.1 T.

molysis of the iron acrylamide complex comprises two ferromagnetic phases, Fe₃C and α -Fe (Table 2). The spectrum of the thermolysis product exhibits two sextets, indicating the formation of a ferromagnetic phase: Fe₃C accounts for 86.87%, α -Fe makes 3.17%, and the rest are paramagnetic phases.

Table 2. Mössbauer spectroscopy data for the acrylamide complex of Fe^{III} nitrate and products of polymerization and thermolysis at 873 K

Sample	IS	QS	Hhf	Phase	Content
	mn	mm s ⁻¹		composition	(wt. %)
Monomer	0.270	0.650	0.0	PPI	85.70
	0.340	1.413	0.0	PPII	14.30
Polymer	0.270	0.650	0.0	PPI	66.63
	0.340	1.413	0.0	PPII	33.37
Thermolysis	0.070	0.000	20.7	Fe ₃ C	86.87
product	0.073	0.000	32.8	α-Fe	3.170
		0.840	0.0	PPI, PPII	Residue

Note. IS is isomer shift, QS is quadrupole splitting, Hhf is hyperfine field, PPI and PPII is paramagnetic phase.





Fig. 8. Hysteresis loops measured at 5 and 300 K in a ± 1.1 T field for the thermolysis product of the Fe^{III} nitrate acrylamide complex at 873 K.



Fig. 7. Magnetization *vs.* temperature in the FC and ZFC modes in a 0.005 T field (*a*) and FC and ZFC hysteresis loops (*b*) measured at 5 K in a ± 1.1 T field for the Fe^{III} acrylate thermolysis product.

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The coercive force decreases from 0.27 to 0.06 T as the temperature increases from 5 to 300 K. The pattern of

Fig. 9. Magnetization *vs.* field curves at temperatures of 5, 75, and 300 K for the thermolysis product of the co-crystallized Fe^{III} and Co^{II} acrylates ($T_{exp} = 643$ K).

variation of the residual magnetization and M_s with temperature implies a certain contribution of the temperature-dependent magnetocrystalline anisotropy of Fe₃C to

Table 3. Measurement of the magnetic characteristics of the solid phase during the thermal transformation of Ni^{II} acrylate ($T_{exp} = 643$ K)

ZFC <u>-</u> 0.3 μ₀*H*/T

∆ <i>m/m</i> 0 (мас.%)	$\sigma_s/G \ cm^3 \ g^{-1}$		$\sigma_F/G \ cm^3 \ g^{-1}$		$\chi_{\sigma} \cdot 10^5/G \text{ cm}^3 \text{ g}^{-1}$		η_F	
	300 K	77 K	300 K	77 K	300 K	77 K	300 K	77 K
0	0.209	_	0.000	_	2.55	_	0	0
19.1	0.235	0.675	0.024	0.041	2.19	6.70	$4.4 \cdot 10^{-4}$	$7.5 \cdot 10^{-4}$
27.1	0.323	1.447	0.084	0.155	2.53	11.80	$1.54 \cdot 10^{-3}$	$2.84 \cdot 10^{-3}$
35.4	_	2.177	_	1.240	_	9.90	_	$2.28 \cdot 10^{-2}$
46.0	0.930	2.184	0.624	1.949	3.24	11.60	$1.14 \cdot 10^{-2}$	$1.74 \cdot 10^{-2}$
51.2	14.360	14.950	12.800	13.780	16.70	12/3	0.235	0.235

Note. $\sigma_s = \sigma$ (9446 Oe) is the magnetization in a 9446 σ field; $\sigma_F \rightarrow \sigma(0)$ is extrapolation of the magnetization to zero field; $\chi_{\sigma} = \chi$ (9446 Oe) is the specific magnetic susceptibility in a 9446 Oe field; $\eta_F = \sigma_F / \sigma_s(Ni)$ is the weight fraction of the Ni metal phase in the sample under the assumption that the ferromagnetism is wholly due to this phase, $M_s(Ni) = 54.5 \text{ G cm}^3 \text{ g}^{-1}$.

the overall magnetic behavior. The FC curves measured in 0.002 and 0.6 T fields show some deviations at low temperatures (at 5 K) similarly to the $M_r(T)$ dependence. This may be related to irreversible magnetization processes at low temperature caused, as discussed above, by the non-collinearity of the spins of surface atoms.

