

# Mössbauer Study of Oxo Derivatives of Iron in the $\text{Fe}_2\text{O}_3\text{--Na}_2\text{O}_2$ System

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**Abstract**—Various compositions of oxo derivatives of iron reacting with sodium peroxide have been studied by Mössbauer spectroscopy. We have examined several mathematical models of the measured spectra. The results obtained are inconsistent with hypotheses made previously that such conditions may lead to the formation of compounds of iron in oxidation states above (6+). We demonstrate that a large excess of an alkali peroxide leads, most likely, to the formation of at least two iron(V) derivatives in tetrahedral coordination. In their Mössbauer spectra, they have isomer shifts of  $-0.45$  and  $-0.51$  mm/s and unusually large quadrupole splittings: 1.32 and 1.94 mm/s (at room temperature).

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## INTRODUCTION

It is common practice to divide the charge states of elements in compounds into lower, medium, and higher oxidation states (OS's). Elements in the most widespread compounds are thought to be in medium OS's. As a rule, they possess high thermodynamic stability under various conditions. The elements in them may exhibit both oxidizing and reducing properties. In compounds of elements in their higher OS's [1], the elements are formally in a high charge state and typically exhibit oxidizing properties. Such compounds usually have low thermodynamic stability or are only stable under certain conditions (temperature, pH, solvent, etc.). Note that the theoretically possible higher OS should be differentiated from the experimentally achievable one. For example, in the case of iron, 2+ and 3+ are commonly thought to be medium OS's. It is known that, in most iron-containing minerals, this element is in these OS's [2]. Compounds containing iron atoms in higher OS's are referred to as higher OS's. In particular, 6+ for iron is thought to be the highest experimentally achievable OS. Only a small number of such substances, ferrates(VI), are known. They possess strong oxidizing properties, and their stability regions are limited by low temperature and by either a solid phase or highly alkaline solutions [3]. There are only a few examples of the OS's intermediate between (3+) and (6+) for iron [4–6]. As a rule, they form and exist under very unusual conditions.

Theoretically, the highest achievable OS of iron is thought to be (8+) [7]. Moreover, there are unconfirmed reports on the synthesis and characterization of the corresponding iron compounds [8, 9]. In spite of the internal contradictions in describing the properties

of materials containing iron in this high charge state, the preparation, stabilization, and practical application of iron compounds in extreme oxidation states have been the subject of patents [10]. Note that Mössbauer spectroscopy has been the only method used to identify the charge state of iron in samples. In particular, in a recent study Dedushenko et al. [11] supposedly confirmed the possibility of formation of iron(VII) and iron(VIII) compounds in the products of spontaneous degradation of iron compounds forming in an excess of sodium peroxide. They arrived at this conclusion by interpreting Mössbauer spectra. Using complex mathematical tools [12], they separated out several resonance lines from poorly resolved spectra, with isomer shifts in the range  $-1.58$  to  $-0.73$  mm/s, which were assigned to compounds of iron in extreme (and exotic) OS's (from 8+ to 5.5+) using extrapolation of data for known iron oxo compounds [11]. The data presented in that report appear, however, superficial and unsystematic, and obviously require further verification.

## EXPERIMENTAL

The iron precursor used was  $^{57}\text{Fe}$ -enriched, activated ferric oxide prepared by a purpose-developed procedure. To this end, a weighed amount of 95%-enriched  $^{57}\text{Fe}_2\text{O}_3$  was dissolved in a very small amount of concentrated hydrochloric acid. After complete dissolution of the oxide, the solution was boiled down to near dryness, and an appropriate amount of a 10% oxalic acid solution was added. As a result, the solution changed color from yellow-brown to apple green. It was then exposed to light from a 250 W incandescent

lamp. After complete reduction of trioxalatoferate(III) to dioxalatoferate(II) under illumination [13], the yellow solution was boiled under the lamp. The resultant bright yellow crystalline iron(II) oxalate precipitate was washed with a small amount of ethanol and dried. The material thus prepared was sequentially heated at temperatures of 130, 370, and 450°C in a silver boat in flowing purified argon. Cooled in flowing argon, the black powder rapidly oxidized when exposed to air to form black-brown substance. According to Mössbauer spectroscopy results, the final synthesis product consisted largely of a magnetically ordered iron(III) oxide.

The activated iron(III) oxide thus prepared was used to prepare solid solutions of iron compounds in sodium peroxide. To this end, a weighed amount of Na<sub>2</sub>O<sub>2</sub> (Lancaster Synthesis, 95% purity) was thoroughly ground with a weighed amount of ferric oxide in a dry chamber and then heated in a tube furnace in a silver boat under a dry oxygen atmosphere to a temperature of 495°C over a period of 5 min. After cooling, the gray sinter cake was slightly ground (so as not to cause a mechanochemical transformation of the products) and then hermetically sealed in plastic cuvettes of a Mössbauer spectrometer. The synthesized solid solutions of iron compounds in sodium peroxide, containing 91.1, 18.9, 9.8, 5.0, 2.5, 1.7, and 1.4 mM Fe/M, were characterized by Mössbauer spectroscopy.

