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XANES AND CRYSTAL FIELD SPECTROSCOPY OF FIVE-COORDINATED NICKEL(II) IN POTASSIUM-NICKEL PHOSPHATE

L. GALOISY and G. CALAS Laboratoire de Minéralogie-Cristallographie, Universités de Paris 6 et 7 et IPGP URA CNRS 09, 75251 PARIS Cedex 05, France

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ABSTRACT

The first spectroscopic data on KNiPO₄ used as reference compound for 5coordinated nickel in crystalline oxide compounds are presented. The Ni-K edge Xray Absorption Near Edge Structure (XANES) spectrum is compared to those of 4and 6-coordinated Ni in NiCr₂O₄ and CaNiSi₂O₆, respectively. The intensity of the pre-edge increases from 6- to 4-coordination while that of the main-edge decreases. Both features are thus sensitive indicators of the Ni coordination state. Crystal field spectra are also different for the three nickel coordination states. The KNiPO₄ crystal field spectrum exhibits a position and relative intensity of the absorption bands similar to those found in the spectra of pentacordinated Ni complexes. They are interpreted using the electron energy level diagram of Ni(II), in a distorted square pyramid crystal field. Criteria for the use of XANES and crystal field spectroscopy to characterize the presence of 5-coordinated Ni in oxide compounds are given. The similar crystal field stabilization energy encountered in 5- and 6coordinated nickel explains the stability of 5-coordinated nickel in phosphates. MATERIALS INDEX : nickel, phosphates, oxides.

1. Introduction

Pentacoordination of transition elements is observed in coordination complexes and has been extensively investigated because of its importance in many reactive intermediate species involved in chemical reactions (1-3). However, five-coordinated transition elements are more seldom in crystalline inorganic compounds. Among 3*d*-elements, nickel exists in pure 5-coordination in a few compounds among which KNiPO4 (4), and in both 5- and 6 coordination in α -Ni₂P₂O₇ (5) and BaNiP₂O₇ (6). 5-coordinated Ni has also been recently described in silicate glasses (7). Undistorted five-coordinated ions can be found either in trigonal bipyramid (TBP, D_{3h}) or square pyramid (SP, C_{4v}) geometry. However, the spectroscopic properties of five-coordinated cations may be difficult to interpret because these ions occur generally in sites of low symmetry, which correspond to the possibility of a continuous transformation from the TBP to the SP geometry by site distortion.

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Spectroscopic methods such as EXAFS are widely used to directly determine the coordination of transition elements in solids. A problem is to decipher among 5-coordinated Ni (⁽⁵⁾Ni) and a mixture of 4-coordinated (⁽⁴⁾Ni) and 6-coordinated Ni (⁽⁶⁾Ni), which give similar average Ni-O distances. X-ray Absorption Near Edge Structure (XANES) and crystal field spectra are sensitive to the local symmetry of the site occupied by Ni. The former has been used to study 5-coordinated Fe(III) (8) and Co(II) (9) in various solids and coordination complexes, as the latter has been extensively used to determine coordination complexes of pentacoordinated transition elements, among which high spin ⁽⁵⁾Ni(II) (2). We have used the complementary data given by both methods on KNiPO₄ -a compound in which nickel exists only in 5-coordination- to derive the characteristic features of ⁽⁵⁾Ni(II) surrounded by oxygen by comparison with ⁽⁴⁾NiCr₂O₄ and CaNi⁽⁶⁾Si₂O₆. Crystal field stabilization energies derived from spectroscopic measurements help explain the presence of the unsusual 5-coordination coordination state of Ni(II).

2. Experimental

2.1 Sample preparation and characterization

KNiPO4 has been prepared from mixtures of Ni-sulfate with KH₂PO4. Sintering was realized at 900°C for 20 hours in a Pt crucible, according to DURIF (pers. comm.). CaNiSi₂O₆ has been prepared by glass devitrification according to (10) and NiCr₂O₄ by solid state reaction between NiO and Cr₂O₃ at 1150°C. All samples have been characterized by electron probe microanalysis and x-ray diffraction.

2.2 Spectroscopic methods

XANES spectra of finely ground powders were recorded at the Ni K-edge in transmission mode, using the station D44 (EXAFS-4) of the LURE-DCI synchrotron source (Orsay, France). Sample thickness was optimized to avoid spectral distortion. A Si (311) double-crystal monochromator was used, providing an overall spectral resolution of 1.9 eV. The energy steps were 0.15 eV for the pre-edge region and 0.5 eV for the main part of the edge, with 3 sec accumulation time. Energy calibration was repeatedly checked and is accurate within 0.3 eV. Absorbance was normalized to the atomic absorption above the absorption threshold, extracted by a polynomial fit of EXAFS. The position of the XANES features was determined with first and second derivative functions, after a smoothing using a second order polynomial function.

