

Synchrotron-based far-infrared spectroscopy of nickel tungstate

A. Kalinko^{1,2}, A. Kuzmin¹, P. Roy³, and R.A. Evarestov⁴

¹*Institute of Solid State Physics, University of Latvia, 8 Kengaraga Str., Riga LV-1063, Latvia*
E-mail: a.kuzmin@cfi.lu.lv

²*Universität Paderborn, Naturwissenschaftliche Fakultät, Department Chemie*
100 Warburger Straße, Paderborn 33098, Germany

³*Synchrotron SOLEIL, l'Orme des Merisiers, Saint-Aubin, BP 48, Gif-sur-Yvette 91192, France*

⁴*Department of Quantum Chemistry, St. Petersburg University*
26 Universitetskiy Prospekt, Stary Peterhof 198504, Russia

Received January 25, 2016, published online May 25, 2016

Monoclinic antiferromagnetic NiWO₄ was studied by far-infrared (30–600 cm⁻¹) absorption spectroscopy in the temperature range of 5–300 K using the synchrotron radiation from SOLEIL source. Two isomorphous CoWO₄ and ZnWO₄ tungstates were investigated for comparison. The phonon contributions in the far-infrared range of tungstates were interpreted using the first-principles spin-polarized linear combination of atomic orbital calculations. No contributions from magnetic excitations were found in NiWO₄ and CoWO₄ below their Néel temperatures down to 5 K.

PACS: **78.30.-j** Infrared and Raman spectra;
71.15.-m Methods of electronic structure calculations.

Keywords: NiWO₄, CoWO₄, ZnWO₄, infrared spectroscopy, first-principles calculations.

Introduction

Synchrotron light sources generate radiation with high flux and brilliance, which spans a wide range of electromagnetic spectrum, including its far-infrared part. Therefore, they are intensively used nowadays in infrared (IR) spectroscopy to probe vibrational properties of single crystalline [1,2], microcrystalline [2,3] and nanocrystalline materials [4–7]. Besides that infrared spectrum can contain information on magnetic excitations, which were observed, for example, in antiferromagnetic metal oxides as CoO, NiO and solid solutions Ni_cMg_{1-c}O and Co_cMg_{1-c}O [2,8]. Here synchrotron-based IR spectroscopy is applied to more complex binary metal oxide such as nickel tungstate (NiWO₄). Recent interests on NiWO₄ have been stimulated by its applications as a catalyst [9,10], in supercapacitors [10,11] and light-controlled bipolar resistive switching devices [12] as well as by numerous possibilities to produce it in nanostructured form [13–20].

The vibrational properties of NiWO₄ in the mid-infrared range 400–2000 cm⁻¹ were studied previously in [21–23]. However, the magnetic structure of NiWO₄ single crystal,

having the Néel temperature $T_N = 67$ K, was probed at 5 K by IR absorption spectroscopy only in Ref. 24. Two antiferromagnetic resonance (AFMR) modes at 17.9 and 22.4 cm⁻¹ were identified, and the third magnetic band was observed at 119 cm⁻¹: a value close to the doubled exchange energy [24]. It was found in [25] for cobalt (CoF₂, CoWO₄) and manganese (MnCO₃, MnF₂, RbMnF₃, KMnF₃) containing compounds that the maximum frequency in the spin-wave spectrum, estimated from the AFMR follows a linear dependence on the Néel temperature. Applying the same procedure to nickel compounds (NiF₂, KNiF₃, NiO), one can estimate a value for NiWO₄ close to 108 cm⁻¹, and thus the value of the doubled exchange energy ~ 216 cm⁻¹, which is nearly two times larger than proposed from AFMR measurements in [24].