Mössbauer absorption spectra were obtained on an MS1104EM express Mössbauer spectrometer (ZAO Kordon, Rostov-on-Don). The gamma sources used were Mössbauer sources containing <sup>57</sup>Co in metallic rhodium, with activities of 3 and 35 mCi (ZAO Ritverts, St. Petersburg). To obtain spectra, the samples enclosed in a plastic cuvette were placed in an evacuated cryostat. The spectra were measured with quality of at least 90 for resolution at 1024 points of each sample at both room temperature and liquid-nitrogen temperature. The samples were thermostated with an accuracy of ±1 K at liquid-nitrogen temperature and ±4 K at room temperature. Reproducibility of the spectra was checked by comparing room-temperature spectra of a given sample before and after a cooling–heating cycle. The measured Mössbauer spectra were analyzed for high-resolution spectra (1024 points) using the Univem MS 9.08 program. The isomer shift was determined relative to α-Fe.

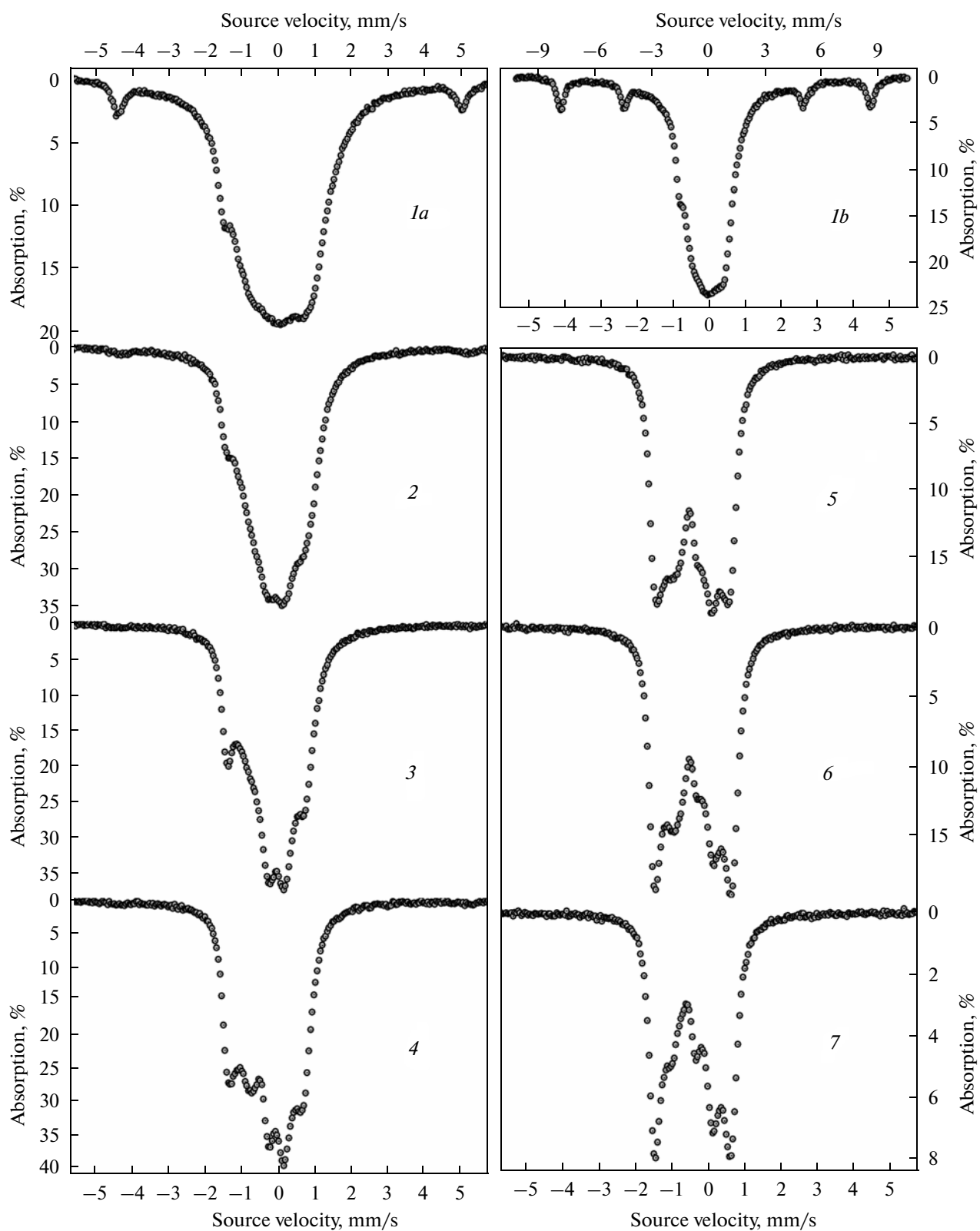
## RESULTS AND DISCUSSION

The shape of the Mössbauer spectra of our samples varied little with temperature. By contrast, varying the iron content produced significant, systematic changes in the spectra (Fig. 1). In the first sample (with the highest iron content), we observed 9% magnetically ordered impurity with the following parameters:  $\delta = 0.20$  mm/s,  $\Delta = 0.09$  mm/s,  $H = 489$  kOe, and  $\Gamma = 0.45$  mm/s. The rest of the spectrum of those samples

had the form of a poorly resolved set of broad subspectra. In spite of the poor resolution, even the spectrum of the first sample contains a well-defined shoulder on the left side, which suggests the presence of a resonance line with an isomer shift of about  $-1.5$  mm/s. According to Perfil'ev et al. [9] and Dedushenko et al. [11], this should be interpreted as evidence for the presence of iron(VIII). In addition, the central part of the spectrum of sample 2 (Fig. 1) contains a narrow doublet with an isomer shift of about  $-0.1$  mm/s. Further reducing the iron content of the mixtures rapidly improves the resolution of the spectra. Even in the spectrum of the third sample, we can reliably distinguish the aforementioned doublet, and the resonance line near  $-1.5$  mm/s has a minimum (Fig. 1). At a concentration of 5 mM/M, the spectrum shows well-defined resonances near  $-1$  and  $0.6$  mm/s (at the liquid-nitrogen temperature). Starting at 2.5 mM/M, the intensity of the central narrow doublet decreases, and it becomes clear that the resonance lines at  $-1.5$  and  $0.6$  mm/s belong to the same doublet, whose contribution increases with decreasing iron content (Fig. 1, sample 7).

As a rule, interpretation of poorly resolved Mössbauer spectra is an intricate, multiparametric problem. A measured spectrum is fitted using a particular model based on available information about the composition, structure, and properties of the sample. A criterion for whether the spectrum has been adequately decomposed into components is the agreement between the obtained parameters and expected ones for realistic physical and chemical models. A criterion for sufficiency is