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Note

Mössbauer Spectra of Iron(III) Iodate and Periodates

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The Mössbauer spectra of iron(III) iodate and periodate are studied at room temperature. The spectrum of iron(III) iodate shows a single line of absorption, while that of iron(III) periodate exhibits quadrupole splitting. The results are discussed in terms of ionic character and covalency of the chemical bond between iron(III) and oxy-anions.

INTRODUCTION

Iron(III) salts of oxyacids represent a large group of compounds in which the chemical bond Fe—O plays an important role. Many of these compounds have been investigated by Mössbauer spectroscopy.

In recent years, there has been considerable interest in the behaviour of all metal iodates, since many crystals of metal iodates can be applied in semiconductor and laser techniques. Abrahams et al.¹ have studied crystallographic, magnetic and some optical properties of Cr(III), Mn(II), Fe(III) and Ni(II) iodates. The crystals of anhydrous iodates of Cr, Mn, Fe, Co and β -Ni form a single isomorphous family. The iodates of Mn(II), Fe(III), α -Ni(II) and β -Ni(II) are antiferromagnetic and their Néel temperatures are 6.5, 17.0, 3.5 and 5.0 K, respectively.

In this paper the Mössbauer spectra of iron(III) iodate and periodates will be presented.

EXPERIMENTAL

Anhydrous iron(III) iodate was prepared by adding ferric nitrate in 4 molar nitric acid to boiling aqueous iodic acid². The IR spectrum of Fe(IO₃)₃ prepared by us was in good agreement with the data of Dasent and Waddington³. Anhydrous iron(III) periodate was prepared with sodium meta-periodate in a strong nitric acid medium and the reaction was performed at room temperature. Iron(III) hydroxide periodate was prepared with sodium meta-periodate and equilibrated at pH 2.10. The samples were protected from atmospheric H₂O. The spectra were recorded by the standard Mössbauer equipment. The Mössbauer source was ⁵⁷Co in Pt. The velocity scale was calibrated by using an α -iron foil as a standard absorber.

RESULTS AND DISCUSSION

The results of Mössbauer studies of iron (III) iodate and periodates are shown in Figures 1 and 2 and Table I. A single resonance line was observed in the spectrum of iron (III) iodate: this line shows a chemical isomer shift of $+ 0.13 \pm 0.03$ mm/s at room temperature and another one of 0.17 ± 0.03 mm/s

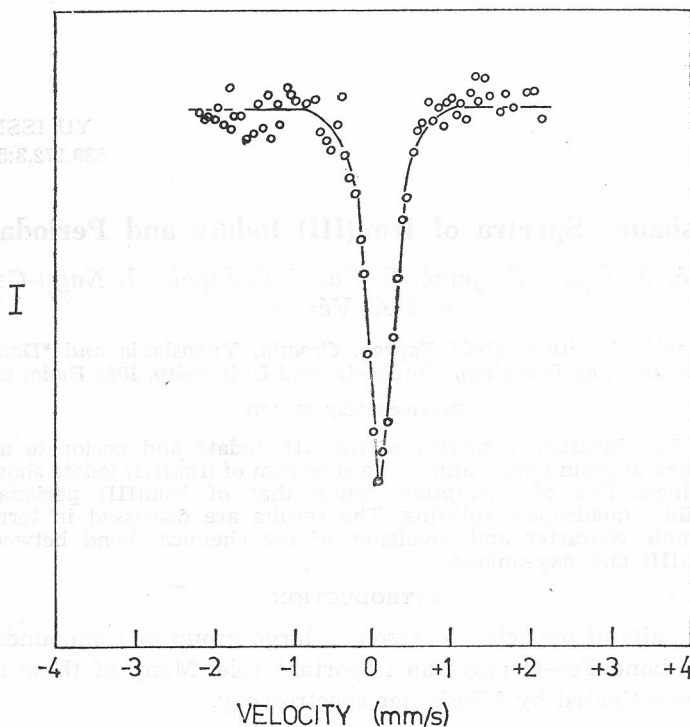


Figure 1. The Mössbauer spectrum of iron(III) iodate at room temperature.