In this study we have performed a temperature dependent (5–300 K) far-infrared (30–600 cm⁻¹) study of polycrystalline NiWO₄ tungstate using the synchrotron radiation from SOLEIL source [26]. A comparison with isostructural non-magnetic ZnWO₄ and antiferromagnetic CoWO₄ ($T_N = 55$ K) compounds and first-principles linear combination of atomic orbital (LCAO) calculations was

used to assign unambiguously the phonon bands with the aim to find possible magnetic excitations [24] and their temperature dependence in antiferromagnetic NiWO₄ phase.

Experimental and calculation details

AWO₄ (A = Co, Ni, Zn) polycrystalline powders were synthesized by co-precipitation technique [27] by mixing the aqueous solutions of A(NO₃)₂·6H₂O and Na₂WO₄·2H₂O salts and post-annealing the precipitate at 800–900°C for 8 hours. The phase purity of the samples was confirmed by x-ray diffraction.

The infrared measurements were performed using the SOLEIL synchrotron light at AILES (advanced infrared line exploited for spectroscopy) beamline [26] in transmission mode. Far-IR spectra were recorded under vacuum in the range 30–600 cm⁻¹ using a Bruker IFS 125 MR Fourier transform spectrometer combined with a bolometer. The temperature range was 5–300 K with variable step. Isomorphous ZnWO₄ and CoWO₄ compounds were measured for comparison. Polycrystalline sample powders were milled in agate mortar, uniformly mixed with 100 mg polyethylene powder and pressed into pellets.

To interpret infrared spectra, the first-principles LCAO calculations of the phonon frequencies in ZnWO₄ and CoWO₄ were performed using the direct (frozen phonon) method by the CRYSTAL09 code [28], whereas the results for NiWO₄ were taken from our work [29]. The accuracy in the evaluation of the Coulomb and exchange series was controlled by a set of tolerances, set at 10⁻⁸, 10⁻⁸, 10⁻⁸, 10⁻⁸, 10⁻¹⁶, to provide high numerical accuracy. The Monkhorst–Pack scheme [30] for 8×8×8 k-point mesh in

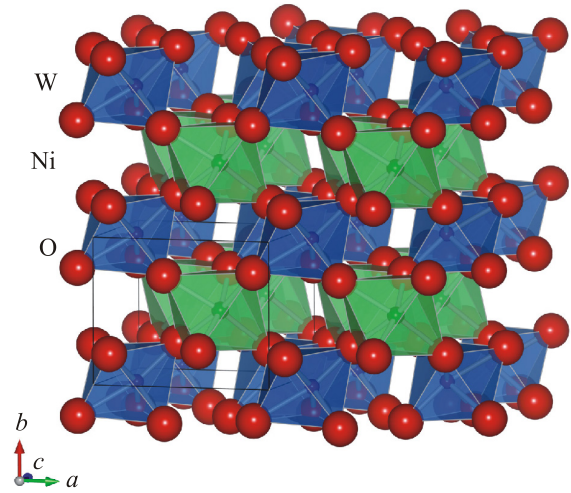


Fig. 1. (Color online) Crystal structure of woframite-type NiWO₄. Crystallographic unit cell is indicated.

the Brillouin zone was applied. The SCF calculations were performed for hybrid Hartree–Fock (HF)/density functional (DFT) Hamiltonian (PBE0-type [31]) with 13% of HF contribution, because they gave the best agreement with the experimental phonon frequencies of NiWO₄ [29]. More details on the calculations can be found in Ref. 32.

Results and discussion

Nickel tungstate has monoclinic wolframite-type structure (Fig. 1) with two formula units per unit cell (space group *P2/c* (13)). It is build up from NiO₆ and WO₆ octahedra joined by the edges, which form zig-zag chains along the *c* axis [33]. At ambient conditions NiWO₄ exists

Table 1. Frequencies and intensities of infrared active modes in AWO₄ (A = Co, Ni, Zn) calculated from first-principles using the LCAO method with hybrid DFT/HF functional PBE0-13%