Crystal field spectra have been recorded at room temperature between 4000 and 30000 cm⁻¹, with an UV-Visible-NIR computerized 2300 CARY spectrophotometer. Samples were prepared as finely ground powders deposited on aluminum sample holders. Diffuse reflectance values (R) were obtained by reference to halon and converted into a remission function F(R) using the Kubelka-Munk formalism. The remission function, already used for other Ni-compounds (7, 11), is proportional to sample absorbance. Crystal field spectra are presented after conversion of wavelengths into wavenumbers and baseline correction.

3. Results and interpretation

3.1 Structural data

In addition to a different coordination geometry, 5-coordinated Ni (⁽⁵⁾Ni) presents Ni-O distances which are intermediate between those of 6-coordinated Ni (⁽⁶⁾Ni) and 4-coordinated Ni (⁽⁴⁾Ni). Ni occurs in 5-coordination in KNiPO₄ and occupies a distorted square pyramid with the following Ni-O distances: 1.95, 1.99, 2.00, 2.08 and 2.18Å (4). The average Ni-O distance is $d(\overline{^{(5)}Ni-O}) = 2.040$ Å and $\sigma=0.082$ Å. This $d(\overline{^{(5)}Ni-O})$ distance is larger than in other ⁽⁵⁾Ni crystalline compounds such as α -Ni₂P₂O₇ in which ⁽⁵⁾Ni occurs also in a square pyramid with $d(\overline{^{(5)}Ni-O}) = 2.005$ Å and $\sigma=0.048$ Å (5). $d(\overline{Ni-O})$ distances are 2.07Å and 1.95Å in Ca⁽⁶⁾NiSi₂O₇ and ⁽⁴⁾NiCr₂O₄, respectively.

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3.2 XANES data

XANES may be divided into two regions (see 12, 13): the first one corresponds to low photoelectron kinetic energies, in which electronic transitions occur from core levels to the bound empty states. It includes the pre-edge and the rising slope of the main edge. At higher photoelectron kinetic energy, the second region corresponds to a multiple scattering of the photoelectrons excited in the continuum. It includes the shape resonance and the multiple resonance features which may be observed in the first tens of eV above the absorption threshold.

3.2.1 Transitions to bound states

In K edge XANES spectra, a weak pre-edge is observed at about 8326 eV, a value which does

not vary with the coordination number. This pre-edge corresponds to transitions of core electrons towards the first empty 3d-like levels (feature A, Fig. 1). As Ni²⁺ is a d⁸ cation, it has almost filled



FIG. 1.

Normalized Ni-K edge XANES spectra of three Ni-compounds. From top to bottom: $Ca^{(6)}NiSi_2O_6$, $K^{(5)}NiPO_4$ and ${}^{(4)}NiCr_2O_4$.

3*d*-orbitals and the K edge pre-edge is less intense than in lower Z transition elements because of a lower transition probability. This low intensity precludes a fitting of the pre-edge with Lorentzian components as for Fe-compounds (14). Only one electronic transition is expected from the *ls*-level, to e_g and t_2 states for Ni²⁺ in 6- and 4-coordination. In octahedral symmetry, this transition is dipole-forbidden and, as only a quadrupolar transition occurs, the pre-edge has a low relative intensity. In tetrahedral symmetry, this transition is dipole allowed. Dipolar transitions are also allowed in 5-coordination. The presence of dipolar transitions in non-centrosymmetric sites explains the enhancement of pre-edge intensity in ⁽⁵⁾- and ⁽⁴⁾Ni XANES (Table 1), as already observed in ⁽⁴⁾Fe- (14) and ⁽⁵⁾Fe-compounds (8). *d-p* hybridization also explains the higher pre-edge intensity in tetrahedral sites. A shoulder B is present on the main edge slope but is weaker in the KNiPO4 spectrum in which it is only detected on the second derivative. The B feature shifts to higher energy from ⁽⁴⁾- to ⁽⁵⁾- and ⁽⁴⁾Ni (from 8336 eV to 8337 and 8339 eV) as in Fe(III) compounds (8). This transition may be assigned to a transition to a *4p*-like level.