provided by statistical parameters of the deviation of results of the proposed model from experimental data. Clearly, a larger number of subspectra in a model and a smaller number of constraints for their components ensure better fitting quality. In some cases, when the iron atoms in a sample have an inhomogeneous environment and parameters of subspectra vary continuously in some range, or spectra contain overlapping components (resonance lines), a model-free description of spectra is used, instead of models [12, 14]. However, a model-free description of spectra also requires an adequate initial hypothesis as to the properties of the substance to be studied. In some cases, even with well-resolved spectra, an incorrect initial hypothesis may entail inadequate interpretation of experimental data [15].

The above considerations refer in full measure to the present Mössbauer spectra (Fig. 1), which can be described in several ways as shown below. Clearly, all of these spectra are the sum of subspectra corresponding to iron atoms in different environments. Given the small width and weak temperature dependence of the resonance lines, it is reasonable to assume that the subspectra at different sample compositions correspond to iron atoms in a particular, fixed environment. Clearly, only the percentages of iron in different environments vary in response to changes in the iron con-



**Fig. 1.** 78 K Mössbauer spectra of iron oxo compounds in sodium peroxide: (1) 91.1, (2) 18.9, (3) 9.8, (4) 5.0, (5) 2.5, (6) 1.7, and (7) 1.4 mM  $\text{Fe}_2\text{O}_3/\text{M Na}_2\text{O}_2$ .

tent of the fusion cakes under consideration. Since we deal, most likely, with highly dilute solid solutions, it cannot be ruled out that iron atoms are localized in different parts of the melt during synthesis. It seems likely that even spectra of mixtures with high sodium peroxide contents reflect “summation” of the states of iron in solutions with different concentrations. Based on this, we think that it is convenient and possible—for demonstrating that the Mössbauer spectra under discussion can be decomposed in different ways—to sum the measured spectra of the materials containing 9.8 to 1.4 mM Fe/M. Such a situation may indeed occur, for example, in the case of poor homogenization of the starting mixture, liquid immiscibility, etc. In our case, such a procedure will make it possible to level off the fractions of various subspectra for preliminary analysis and increase the statistical weight of components that are encountered in different samples, minimizing the effect of impurity phases on the model. Consider possible decompositions of the obtained sum spectrum into components.

The simplest mathematical model, with the minimum number of spectral components, is a superposition of three doublets (table, model 1), one of which differs significantly in isomer shift and quadrupole splitting from the other two, which are relatively close in isomer shift and have appreciable quadrupole splittings.

The addition of singlet with an isomer shift of about  $-0.8$  mm/s to the above model reduces the residual only slightly (table, model 2; Fig. 2).