NiWO ₄		CoWO ₄		ZnWO ₄	
Frequency, cm ⁻¹	Intensity	Frequency, cm ⁻¹	Intensity	Frequency, cm ⁻¹	Intensity
187	2.54	170	2.26	141	12.11
219	8.83	199	10.47	151	10.95
226	3.49	208	7.03	174	10.74
267	34.07	250	22.61	247	35.82
280	20.36	271	40.53	262	33.68
313	35.75	301	24.95	279	0.99
331	30.02	326	24.23	320	9.58
349	8.41	344	6.88	340	16.18
446	8.76	434	5.15	431	4.16
457	8.95	444	18.38	458	8.02
514	19.80	505	23.89	516	18.54
560	97.25	535	98.43	554	100.00
677	45.47	651	51.43	661	46.17
745	100.00	742	100.00	762	83.65
862	14.69	854	14.40	866	12.67

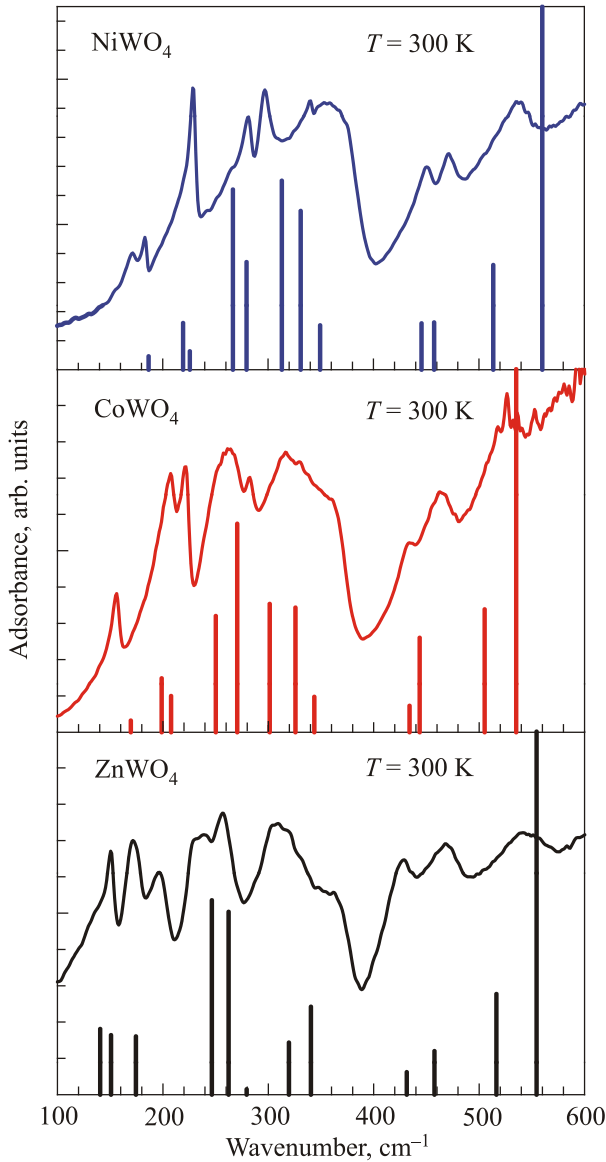


Fig. 2. (Color online) Far-IR absorption spectra measured at $T = 300$ K for isostructural wolframite-type compounds AWO_4 ($A = \text{Co}, \text{Ni}, \text{Zn}$). Spectra are vertically shifted for clarity. Vertical bars indicate the phonon modes from the first-principles LCAO calculations.

in the paramagnetic phase, while below the Néel temperature $T_N = 67$ K the spins on nickel ions order antiferromagnetically [34] leading to the doubling of the crystallographic unit cell along the a axis.