Characteristic features of the magnetic properties of nanocomposites obtained by thermolysis of the co-crystal-



lized cobalt(II) and iron(III) acrylate. The solid products of thermal transformations of co-crystallized Co^{II} and Fe^{III} acrylates with a Fe : Co atomic ratio of 2 : 1 (Fe₂CoAcr) have a non-uniform phase composition (CoFe₂O₄, Fe₃O₄, CoO) of the nanocrystalline particles characterized by rather narrow size distribution (average size 12 nm) in the formed matrix space. The nanoparticle composition and structure are also reflected in the complex character of the sample magnetic properties. Thus hysteresis loops below 200 K are open and shifted toward negative magnetic field (Fig. 9). This can be attributed to strong irreversible magnetic processes. An additional contribution of the effects related to "freezing" of the disordered surface spins of the nanoparticles occurring under close interaction with the matrix carbon molecules cannot be ruled out either.²⁰



Fig. 10. Magnetization *vs.* magnetic field curves measured in the temperature range of 90–300 K for the products of thermolysis of the acrylamide complex of Ni^{II} nitrate formed at temperatures of 673 (*a*), 773 (*b*), and 873 (*c*).

Fig. 11. Magnetization *vs.* temperature in the FC and ZFC modes in a 8 kA m⁻¹ field (0.008 T) for the products of thermolysis of the acrylamide complex of Ni^{II} nitrate formed at temperatures of 673 (*a*), 773 (*b*), and 873 K (*c*).

In the temperature range of 200–300 K, the coercive force H_c and residual magnetization decrease and at room temperature they are 0.035 T and 7.49 mT, respectively.

Magnetic properties of nickel-containing nanocomposites. For more detailed investigation of the magnetic phase formation during the thermal transformations of metalcontaining monomers, the dependence of the magnetic characteristics on the reaction time was studied in relation to the products of thermolysis of Ni^{II} acrylate with various weight losses. The magnetization of the starting Ni^{II} acrylate (NiAcr₂) is $\sigma_s(300 \text{ K}) = 0.209 \text{ G cm}^3 \text{ g}^{-1}$ and the specific magnetic susceptibility is $\chi_{\sigma}(300 \text{ K}) =$ $= 0.255 \cdot 10^{-4} \text{ cm}^3 \text{ g}^{-1}$. The magnetic moment for NiAcr₂ is $\mu_{\text{eff}} = 3.40 \ \mu_{\text{B}}$; this is close to the purely spin value $\mu_s = 2.83 \ \mu_{\text{B}}$, which is typical of the octahedral symmetry of Ni²⁺. During the thermolysis, σ_s and χ_{σ} change. The pattern of their change is illustrated by the data presented in Table 3.

The observed nonmonotonic dependence of σ_s and σ_F on the time of thermolysis (degree of weight loss by the sample) is probably due to the sharp increase in the rate of formation of the ferromagnetic phase at the end of transformation and indicates that the metal-containing products formed during the transformation occur for a long period in a weakly magnetic phase. At the final stages of thermolysis, $\eta_F \approx 0.23-0.25$, *i.e.*, only ~25% of the Ni atoms occur in the ferromagnetic phase, while the other Ni atoms occur in the weakly magnetic phase. The final transformation product has the following magnetic characteristics: $M_s(300 \text{ K}) = 14.36 (300 \text{ K}), 14.95 (77 \text{ K})$ G cm³g⁻¹; $\chi_{\sigma} \cdot 10^5 = 16.7 (300 \text{ K}), 12.3 (77 \text{ K}) \text{ cm}^3 \text{ g}^{-1}$; $H_c = 8.94 (300 \text{ K}), 53.6 (77 \text{ K}) \text{ Oe}; j_r = 0.02 (300 \text{ K}),$ $0.133 (77 \text{ K}), where j_r is the squareness ratio.$



Fig. 12. Photomicrographs of the product of thermolysis of acrylamide complex of Ni^{II} nitrate formed at 673 K.