Another possible decomposition, into two singlets and two doublets, is presented as model 3 (table, Fig. 2). Note that the isomer shifts of the two doublets and one singlet differ little and can obviously correspond to iron atoms in the same OS.

Finally, the best residual factor can be ensured using model 4 (table), which contains two singlets with small isomer shifts (Fig. 2). Note that the singlets in model 4 are on the whole similar to those reported by Dedushenko et al. [11], who assigned them to iron atoms in the OS (8+).

To assign the corresponding subspectra to particular charge states of iron in the samples, consider the isomer shift as a function of formal OS for various oxo iron compounds. To this end, in plots of the isomer shift against OS we indicate the average of the experimentally observed isomer shifts for oxo compounds of iron in different OS's in the most widespread coordination polyhedra—tetrahedra and octahedra—at a particular temperature (Fig. 3). Data were selected over all values presented in the classic review by Menil [16] and were supplemented by more recent data [4, 17] for compounds of iron in higher oxidation states. On the whole, we used about 240 experimental data points in constructing the plot (Fig. 3). It is seen from the diagram thus obtained that, for most iron-containing oxo clusters with a given symmetry, the isomer shift is roughly a linear function of the OS of the central

atom. Despite the small amount of data for compounds of iron in OS's other than (2+) and (3+), such an empirical relation, is often used in predicting the isomer shift for compounds of iron in extreme OS's [11, 15] and builds on its connection with the electron density at the Mössbauer nucleus [18–20].

Nevertheless, analysis of the data in Fig. 3 leads to some useful observations for interpretation of Mössbauer parameters of iron oxide compounds. In particular, in the case of iron oxo compounds a change in OS by (1+), with no symmetry changes, leads to a reduction in isomer shift by 0.34–0.41 mm/s (except for the 2+  $\rightarrow$  3+ transition). Further, raising the temperature from liquid-nitrogen temperature to room temperature leads to a reduction in isomer shift by 0.05–0.26 mm/s. Finally, the isomer shift of iron atoms in tetrahedral coordination is typically smaller than that of iron atoms in octahedral coordination by 0.19–0.25 mm/s when there is no changes in the charge state of the central atom. (Although the difference is perhaps much smaller for compounds in the OS's (5+) and (6+) (see Fig. 3)).

Thus, analysis of the literature leads us to conclude that doublet 1 in models 1 and 2, with an area of about 13% and a room-temperature isomer shift of  $-0.22$  mm/s, corresponds to iron(IV) atoms in tetrahedral coordination, which fits well with published data for  $\text{Na}_4\text{FeO}_4$  [4]. The singlet with a negative isomer shift in models 2 and 3 (table) is obviously due to iron(VI) atoms in the form of ferrate ions [21], which readily form under the conditions in question [22]. The singlet with a positive isomer shift in model 3 may arise from iron(III) atoms in octahedral coordination [16].

Doublets 2 and 3 in models 1 and 2 possess unusual parameters which have no analogues in the literature. According to Fig. 3, doublets with such isomer shifts may equally be due to iron(V) atoms in tetrahedral and octahedral coordination. The unusually high quadrupole splitting values may result from both the lattice contribution to the electric field gradient (see below) and the formation of tetrahedral high-spin iron-containing clusters in the  $e^2t_2^1$  electronic configuration (for example, no quadrupole splitting was detected for iron(V) in octahedral coordination ( $t_{2g}^3e_g^0$ ) [6]). At the same time, the splitting is a weak function of temperature in the temperature range studied, in contrast to what would be expected for the  $e^2t_2^1$  configuration.

It is worth noting that, whereas the isomer shifts of the doublets for iron(V) differ little (table, models 1, 2), their quadrupole splittings differ by about 0.75 mm/s. This indicates that there are significant distinctions between the environments of the resonance atoms. Given that the system under consideration is rather simple, we cannot rule out the formation of iron compounds with dioxygen ligands [23–25], for example, peroxide or superoxide ions, under

Parameters of various models for describing the Mössbauer spectrum of iron oxo compounds in Na<sub>2</sub>O<sub>2</sub>