3.2.2 Multiple scattering events

The shape resonance corresponds to the superposition of multiple scattering (MS) resonances of the different orders. As a consequence, a site distortion prevent the various MS contributions from being in phase and the shape resonance will be split, as in CaNiSi₂O₆.

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In highly symmetric structures, such as NiCr₂O₄ spinel, XANES MS resonances partly arise from the contribution of atomic shells located beyond the Ni-coordination shell. Such MS features cannot be related unequivocally to the coordination geometry of nickel. The position of the shape resonance is the same in CaNiSi₂O₆ and KNiPO₄, but is shifted by 5eV towards higher energy in NiCr₂O₄.

TABLE 1					
Intensity of the pre-edge and main-edge XANES features.					

	CaNiSi2O6	NiCr2O4	KNiPO4
pre-edge	0.035	0.13	0.045
main-edge	1.7	1.37	1.53

This is explained by the inverse relationship between interatomic distances and the position of MS resonances (8, 16), as Ni-O distances are similar in CaNiSi₂O₆ and KNiPO₄ but are reduced by about 0.1Å in NiCr₂O₄. Another important variation concerns the intensity of the shape resonance which decreases from ⁽⁶⁾- to ⁽⁵⁾- and ⁽⁴⁾Ni (Table 1). This is expected from an increasing *p-d* hybridization from 6- to 4-coordination which decreases the transition probability of the electric dipole transitions from the *ls*-ground state (9).

3.3 Crystal field spectra

The crystal field spectrum of ⁽⁵⁾Ni in KNiPO₄ (Fig.2) shows three main groups of absorption bands as $^{(6)}$ Ni in CaNiSi₂O₆ (7) and $^{(4)}$ Ni in β -Al₂O₃:Ni (15), a general property of high spin Ni²⁺ (17), first, an unsplit transition near 5000 cm⁻¹ occurs at a similar position in (4)Ni with the same linewidth (1500 cm⁻¹ wide in β -Al₂O₃:Ni) and almost twice narrower than the crystal field transition of $^{(6)}$ Ni in CaNiSi₂O₆ (2700 cm⁻¹). This small linewidth is due to the weakly antibonding character of the molecular orbitals located above the non-bonding orbitals in 5-coordination (1). second, the broad band near 10000 cm⁻¹ arises from partly overlapping absorption bands which impart this asymmetric band an overall linewidth larger than 3000 cm⁻¹. The most intense absorption band, at 22100 cm⁻¹, shows a shoulder at 18800 cm⁻¹ as in all ⁽⁵⁾Ni crystal field spectra because it corresponds to two distinct transitions. The position of the maximum is intermediate between that measured in ⁽⁴⁾Ni and ⁽⁶⁾Ni spectra. A narrow spin-forbidden transition $({}^{3}B({}^{3}F) \rightarrow {}^{1}A_{1}({}^{1}D))$ is observed at 13600 cm⁻¹. There is a good agreement between the experimental position of the optical transitions and the values predicted using the electron energy levels diagrams of Ciampolini (2) (Table 2), by adjusting the values of the crystal field splitting parameter Dq, the O_{bas} -Ni- O_{ap} angle α (O_{bas} and O_{ap} represent basal and apical oxygen, respectively), the Racah parameter B and the radial integrals B2 and B4. The crystal field splitting has been assumed to be the same for the basal (D_{qbas}) and apical (D_{qap}) oxygen ligands. The relative intensity of the two ³P components depends on Ni-site symmetry because the low wavenumber component arises from a symmetry-forbidden transition (2). The same argument holds for the transitions to the ${}^{3}B_{2}$ and ${}^{3}A_{2}(F)$ levels and explains the low intensity of the component at 8300 cm⁻¹.

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4. Discussion

The coexistence of $(^{4})$ Ni and $(^{6})$ Ni gives average d(Ni-O) distances close to d($^{(5)}$ Ni-O) distances. Structural data from spectroscopic methods such as EXAFS need thus to be completed by symmetry-sensitive methods such as XANES and crystal field spectroscopy. As already observed for $^{(5)}$ Fe³⁺ (8), XANES spectroscopy provides the possibility of identifying 5-coordinated ions.



FIG. 2.

Crystal field spectrum of KNiPO₄. The transitions observed in CaNiSi₂O₆ (O) and NiCr₂O₄ (T) are shown at the top and bottom, respectively. Forbidden transitions have been shown in italic in the three Ni-coordination states.

TABLE 2Optical transitions of (5)Ni²⁺ in KNiPO4.

