Valleriite, a Natural Two-Dimensional Composite: X-ray Absorption, Photoelectron, and Mössbauer Spectroscopy, and Magnetic Characterization

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ABSTRACT: Valleriite is of interest as a mineral source of basic and precious metals and as an unusual material composed of two-dimensional (2D) Fe–Cu sulfide and magnesium hydroxide layers, whose characteristics are still very poorly understood. Here, the mineral samples of two types with about 50% of valleriites from Noril’sk ore provenance, Russia, were examined using Cu K- and Fe K-edge X-ray absorption fine structure (XAFS) spectroscopy, X-ray photoelectron spectroscopy (XPS), 57Fe Mössbauer spectroscopy, and magnetic measurements. The Cu K X-ray absorption near-edge structures (XANES) spectra resemble those of chalcopyrite, however, with a higher electron density at Cu+ centers and essentially different from those of bornite CuFeS2; the Fe K-edge was less informative because of accompanying oxidized Fe-containing phases. The post-edge XANES and extended XAFS (EXAFS) analysis reveal differences in the bond lengths, e.g., additional metal–metal distances in valleriites as compared with chalcopyrite. The XPS spectra confirmed the Cu+ and Fe3+ state in the sulfide sheets and suggest that they are in electron equilibrium with (Mg, Al) hydroxide layers. Mössbauer spectra measured at room temperature comprise central doublets of paramagnetic Fe3+, which decreased at 78 K and almost disappeared at 4.2 K, producing a series of hyperfine Zeeman sextets due to internal magnetic fields arising in valleriites. Magnetic measurements do not reveal antiferromagnetic transitions known for bornite. The specific structure and properties of valleriite are discussed in particular as a platform for composites of the 2D transition metal sulfide and hydroxide (mono)layers stacked by the electrical charges, promising for a variety of applications.

INTRODUCTION

Valleriite is a mineral with an unusual structure formed by alternating quasi-monolayers of brucite-type yMg(OH)2·zAl-(OH)3 and sulfide monolayers close to CuFeS2.1–11 Found in many locations since 1960s, valleriite is not abundant and, generally, has limited commercial importance. At the same time, so-called “coppery” ores of Noril’sk ore provenance in Russia (5–8% of total deposits) contain up to 20% of valleriite, industrial values of copper, nickel, and platinum group metals.12–14 Valleriite is densely overgrown with serpentines, pyrrhotite, chalcopyrite, aluminosilicates, etc., and the beneficiation of valleriite-containing ores using froth flotation and other separation techniques is poor due to special and scarcely understood properties of valleriite and a depressing effect of serpentines. Direct extraction of metals and chemical conversion of valleriite to simple sulfide phases have been suggested but not implemented in any technologies (see ref1 and references therein). On the other hand, low-dimensional materials, such as graphene, van der Waals crystals, MAX and MXenes, transition metal dichalcogenides, and ternary chalcogenides,15–24 attract huge attention owing to their unique physical properties, including magnetic, and much efforts are being taken to discover new two-dimensional (2D) materials nowadays. Naturally occurring minerals like valleriite, which is composed of “noncommensurate” sulfide and hydroxide quasimonolayers1 with very diverse chemical, electronic and magnetic characters, may offer some clues as promising prototypes of the novel (nano)composite materials (see, for example, refs 24–26).

The composition of valleriites depends on their origin.11,27–30 The brucite-like layers, which are believed to contain some Fe2+/Fe3+ ions substituting Mg2+ and Al3+ cations in octahedral coordination to OH− anions, can be
described as \[ m[Mg, Fe(OH)_2]+n(Al, Fe)(OH)_3, \] where \( 1.3 \leq m \leq 1.6 \) and \( 0 \leq n \leq 0.3 \). The sulfide part \( Cu_2FeS_2 \) usually has \( x \) and \( y \) within the range 1 ± 0.3 or narrower; in particular, Hughes et al. have found that synthetic valleriites were stable in the range from \( [CuFeS_2]_{1.67} [Mg_{0.70}Al_{0.30}(OH)_3]_{1.35} - [Mg_{0.74}Al_{0.26}(OH)_2]_{1.34} \). X-ray diffraction (XRD) studies have confirmed that the sulfide sublattice is rhombohedral (space group \( R3m \)) with hexagonal axes \( a = 0.3792 \) nm and \( c = 0.341 \) nm; the hydroxide layers have hexagonal lattice (space group \( P\overline{3}m1 \)) with \( a = 0.307 \) nm and \( c = 1.137 \) nm. Cu and Fe atoms are considered randomly occupying all of the tetrahedral sites within a pair of close-packed atomic S layers. The hydroxide layers are believed to bear a positive electric charge caused by the substitution of \( Mg^{2+} \) with \( Al^{3+} \); correspondingly, the sulfide layers are charged negatively. The layers have been found to be partially mismatched in both natural and synthetic valleriite samples. X-ray photoelectron spectroscopy (XPS) studies suggest that the nominal oxidation states of metals in the sulfide layers seem to be \( Cu^{+} \) and \( Fe^{3+} \), similar to chalcopyrite. However, antiferromagnetic ordering is absent; room-temperature \( 57Fe \) Mössbauer spectroscopy studies have found paramagnetic signals from a series of \( Fe^{++}/Fe^{3+} \) centers preferentially coordinated with \( S \) but occurring also in the brucite-like layers, along with chalcopyrite, magnetite, and other impurities both in natural and synthetic samples.