Model	Temperature, K	Subspectrum no.	Proposed OS	Isomershift $\delta$ , mm/s	Quadrupole splitting $\Delta$ , mm/s	Linewidth $\Gamma_{\text{exp}}$ , mm/s	Relative area $S/S_0$ , %	$\chi^2$	$\delta_{298} - \delta_{78}$ , mm/s		
1	78	1	+4	-0.13	0.40	0.35	11	3.93			
		2	+5	-0.39	1.27	1.02	71				
		3	+5	-0.44	2.10	0.33	18				
	298	1	+4	-0.21	0.36	0.30	12			2.76	-0.08
		2	+5	-0.45	1.18	0.90	72				
		3	+5	-0.51	1.95	0.29	16				
2	78	1	+4	-0.13	0.41	0.37	14	3.60			
		2	+5	-0.39	1.34	1.03	69				
		3	+5	-0.44	2.10	0.33	17				
		4	+6	-0.79		0.32	1				
	298	1	+4	-0.22	0.38	0.35	19			2.17	-0.09
		2	+5	-0.45	1.32	0.89	63				
		3	+5	-0.51	1.94	0.28	14				
		4	+6	-0.87		0.38	4				
3	78	1	+3	0.57		0.51	26	5.53			
		2	+6	-0.74		0.22	2				
		3	+6	-0.68	0.66	0.54	36				
		4	+6	-0.69	1.57	0.42	36				
	298	1	+3	0.42		0.50	26			2.90	-0.15
		2	+6	-0.78		0.21	2				
		3	+6	-0.71	0.62	0.48	38				
		4	+6	-0.73	1.45	0.37	34				
4	78	1	+3	0.35	0.50	0.38	19	1.93			
		2	+4	0.12	0.70	0.74	40				
		3	+5	-0.57	0.38	0.32	7				
		4	+6	-1.06		0.58	18				
		5	+7	-1.49		0.37	16				
	298	1	+3	0.23	0.47	0.30	15			1.49	-0.12
		2	+4	-0.03	0.64	0.74	49				
		3	+5	-0.63	0.39	0.21	3				
		4	+6	-1.06		0.50	18				
		5	+7	-1.47		0.35	15				

the synthesis conditions of this study. On the one hand, this would be expected to change the symmetry of the environment of the iron atom and, accordingly, the quadrupole splitting. On the other, this would change the isomer shift because of the displacement of

the electron density along the metal–dioxygen bond, since the electrons of the  $\pi^*$  orbital of the dioxygen ligand are extremely mobile and can change the charge state of the central ion [26]. In particular, ab initio calculations for platinum superoxo complexes

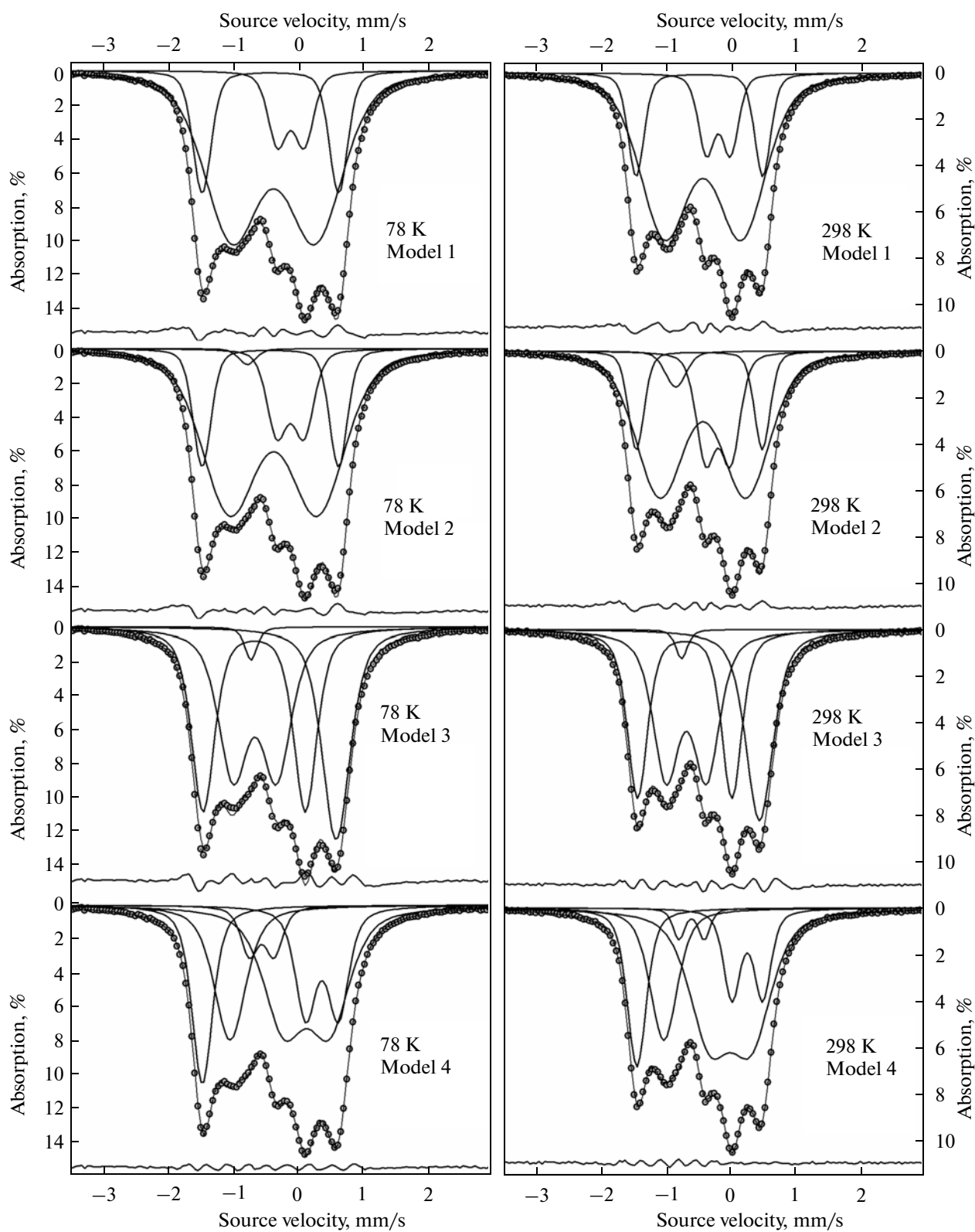
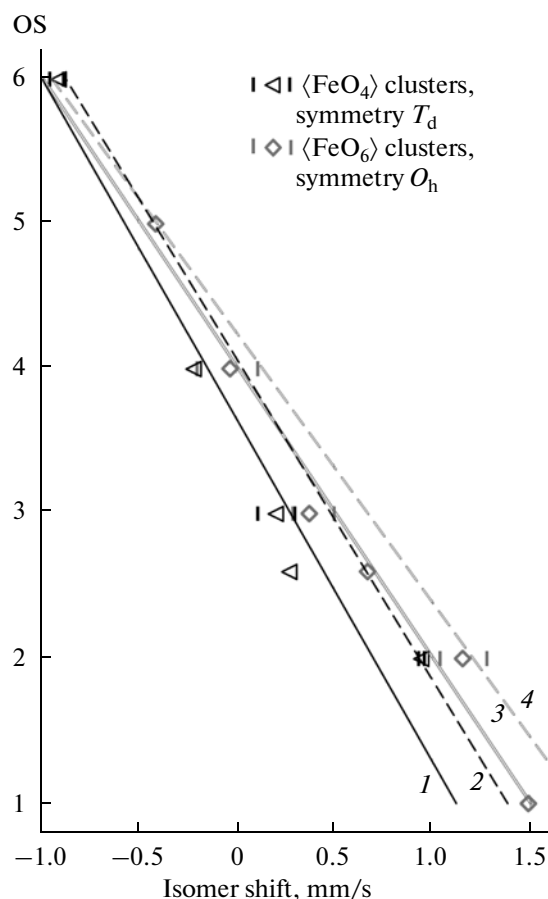