The atomic and electronic structures as well as phonon properties in Γ -point of the Brillouin zone of NiWO_4 were studied in details by us using the first-principles spin-polarized LCAO calculations based on the hybrid HF/DFT scheme [29]. The obtained results were in good agreement with the available experimental data. In particular, we found that a correct account for the magnetic ordering gives also the best results for the vibration frequencies probed by Raman spectroscopy [29]. Therefore, we have

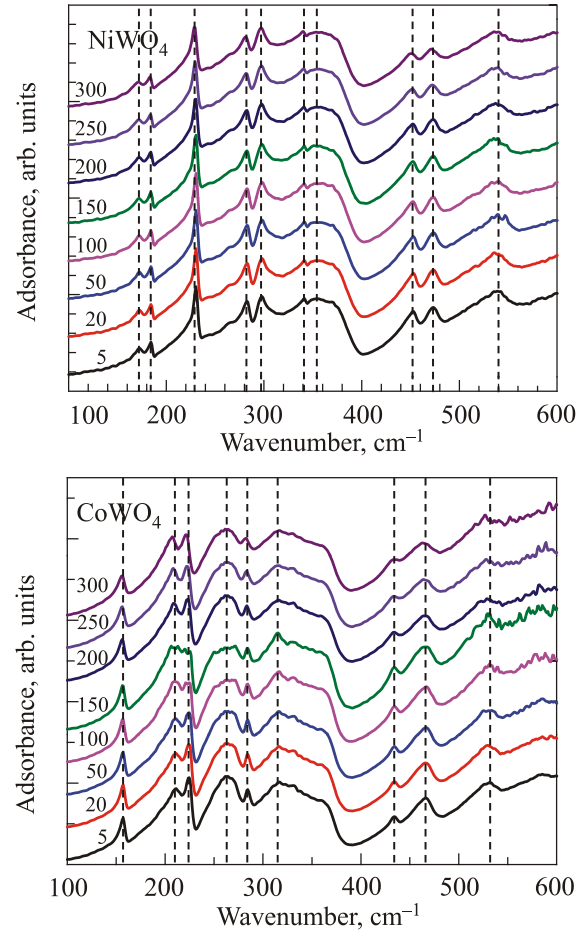


Fig. 3. (Color online) Temperature dependent (5–300 K) far-IR absorption spectra of NiWO_4 . The positions of vibrational bands are indicated by vertical dashed lines.

utilized similar approach to calculate phonon modes in CoWO_4 with the Néel temperature $T_N = 55$ K [35], whereas non-magnetic LCAO calculations were performed for ZnWO_4 .

The group theory predicts 36 lattice modes for space group $P2_1/c$: 3 acoustic modes, 18 Raman active modes and 15 IR active modes. Twelve IR active modes ($5A_u + 7B_u$) are observed experimentally in isostructural NiWO_4 , CoWO_4 and ZnWO_4 below 600 cm^{-1} in Fig. 2 and are compared with the theoretical ones (vertical bars) obtained from the first-principles spin-polarized LCAO calculations [29,36]. The position and the height of the bars indicate calculated mode frequency and intensity, respectively. Full set of calculated frequencies and intensities for all IR-active modes in tungstates is given in Table 1. While one can notice a good qualitative agreement between the theory and the experiment in Fig. 2, the absolute values of vibrational frequencies can differ by $\pm 25 \text{ cm}^{-1}$.

The vibrational properties of NiWO_4 in the mid-infrared range $400\text{--}2000 \text{ cm}^{-1}$ were studied previously in [21–23]. Our temperature dependence of the far-IR absorption spectrum of NiWO_4 is shown in Fig. 3 in comparison

with the results for CoWO₄. Upon temperature increase from 5 K to 300 K, the only noticeable changes are observed in the positions of vibrational bands. They shift slightly due to lattice expansion and anharmonic effects that reflects the rigidity of the tungstate lattice. No new bands are observed in Fig. 3 that confirms the absence of any structural phase transition in NiWO₄ and CoWO₄ at atmospheric pressure from 5 to 300 K. Finally, we did not observe in our polycrystalline NiWO₄ sample any absorption related to magnetic excitations at 119 cm⁻¹, which was found previously in [24]. Also no AFMR modes, observed in [24] at 67 and 79.3 cm⁻¹, were found in IR-spectra of CoWO₄.