T	ransitions	Predicted ⁽¹⁾ (cm ⁻¹)	Observed (cm ⁻¹)
	³ E(F) ³ B ₂ , ³ A ₂ (H	4500 F) 8700	4800 8300
$^{3}B_{1}(F)-$	\rightarrow ³ E(F)	11300	10700
	$^{3}A_{2}(P)$	19500	18800
	$^{3}E(P)$	22200	22100

(1) Using Dq_{bas}= Dq_{ap}=1000 cm⁻¹, α = 105°, B2/B4=2.0 and B= 825 cm⁻¹.

In the absence of features peculiar to 5-coordination, the intensity of both pre-edge and main edge features is a reliable indication of the nickel coordination. In ⁽⁵⁾Ni K-edge XANES spectra, this

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intensity is intermediate between that observed in ⁽⁴⁾Ni and ⁽⁶⁾Ni and is thus sensitive to the noncentrosymmetric character of the 5-coordination. XANES provides a quantitative method to decipher among ⁽⁵⁾Ni, ⁽⁶⁾Ni and ⁽⁴⁾Ni, and has been used recently to detect the presence of ⁽⁵⁾Ni in Ni-bearing silicate glasses (7, 18). ⁽⁵⁾Ni crystal field spectra present a higher number of allowed transitions -five and six in TBP and SP sites, respectively- than undistorted ⁽⁶⁾Ni and ⁽⁴⁾Ni for which only three optical transitions are allowed.





3a (left). Electron energy level diagram for $^{(5)}$ Ni in a square pyramidal field (with $\alpha = 100^{\circ}$) (after (2), modified); 3b (right) Splitting of the 3*d*-orbitals in a square pyramid, as compared to the splitting in an octahedral field (only the three unpaired electrons acting in the crystal field stabilization energy have been represented) (after (3)).

The spectra of $^{(5)}$ Ni in KNiPO₄ is similar to those observed in coordination complexes (2) and may be interpreted using the same electron energy level diagrams (Fig. 3a). The most peculiar characteristics of $^{(5)}$ Ni crystal field spectra are: (i) the presence of an unsplit narrow transition near

5000 cm⁻¹ because of the low slope of the ${}^{3}E(F)$ level relative to the ${}^{3}B_{1}(F)$ ground level; (ii) an intense absorption band near 22000 cm⁻¹, at a position intermediate between that measured in ${}^{(4)}Ni$ and ${}^{(6)}Ni$ spectra, split because of the existence of two separate ${}^{3}A_{2}(P)$ and ${}^{3}E(P)$ levels in ${}^{(5)}Ni$; (iii) a broad transition near 8000-10000 cm⁻¹ corresponding to three partly resolved, overlapping transitions. The two absorption bands occurring at low wavenumber have thus strongly different linewidths in ${}^{(5)}Ni$ by contrast to ${}^{(6)}Ni$ and ${}^{(4)}Ni$ in which their linewidths are similar. Indeed, in 6-and 4-coordination the two absorption bands occurring at low wavenumber correspond to only one electronic transition.

5. Conclusions

Divalent nickel receives a stronger crystal field stabilization energy (CFSE) in octahedral coordination than in 4-coordination which explains why 6-coordination is the most common coordination state of this cation. CFSE is 12Dq and 10Dq for ⁽⁶⁾Ni and ⁽⁵⁾Ni, respectively, Dq being the crystal field splitting parameter (Fig. 3b). This small difference explains the existence of ⁽⁵⁾Ni as a reactive intermediate in chemical reactions involving ligand exchange (3). By using the

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crystal field value used for interpreting the crystal field spectrum of KNiPO₄ and the value of the low energy transition (i.e. crystal field transition) observed in CaNiSi₂O₆, the calculated CFSE is 117.8 kJ.mole⁻¹ in CaNiSi₂O₆ and 119 kJ.mole⁻¹ in KNiPO₄. The CFSE of divalent Ni is thus similar in these two crystalline compounds despite the different Ni-coordination. This explains why ⁽⁵⁾Ni is encountered in other phosphates (see Introduction). The similar CFSE of ⁽⁵⁾Ni and ⁽⁶⁾Ni explains also the analogy of the phase relations in Mg₂P₂O₇ and Ni₂P₂O₇. Both systems have a low temperature form in which both 5- and 6-coordinated cations coexist and high temperature phases which contain only 6-coordinated cations. The similarity of the transformations encountered in both systems shows that CFSE does not play he most important role in the phase transition in favoring the phases which contain exclusively ⁽⁶⁾Ni.

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