Fig. 2. Possible models for describing of sum Mössbauer spectra at different temperatures.



**Fig. 3.** Ranges and average of the isomer shift for iron atoms in different OS's in (1, 2) tetrahedral and (3, 4) octahedral interstices of oxo compounds at room temperature, and approximation of average straight lines for (1, 3) room temperature and (2, 4) liquid-nitrogen temperature (data are not presented) according to published data.

demonstrate that the electron density is displaced from the platinum(IV) atom to the  $\pi^*$  orbital of the dioxygen ligand [27]. In contrast, in the case of tin(IV) hexahydroperoxo complexes the electron density is displaced from the  $\pi^*$  orbitals to the complex-forming ligand, leading to an increase in isomer shift in the Mössbauer spectrum by 0.22 mm/s relative to tin(IV) hexahydroxo complexes [28, 29]. It is reasonable to assume that an excess of peroxide ions in a solid solution may result in the formation of single and doubly substituted iron(V) peroxo complexes, for example,  $\text{FeO}_2(\text{O}_2^{2-})^-$  and  $\text{Fe}(\text{O}_2^{2-})_2^+$ . Then, the chemical model under consideration suggests that the former complex should correspond to the doublet with the smaller isomer shift and larger quadrupole splitting. By contrast, because of the larger number of donor ligands, the doubly substituted complex should have a larger isomer shift and smaller quadrupole splitting owing to the higher symmetry coordination of the complex-forming atom.

Similar reasoning applies to the origin of the doublets of iron(VI) in model 3 (table). Indeed, according to this model, the samples contain, in addition to the conventional ferrate ion, iron(VI) atoms in a heavily distorted coordination. The distortion may be produced, for example, by the peroxo ions bonded directly to these atoms. Note, however, that this model, first, assumes coexistence of Fe(III) and Fe(VI) in one sample. Second, even though this model describes experimental data using six resonance lines of which four are independent, its residual factor is considerably poorer than, for example, that of model 1 (table), which also includes six resonances, but only three of them are independent.