at the temperature of liquid nitrogen. The value of the isomer shift indicates the possible ionic character of iron(III). The lack of quadrupole splitting indicates high symmetry of this compound. This feature may be accounted for by the presence of the Fe(III) ion and by the fact that the electric field gradient receives no contributions from the lattice. The lower isomer shift for iron(III) periodate shows that the *s* electron density increases at the iron nucleus and this may be interpreted by a covalency effect of the Fe—O—IO₃ bond. The ap-

TABLE I

The Mössbauer Parameters of Iron(III) Iodate and Periodates at Room Temperature

Compound	$\delta/\text{mm/s}$ (± 0.03)	$\Delta/\text{mm/s}$ (± 0.03)
Fe(IO ₃) ₃	+0.13	0.00
Fe(IO ₄) ₃	+0.01	0.73
Fe(OH)(IO ₄) ₂	+0.05	0.78
*Fe(OH)(IO ₄) ₂	+0.22	0.81

* in contact with air for 45 days

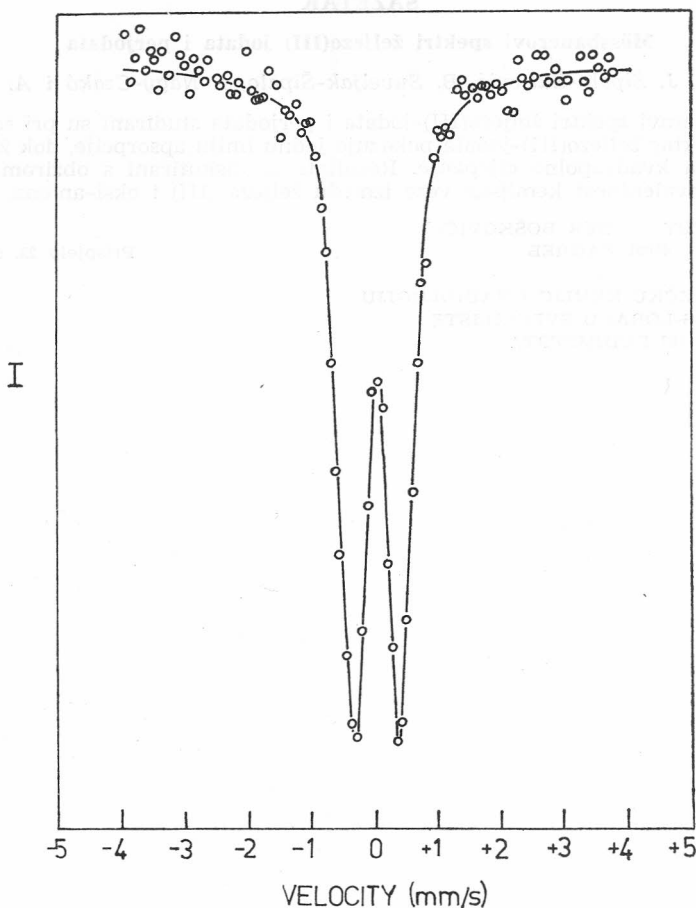


Figure 2. The Mössbauer spectrum of iron(III) periodate at room temperature.

pearance of quadrupole splitting of iron(III) periodate also indicates, that the electronic structure of the iron atoms is not symmetrical and the influence of oxy-anion on the $3d^5$ electrons is more pronounced than in the case of iron(III) iodate. In comparison with iron(III) periodate, the Mössbauer parameters of iron(III) hydroxide periodate have not changed significantly and it means that there is no essential influence of the hydroxide group on the properties of a chemical bond between the iron and the periodate anion. Iron(III) hydroxide periodate in contact with air for 45 days shows a higher isomer shift. The presence of absorbed water molecules in the inner ligand sphere of iron(III) increases the isomer shift to $+0.22 \pm 0.3$ mm/s.

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SAŽETAK**Mössbauerovi spektri željezo(III) jodata i perjodata**

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Mössbauerovi spektri željezo(III)-jodata i perjodata studirani su pri sobnoj temperaturi. Spektar željezo(III)-jodata pokazuje jednu liniju apsorpcije, dok željezo(III)-perjodat ima kvadrupolno cijepanje. Rezultati su diskutirani s obzirom na ionski karakter i kovalentnost kemijske veze između željeza (III) i oksid-aniona.

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