At the end, we note that this article is another example of the use of synchrotron radiation, which we have used in our previous papers for study of the VUV spectroscopic properties of NiWO₄ [37,38].

Conclusions

Temperature dependent (10–300 K) far-infrared (30–600 cm⁻¹) study of polycrystalline monoclinic NiWO₄ was performed in comparison with isomorphous CoWO₄ and ZnWO₄ tungstates using the synchrotron radiation from SOLEIL source. The phonon contributions into far-IR absorption spectra of tungstates were successfully interpreted using the first-principles spin-polarized LCAO calculations. Weak temperature dependence of the far-IR absorption in NiWO₄ and CoWO₄ was found and attributed to the rigidity of their lattices. At the same time, no magnetic contributions were observed down to 5 K in both tungstates.

This work was supported by Latvian Science Council Grant No. 187/2012. The infrared measurements have been supported by synchrotron SOLEIL (Proposal 20110863).

- I. Bolesta, S. Velgosh, Y. Datsiuk, I. Karbovnyk, V. Lesivtsiv, T. Kulay, A.I. Popov, S. Bellucci, M. Cestelli Guidi, and A. Marcelli, *Radiat. Meas.* **42**, 851 (2007).
- N. Mironova-Ulmane, U. Ulmanis, A. Kuzmin, I. Sildos, M. Pars, M. Cestelli Guidi, M. Piccinini, and A. Marcelli, *Phys. Solid State* **50**, 1657 (2008).
- I. Karbovnyk, S. Piskunov, I. Bolesta, S. Bellucci, M. Cestelli Guidi, M. Piccinini, E. Spohr, and A.I. Popov, *Eur. Phys. J. B* **70**, 443 (2009).
- C. Balasubramanian, S. Bellucci, G. Cinque, A. Marcelli, M. Cestelli Guidi, M. Piccinini, A. Popov, A. Soldatov, and P. Onorato, *J. Phys.: Condens. Matter* **18**, S2095 (2006).
- S. Bellucci, A.I. Popov, C. Balasubramanian, G. Cinque, A. Marcelli, I. Karbovnyk, V. Savchyn, and N. Krutyak, *Radiat. Meas.* **42**, 708 (2007).
- A. Voloshynovskii, P. Savchyn, I. Karbovnyk, S. Myagkota, M. Cestelli Guidi, M. Piccinini, and A.I. Popov, *Solid State Commun.* **149**, 593 (2009).
- P. Savchyn, I. Karbovnyk, V. Vistovskyy, A. Voloshynovskii, V. Pankratov, M. Cestelli Guidi, C. Mirri, O. Myahkota, A. Riabtseva, N. Mitina, A. Zaichenko, and A.I. Popov, *J. Appl. Phys.* **112**, 124309 (2012).
- N. Mironova-Ulmane, A. Kuzmin, M. Cestelli Guidi, M. Piccinini, and A. Marcelli, *Phys. Status Solidi C* **2**, 704 (2005).
- J.M. Quintana-Melgoza, J. Cruz-Reyes, and M. Avalos-Borja, *Mater. Lett.* **47**, 314 (2001).
- U. Nithiyantham, S.R. Ede, S. Anantharaj, and S. Kundu, *Cryst. Growth Des.* **15**, 673 (2015).
- L. Niu, Z. Li, Y. Xu, J. Sun, W. Hong, X. Liu, J. Wang, and S. Yang, *ACS Appl. Mater. Interfaces* **5**, 8044 (2013).
- B. Sun, W. Zhao, L. Wei, H. Li, and P. Chen, *Chem. Commun.* **50**, 13142 (2014).