Finally, consider the fourth model, which includes singlet lines with very small isomer shifts (table). Note, first of all, that this model is in part similar to models proposed in studies that assumed the formation of iron(VIII) compounds [9, 11]. Based on our data in Fig. 3, it is reasonable to assume that subspectra 1, 3, and 4 (table, model 4) correspond to Fe(III), Fe(V) and Fe(VI) atoms in tetrahedral coordination, whereas subspectrum 2 corresponds to Fe(IV) in octahedral coordination. It can be shown by extrapolating the straight lines in Fig. 3 to smaller isomer shifts that the parameters of singlet 5 in model 4 (table) should correspond to a compound of iron in the OS (7+) or higher. We think, however, that this model for experimental data is inherently incorrect, even though it has a better residual factor. Indeed, as mentioned above a change in the temperature of Mössbauer measurements should lead to a second-order Doppler shift [30]. The second-order Doppler shift is negative, and its theoretical value in the temperature range in question is  $-0.15 \pm 0.5$  mm/s for substances with Debye characteristic temperatures between 100 and 700 K [16]. In practice, slight deviations from the theoretical value take place, but similar compounds differ little in temperature shift. At the same time, in model 4 the temperature shifts of different components have drastically different variations, and the shift for the most questionable singlet is positive (table, model 4). This provides further evidence that such interpretation of experimental data is inadequate from the viewpoint of both chemical and physical models.

We think that, among the above models for analysis of measured Mössbauer spectra, model 2 is the most consistent in terms of both physical and chemical models and satisfies the statistical criterion for sufficiency. It assumes coexistence of Fe(IV) and Fe(V) compounds and the presence of trace levels of Fe(VI) impurities.

## CONCLUSIONS

Using Mössbauer measurements at different temperatures, we have studied solid solutions of  $\text{Fe}_2\text{O}_3$  in sodium peroxide at mole fractions of iron from  $91.1 \times 10^{-3}$  to  $1.4 \times 10^{-3}$ . We have examined different

descriptions of the sum spectrum for samples with a mole fraction of iron from  $9.8 \times 10^{-3}$  to  $1.4 \times 10^{-3}$  and showed that models which assume the formation of compounds containing iron in OS's above (6+) are inadequate. Solid peroxide fusion cakes contain over 80% Fe(V) compounds, possibly with dioxygen ligands, which have an unusually large quadrupole splitting.