The Ni-containing nanocomposites obtained during the thermal transformations of the acrylamide complex $[Co(CH_2=CHCONH_2)_4(H_2O)_2](NO_3)_2$ (NiAAm), have higher dispersity of the metal phase and more homogeneous distribution in the matrix space (the experimental data that substantiate this conclusion are not given in the paper) than the Co- and Fe-containing nanocomposites, especially at lower thermolysis temperatures. It could be expected that in these systems, the assembly of Ni nanoparticles would show superparamagnetic behavior.

The dependences of the magnetization of the obtained Ni-containing nanocomposites on the applied magnetic field strength in the temperature range of 90–300 K are



Fig. 13. Coercive force H_c (*a*), saturation magnetization (M_s), and residual magnetization (M_r) of the product of thermolysis of acrylamide complex of Ni^{II} nitrate *vs.* thermolysis temperature.

presented in Fig. 10. The hysteresis loops for the products obtained at 673 and 773 K attest to the formation of superparamagnetic particles, whereas the product of thermolysis at 873 K shows a ferromagnetic behavior, which is also supported by the thermomagnetic characteristics of the Ni nanoparticle assembly in the systems in question (Fig. 11). It can be seen that an inflection corresponding to the blocking temperature appears in the ZFC curves: the product obtained at 673 K at $T > T_b$ ($T_b \approx 40$ K is the characteristic blocking temperature for magnetic nanoparticles) is a superpramagnetic material. According to the measurements, magnetization of an assembly in a strong magnetic field at $T \le T_b$ is ~3 emu g⁻¹; with allowance made for the saturation magnetization $M_{\rm s} = 500 \text{ emu g}^{-3}$ and the nickel density $\rho = 8.9 \text{ g cm}^{-3}$, this corresponds to the magnetization of an assembly of nickel particles with an average diameter d = 7 nm located at distances $d \approx 20$ nm. This conclusion is in satisfactory agreement with the electron microscopy data (Fig. 12). The experimental value of the blocking temperature $T_{\rm b} = 40$ K can be explained by the presence of nickel particles with greater diameters (d = 14 - 16 nm) or by the effect of the surface anisotropy of particles.

The temperature dependences of H_c indicate the decrease in the coercive force for the thermolysis product at 773 K from 0.0077 T (7.7 kA m⁻¹) at 90 K to nearly zero at 300 K. The M_s and M_r values for all products differ little with temperature.

An increase in the thermolysis temperature results in an increase in the particle size of Ni-containing nanocomposites from 6–7 nm (673 K) to 8–14 nm (773 K) and 12–17 nm (873 K). The key magnetic characteristics of these products at room temperature are also consistent with different types of their magnetic behavior (Fig. 13). The sharp increase in H_c for the product obtained at 873 K indicates that at this temperature, the material switches from superparamagnet to ferromagnet.

Thus, the advantage of the polymerization—destruction synthesis of metal nanoparticles is not only the fact that this provides stabilized magnetic nanoparticles resistant to oxidation and aggregation; this approach also allows for the effective control of nanoparticle size and, finally, magnetic properties. Indeed, the nanocomposites based on acrylamide metal complexes, unlike those formed from carboxylate precursors, are characterized by higher dispersity and contain metal nanoparticles, and only at high synthesis temperatures, carbide phases appear. The metal-containing nanocomposites are magnetic materials with ferro- and superparamagnetic properties.

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