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# A magnetochemical study of sodium ferrate

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**A magnetochemical study of sodium ferrate samples obtained by heating sodium peroxide and iron(III) oxide at about 480 °C and in a 10:1 molar ratio of sodium to iron has shown that there exists a phase of iron in a higher oxidation state which, in terms of quenched orbital magnetism theory, can be considered as a high-spin oxocomplex of tetravalent iron, which is antiferromagnetic with a Neel temperature of about 14 K.**

Various derivatives of iron in higher oxidation states in Na–Fe–O systems have often been investigated,[1–3] but the data reported are controversial. This can be explained both by the difficulty in synthesising the pure compounds and by the instability of the substances obtained, which results in the samples always containing impurities from decomposition products. This greatly influences the results of chemical analysis and magnetic and other characteristics. In addition, sodium ferrates were observed to be amorphous in a number of cases.

Sodium peroxides, as well as oxides, have no paramagnetic properties and paramagnetic sodium superoxide can be formed only under extreme conditions.[4,5] That is why magnetochemistry is a convenient research method for studying iron compounds in the Na–Fe–O system. In particular, it can define the oxidation state of the transition element.

An earlier study of the Na–Fe–O system allowed us to obtain new information about compounds of iron in higher oxidation states.[6] The room temperature Mössbauer spectrum of one of them was a doublet with a chemical shift relative to sodium nitroprusside $\delta = -0.01\pm0.01$ mm s$^{-1}$, quadrupole splitting $E =$ $= 0.40\pm0.01$ mm s$^{-1}$ and width of lines at half height $\Gamma_{1/2} =$ $= 0.24\pm0.01$ mm s$^{-1}$. At 5 K this doublet changed into a six-line spectrum typical of magnetoordering phases ($\delta =$ $= 0.09\pm0.02$ mm s$^{-1}$, $E = 0.21\pm0.02$ mm s$^{-1}$, hyperfine magnetic field $H = 25.7\pm0.1$ T and $\Gamma_{1/2} = 0.27\pm0.02$ mm s$^{-1}$ for central lines). These values of chemical shifts and hyperfine magnetic field might be related to the oxidation states of iron +4 or +5 with high-spin d$^4$ or d$^3$ configurations, respectively[6,7] which did not allow us to draw a final conclusion about the oxidation state.

The use of different X-ray diffraction techniques did not allow any information about the crystal structure to be obtained. According to the results of this method the substance was amorphous. Various attempts to study the geometry of the iron coordination polyhedron by IR and Raman spectroscopies showed no positive result owing to the quick decomposition of the samples while measurements were being carried out.[†]

In the present paper the results of the magnetochemical study of the phase obtained by us earlier[6] are presented.

The dependence of the magnetization of the sample on an external magnetic field at liquid helium and room temperatures was linear, neither hysteresis nor remanence being observed. That indicates the absence of ferri- and ferromagnetic clusters in the samples.

The temperature dependence of reciprocal molar magnetic susceptibility is shown in Figure 1. Above 50 K that dependence obeys the Curie–Weiss law well ($\theta = -36$ K). The calculated value of the room temperature effective magnetic moment $p_{\mathrm{eff}}$ is $5.0\pm0.2\,\mu_{\mathrm{B}}$.

At about 14 K (the minimum of the reciprocal susceptibility) an antiferromagnetic transition takes place.

The increase of magnetization below 7 K might be explained by the presence of paramagnetic impurities. These impurities can probably be related to the decomposition product of the initial phase. In fact, at 77 K in the EPR spectra an anisotropic signal with parameters $g_{\parallel} = 2.190\pm0.001$, $g_{\perp} = 1.999\pm0.001$ was observed, the intensity of the signal increasing with the decomposition of the substance.[6] However, it is not possible to estimate the impurity content quantitatively.

The magnetic properties of 3d-transition element ions with open valent shells can be satisfactorily described in terms of a so-called 'quenched orbital magnetism' model.[9] According to this model the magnetic moment of an ion is determined only by the spin component and is independent of orbital moment[8,9] and the effective magnetic moment $p_{\mathrm{eff}} = 2[S(S+1)]^{1/2}$.

Within the framework of that supposition, an Fe$^{4+}$ ion with four unpaired electrons in the d-level and ground term $^5$D must have an effective magnetic moment $4.90\,\mu_{\mathrm{B}}$. The values given in the literature[8] are in the interval 4.8–5.0 $\mu_{\mathrm{B}}$.

The effective magnetic moment for Fe$^{5+}$ ions with three unpaired electrons and ground term $^4$F must be equal to $3.87\,\mu_{\mathrm{B}}$. The literature values[8] are 3.7–3.9 $\mu_{\mathrm{B}}$.

Owing to the theoretical and experimental values of the effective magnetic moment for high-spin 3d$^4$ and 3d$^3$ configurations

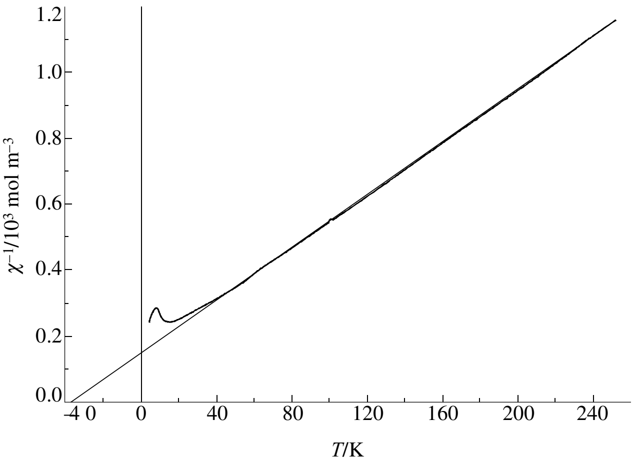

**Figure 1** Temperature dependence of the reciprocal molar magnetic susceptibility of sodium ferrate.

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[†] The sodium peroxide used in this work and the reaction products are extremely reactive and interact easily with water and carbon dioxide which are present in the air. All manipulations with the substances were therefore performed in glove boxes under a dry air atmosphere free from CO$_2$. Specimens for measurements were enclosed in a hermetically sealed special plastic container.

To obtain the substance, a mixture of Na$_2$O$_2$ and Fe$_2$O$_3$ in a 10:1 molar ratio of these oxides was thoroughly ground to powder and poured into a covered silver boat. The mixture was heated to about 480 °C in a special reactor with oxygen passing over it.

Quantitative atomic absorption analysis on iron was carried out with a 'Carl Zeiss, Jena' AAS1N-spectrometer.

Magnetic measurements in the interval 4.2–291 K in a field up to 0.5 T were obtained with a PARC-155 vibration magnetometer. The magnetometer was calibrated by the saturation magnetic moment of a cylindric nickel sample in a high magnetic field. Sensitivity at the magnetic moment was better than $5\times10^{-8}$ A m$^2$.

presented here, the obtained value of $p_{\text{eff}} = 5.0 \pm 0.2\,\mu_{\text{B}}$ is attributed to a high-spin $d^4$-configuration and consequently to the oxidation state +4.

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