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#### REFERENCES

- Riedel, S. and Kaupp, M., The highest oxidation states of the transition metal elements, *Coord. Chem. Rev.*, 2009, vol. 253, p. 606.
- Wilke, M., Farges, F., Petit, P.-E., et al., Oxidation state and coordination of Fe in minerals: An Fe K-XANES spectroscopic study, *Am. Mineral.*, 2001, vol. 86, p. 714.
- Perfiliev, Yu.D., Benko, E.M., Pankratov, D.A., et al., Formation of iron(VI) in ozonolysis of iron(III) in alkaline solution, *Inorg. Chim. Acta*, 2007, vol. 360, p. 2789.
- Jeannot, C., Malaman, B., Gérardin, R., and Oulladi, B., Synthesis, crystal and magnetic structures of the sodium ferrate(IV)  $\text{Na}_4\text{FeO}_4$  studied by neutron diffraction and Mössbauer techniques, *J. Solid State Chem.*, 2002, vol. 165, no. 2, p. 266.
- Dedushenko, S.K., Perfiliev, Yu.D., Tchekoukov, D.E., et al., Moessbauer study of pentavalent iron in vanadium(V) oxide matrix, *Mendeleev Commun.*, 1999, vol. 5, p. 211.
- Demazeau, G., Buffat, B., Menil, F., et al., Characterization of six-coordinated iron(V) in oxide lattice, *Mater. Res. Bull.*, 1981, vol. 16, p. 1465.
- Gutsev, G.L., Khanna, S.N., Rao, B.K., and Jena, P.,  $\text{FeO}_4$ : A unique example of a closed-shell cluster mimicking a superhalogen, *Phys. Rev. A*, 1999, vol. 59, no. 5, p. 3681.
- Goralevich, D.K., Studies of higher group VIII oxygen compounds, *Zh. Ros. Fiz.-Khim. O-va, Ser. Khim.*, 1926, vol. 58, no. 8, p. 1129.
- Perfil'ev, Yu.D., Kopelev, N.S., Kiselev, Yu.M., and Spitsyn, V.I., Mössbauer study of octavalent iron, *Dokl. Akad. Nauk SSSR*, 1987, vol. 296, no. 6, p. 1406.
- Dedushenko, S.K., Perfil'ev, Yu.D., and Kornilova, A.A., RF Patent 2 448 055.
- Dedushenko, S.K., Perfil'ev, Yu.D., Chuev, M.I., et al., Identification of iron oxidation states in the products of interaction of  $\text{Na}_2\text{O}_2$  and  $\text{Fe}_2\text{O}_3$  by Mössbauer absorption spectroscopy, *Russ. J. Inorg. Chem.*, 2010, vol. 55, no. 6, p. 942.
- Afanas'ev, A.M. and Chuev, M.A., Discrete versions of Mössbauer spectra, *Zh. Eksp. Teor. Fiz.*, 1995, vol. 107, no. 3, p. 989.
- Cooper, G.D. and DeGraff, B.A., Photochemistry of ferrioxalate system, *J. Phys. Chem.*, 1971, vol. 75, no. 19, p. 2897.
- Matsnev, M.E. and Rusakov, V.S., Spectrrelax: An application for Mössbauer spectra modeling and fitting, *AIP Conf. Proc.*, 2012, vol. 1489, p. 178.
- Kopelev, N.S., Kiselev, Yu.M., and Perfiliev, Yu.D., Mossbauer spectroscopy of the oxocomplexes iron in higher oxidation states, *J. Radioanal. Nucl. Chem.*, 1992, vol. 157, p. 401.
- Menil, F., Systematic trends of the  $^{57}\text{Fe}$  Mossbauer isomer shifts in  $(\text{FeO}_n)$  and  $(\text{FeF}_n)$  polyhedra. Evidence of a new correlation between the isomer shift and the inductive effect of the competing bond T-X ( $\rightarrow\text{Fe}$ ) (where X is o or F and T any element with a formal positive charge), *J. Phys. Chem. Solids*, 1985, vol. 46, p. 763.
- Takeda, Y., Kanno, K., Takada, T., et al., Phase relation in the oxygen nonstoichiometric system,  $\text{SrFeO}_x$  ( $2.5 \leq x \leq 3.0$ ), *J. Solid State Chem.*, 1986, vol. 63, p. 237.
- Walker, L.R., Wertheim, G.K., and Jaccarino, V., Interpretation of the  $\text{Fe}^{57}$  isomer shift, *Phys. Rev. Lett.*, 1961, vol. 6, no. 3, p. 98.
- Neese, F., Prediction and interpretation of the  $^{57}\text{Fe}$  isomer shift in Mossbauer spectra by density functional theory, *Inorg. Chim. Acta*, 2002, vol. 337, p. 181.
- Filatov, M., First principles calculation of Mossbauer isomer shift, *Coord. Chem. Rev.*, 2009, vol. 253, p. 594.
- Shinjo, T., Ichida, T., and Takada, T.,  $\text{Fe}^{57}$  Mossbauer effect and magnetic susceptibility of hexavalent iron compounds;  $\text{K}_2\text{FeO}_4$ ,  $\text{SrFeO}_4$  and  $\text{BaFeO}_4$ , *J. Phys. Soc. Jpn.*, 1970, vol. 29, no. 1, p. 111.
- Wallace, T. and Fleck, A., Some properties of fused sodium hydroxide, *J. Chem. Soc.*, 1921, vol. 119, p. 1839.
- Gutsev, G.L., Weatherford, C.A., Pradhan, K., et al., Structure and spectroscopic properties of iron oxides with the high content of oxygen:  $\text{FeO}_n$  and  $\text{FeO}_n^-$  ( $n = 5-12$ ), *J. Phys. Chem. A*, 2010, vol. 114, no. 34, p. 9014.
- Tran, V.T. and Hendrickx, M.F.A., Description of the geometric and electronic structures responsible for the photoelectron spectrum of  $\text{FeO}_4^-$ , *J. Chem. Phys.*, 2011, vol. 135, paper 094 505.
- Atanasov, M., Theoretical studies on the higher oxidation states of iron, *Inorg. Chem.*, 1999, vol. 38, p. 4942.
- Pankratov, D.A., Komozin, P.N., and Kiselev, Yu.M., EPR spectroscopy of transformations of iridium(III) and iridium(IV) hydroxo complexes in alkaline media, *Russ. J. Inorg. Chem.*, 2011, vol. 56, no. 11, p. 1794.
- Pankratov, D.A., Dement'ev, A.I., and Kiselev, Yu.M., Ab initio calculations of hydroxoplatinum compounds: II. Binuclear platinum(IV) superoxo complexes, *Russ. J. Inorg. Chem.*, 2008, vol. 53, no. 2, p. 247.
- Ippolitov, E.G., Tripol'skaya, T.A., Prikhodchenko, E.G., and Pankratov, D.A., Potassium hexahydroperoxostannate: Synthesis and structure, *Russ. J. Inorg. Chem.*, 2001, vol. 46, no. 6, p. 851.
- Pankratov, D.A., Prikhodchenko, P.V., Perfil'ev, Yu.D., et al., Mössbauer spectroscopy of alkali hydroperoxostannates, *Izv. Ross. Akad. Nauk, Ser. Fiz.*, 2001, vol. 65, no. 7, p. 1043.
- Josephson, B.D., Temperature-dependent shift of  $\gamma$ -rays emitted by a solid, *Phys. Rev. Lett.*, 1960, vol. 4, p. 341.

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