Niobium chalcogenide halides. Crystal structure and electronic structure.
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INTRODUCTION AND SUMMARY.

The aim of this investigation was to study chalcogenides and halides of niobium in the oxidation state +4 (electron configuration 4d\(^1\)). It was known that Nb\(^{4+}\) in the tetrahalides Nb\(_4\)\(\text{Y}_4\) (Y = Cl, Br, I) and in the oxide halides Nb\(\text{O}\)\(\text{Y}_2\) occurs in pairs with Nb-Nb distances in the range 3.03 to 3.31 Å, which is somewhat longer than in niobium metal (Nb-Nb = 2.86 Å); the compounds mentioned are diamagnetic semiconductors [1]. In the disulfide and diselenide Nb\(_2\)\(\text{X}_2\) (X = S, Se), in contrast, no pairs of metal atoms can be distinguished; these compounds are metallic with (nearly) temperature-independent paramagnetism [2].

We first wanted to investigate the compounds Nb\(_2\)\(\text{X}_2\) (X = S, Se; Y = Cl, Br, I) which had been reported by Beckmann and Schäfer [3]. The crystal structure of NbS\(_2\)\(\text{Cl}_2\) had been determined [4]; it showed that both the sulfur and the niobium atoms are present in pairs. The diamagnetic compound was formulated as Nb\(^{4+}\)(S\(_2\))\(^2-\)\(\text{Cl}_2^-\). The vibrational spectra of NbS\(_2\)\(\text{Y}_2\) (Y = Cl, Br, I) were studied by Madame Perrin et al [5,6].

When we started our investigation, the compounds Nb\(_2\)\(\text{X}_2\)\(\text{Y}_2\) (and Nb\(\text{X}_3\)) \(\text{Y}_3\) (Y = Cl, Br) in the gas phase) were the only niobium chalcogenide halides that had been reported. When studying the best conditions to prepare the compounds Nb\(_2\)\(\text{X}_2\)\(\text{Y}_2\) we discovered, however, a very large number (at least seventy) of new phases. Only a limited number of these phases have so far been fully characterized and studied in some detail. The results are described in this thesis.

The synthesis and structures of the compounds Nb\(_2\)\(\text{X}_2\)\(\text{Y}_2\) (X = S, Se; Y = Cl, Br, I) is described in CHAPTER 1. It was found that most of these compounds exist in two forms: a triclinic low-temperature form and a monoclinic high-temperature form. The crystal structure of triclinic NbSe\(_2\)\(\text{Cl}_2\) has been determined, that of (monoclinic) NbS\(_2\)\(\text{Cl}_2\) corrected and refined. Magnetic and electrical properties of Nb\(_2\)\(\text{X}_2\)\(\text{Y}_2\) (and of Mo\(_2\)\(\text{Cl}_2\)) are also included in CHAPTER 1. XPS and optical absorption spectra of Nb\(_2\)\(\text{X}_2\)\(\text{Y}_2\) (including the vibrational spectra of NbSe\(_2\)\(\text{Y}_2\)) are described in CHAPTERS 6, 7 and 8, respectively, the electronic structure is discussed in CHAPTER 9.

The compounds Nb\(_2\)\(\text{X}_2\)\(\text{Y}_2\) were the only compounds for which large single crystals could be obtained of a sufficiently high perfection to justify a detailed study of their optical properties. Most crystals of the other compounds were badly faulted or at least heavily twinned. For some compounds, however, it was possible to find some crystals of sufficient quality to study them by X-ray diffraction.

The structure and physical properties of the mixed-valence compound Nb\(_3\)\(\text{Se}_5\)\(\text{Cl}_7\) are described and discussed in CHAPTER 2, the XPS spectrum in CHAPTER 6; Nb\(_3\)\(\text{Se}_5\)\(\text{Br}_7\) is isotypic with the chloride.
Phases with compositions about Nb$_3$X$_{12}$Y are described in CHAPTER 5; the crystal structure of Nb$_3$Se$_{12}$I (and the isotypic bromide) has recently been reported by Meerschaut [7]. CHAPTER 5 also describes a study of phases of composition close to NbX$_3$Y, in particular of NbSe$_3$Cl; this study was performed in pleasant collaboration with Mr G. J. de Lange.

The synthesis and infrared spectra of the compounds NbX$_3$Y (X = S, Se; Y = Cl, Br) have been reported by Fowles et al [8].

As a by-product of our study we obtained single crystals of NbS$_3$ and NbOI$_2$ of sufficient quality to study their crystal structures. The determination of the structure of NbS$_3$ is reported in CHAPTER 4, the refinement of the structure of NbOI$_2$ in CHAPTER 3. While NbS$_3$ contains pairs of metal atoms, the related compound NbSe$_3$ does not [9]. The XPS spectra of these compounds are given and discussed in CHAPTER 6, as are the spectra of 2s-NbX$_2$ (X = S, Se), NbX$_2$Y$_2$ (X = S, Se; Y = Cl, Br, I), Nb$_3$Se$_5$Cl$_7$, γ-NbSe$_3$Cl and of the halides NbY$_4$ and NbY$_5$.

References

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