- P.S. Pandey, N.S. Bhave, and R.B. Kharat, *Electrochim. Acta* **51**, 4659 (2006).
- Y. Bi, H. Nie, D. Li, S. Zeng, Q. Yang, and M. Li, *Chem. Commun.* **46**, 7430 (2010).
- A. Anspoks, A. Kalinko, J. Timoshenko, and A. Kuzmin, *Solid State Commun.* **183**, 22 (2014).
- Y. Jiang, B. Liu, Z. Zhai, X. Liu, B. Yang, L. Liu, and X. Jiang, *Appl. Surf. Sci.* **356**, 273 (2015).
- R. Karthiga, B. Kavitha, M. Rajarajan, and A. Suganthi, *Mater. Sci. Semicond. Proc.* **40**, 123 (2015).
- G. Nagaraju, R. Kakarla, S.M. Cha, and J.S. Yu, *Nano Res.* **8**, 3749 (2015).
- K.P.F. Siqueira and A. Dias, *J. Nanopart. Res.* **13**, 5927 (2011).
- Y. Wang and Y. Wang, *Adv. Mater. Res.* **311**, 545 (2011).
- M.N. Mancheva, R.S. Iordanova, D.G. Klissurski, G.T. Tyuliev, and B.N. Kunev, *J. Phys. Chem. C* **111**, 1101 (2007).
- A.L.M. de Oliveira, J.M. Ferreira, M.R.S. Silva, G.S. Braga, L.E.B. Soledade, M.A.M.M. Aldeiza, C.A. Paskocimas, S.J.G. Lima, E. Longo, A.G. de Souza, and I.M.G. dos Santos, *Dyes Pigments* **77**, 210 (2008).
- A.L.M. de Oliveira, J.M. Ferreira, M.R.S. Silva, S.C. de Souza, F.T.G. Vieira, E. Longo, A.G. Souza, and I.M.G. Santos, *J. Therm. Anal. Calorim.* **97**, 167 (2009).
- V. Eremenko, V. Naumenko, A. Zvyagin, and A. Maslennikov, *IEEE T. Microw. Theory* **22**, 1069 (1974).
- V.V. Eremenko and V.M. Naumenko, *ZhETF Pis'ma* **7**, 416 (1968).
- P. Roy, M. Rouzies, Z. Qi, and O. Chubar, *Infrared Phys. Techn.* **49**, 139 (2006).
- A. Kalinko and A. Kuzmin, *J. Lumin.* **129**, 1144 (2009).
- R. Dovesi, V.R. Saunders, R. Roetti, R. Orlando, C.M. Zicovich-Wilson, F. Pascale, B. Civalleri, K. Doll, N.M. Harrison, I.J. Bush, P. D'Arco, and M. Llunell, *CRYSTAL09 User's Manual*, University of Torino (2009).
- A. Kuzmin, A. Kalinko, and R.A. Evarestov, *Centr. Eur. J. Phys.* **9**, 502 (2011).
- H.J. Monkhorst and J.D. Pack, *Phys. Rev. B* **13**, 5188 (1976).
- J.P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).

32. A. Kuzmin, A. Kalinko, and R.A. Evarestov, *Acta Mater.* **61**, 371 (2013).
33. R.O. Keeling, *Acta Crystallogr.* **10**, 209 (1957).
34. C.P. Landee and E.F. Westrum, *J. Chem. Thermodyn.* **8**, 471 (1976).
35. H. Weitzel, *Solid State Commun.* **8**, 2071 (1970).
36. A. Kalinko, A. Kuzmin, and R.A. Evarestov, *Solid State Commun.* **149**, 425 (2009).
37. A. Kalinko, A. Kotlov, A. Kuzmin, A. Pankratov, A.I. Popov, and L. Shirmane, *Centr. Eur. J. Phys.* **9**, 432 (2011).
38. A. Kuzmin, V. Pankratov, A. Kalinko, A. Kotlov, L. Shirmane, and A.I. Popov, *Fiz. Nizk. Temp.* **42**, 694 (2016) [*Low Temp. Phys.* **42**, No. 7 (2016)].