The complex composition of natural samples makes the separation of pure vallerite and exploration of its electronic structure, chemical and physical characteristics difficult. Thermal or hydrothermal syntheses of vallerite also have yielded less than 50% of vallerite mixed with metal (hydro)oxides and sulfides. In the current research, we performed the element-specific X-ray absorption fine structure (XAFS) spectroscopy of the Cu- and Fe-K-edges, XPS, and \( 57Fe \) Mössbauer spectroscopy in conjunction with magnetic susceptibility measurements at room and cryogenic temperatures in order to elucidate the structure of vallerites in two types of mineral assemblages from the Noril’sk ore deposit. The mineral samples were thoroughly characterized using mineralogical analysis, electron microscopy, and related analytical techniques (energy dispersive X-ray (EDX), elemental mapping), XRD, transmission electron microscopy (TEM), and so on. This approach allowed to reveal, particularly, a set of magnetic hyperfine interactions involving Fe centers in the sulfide layers at reduced temperatures, which depict vallerite as a new 2D material with, among others, interesting magnetic properties. The results are also important for understanding the origin and behavior of vallerite in nature and mineral processing.

## EXPERIMENTAL SECTION

### Materials

Natural valleriites from two locations of the Talnakh deposit (Noril’sk ore field, Russia) were used in the experiments. Vallerite of the first type (vallerite-1) is mainly represented by grains associated with pyrrhotite (preferentially hexagonal \( Fe_9S_8 \), silicates, and aluminosilicates. The second type of mineral samples (vallerite-2) is composed of vallerite veins in Mg-bearing serpentines (lizardite and others) and chalcopyrite \( CuFeS_2 \). Figure 1 shows scanning electron micrographs (SEMs) of the sample sections and an example of a high-resolution TEM image of a layered vallerite nanocrystal.

### CHARACTERIZATION

**Electron Microscopy and X-ray Diffraction.** The samples were embedded in epoxy resin, polished, and characterized using scanning electron microscopy (SEM), backscattered electron imaging microanalysis (SEM–BSE), and energy-dispersive X-ray analysis (EDX) utilizing a Hitachi TM 3000 instrument operated at an acceleration voltage of 15 kV.
kV, equipped with a Bruker Quantax 70 EDX analyzer. Transmission electron microscopy (TEM) images, EDX, and selected area electron diffraction patterns (SAED) were acquired from ground samples using a JEM-2100 instrument (JEOL) operated at 200 kV. For the TEM experiment, the particles were dispersed in ethanol, and then a droplet of the suspension was placed on a carbon-coated copper grid and allowed to dry at room temperature. X-ray powder diffraction patterns were recorded using a PANalytical X’Pert Pro diffractometer with Cu Ka radiation.

**X-ray Absorption Spectroscopy.** Cu K-edge and Fe K-edge X-ray absorption near-edge structures (XANES) and extended X-ray fine structures (EXAFS) were measured at the bending magnet beamline BM23 (European Synchrotron Radiation Facility, Grenoble, France) at room temperature in the fluorescence mode using a Vortex silicon drift X-ray detector. The storage ring operated in the 1.0 bunch mode with an average current of 90 mA. X-ray irradiation was monochromatized with a double-crystal Si(111) monochromator and an Rh mirror to reject the harmonics; the size of the beam at a sample was 0.1 × 0.3 mm². The monochromator was calibrated to the first maximum in the first derivative of the Cu K-edge absorption spectrum of a metallic copper foil and the Fe K-edge spectrum of an iron foil, respectively, which were continuously collected in the transmission mode during sample measurements. The EXAFS data were collected up to 15 Å⁻¹, with a variable sampling step in energy (5 eV in the pre-edge region, 0.5 eV in the XANES region, and Δk constant in the EXAFS region with 0.03 Å⁻¹ step), and an integration time of 3 s. Typically, 2–3 specimens of each mineral were examined, and 2–3 scans were averaged for each spectrum. Both Cu K- and Fe K-edge XAFS spectra were treated applying standard procedures implemented in the Demeter software package (version 0.9.26) based on the IFEFFIT program, version 1.2.12. The k²-weighted Cu K-EXAFS oscillations were processed with the photoelectron wavevector k in the range 2.3–11.5 Å⁻¹, using a Hanning window with a sill width of 3 Å⁻¹. The Fourier transformed R-space data were windowed in the range of 1.0–2.314 and 3.082 Å for valleriites and chalcopyrite, respectively. The photoelectron threshold energy E₀ was first fitted from the data and then kept constant. The EXAFS signals were simulated utilizing a single-path scattering approach.

**X-ray Photoelectron Spectroscopy.** The photoelectron spectra presented here were recorded with a SPECS spectrometer equipped with a PHOIBOS 150 MCD9 hemispherical energy analyzer using Mg Kα radiation of the dual anode X-ray tube at an analyzer transmission energy of 20 eV for the survey spectra or 8 eV for narrow scans. The binding energies were calibrated against the C 1s line of the adventitious carbon (285.0 eV); a low-energy electron source FG 20 (SPECS), applied to eliminate heterogeneous electrostatic charging, was operated with an electron energy of 0.05 eV and a current of 10 μA. The spectra were fitted after subtraction of the Shirley-type nonlinear background using the CasaXPS software package.

**Mössbauer Spectroscopy.** Transmission Mössbauer experiments were carried out using an MC-1104Em spectrometer with a ⁵⁷Co(Rh) source; the source was kept at room temperature, while the absorber was either at the ambient temperature or cooled down to liquid nitrogen (78 K) and liquid helium (4.2 K) temperatures. The powder samples (about 3 mg/cm² of Fe in thickness) sealed with Kapton tape were attached to an Al sample holder. Isomer shifts (IS) are given relative to α-iron at room temperature. Probabilities P of the quadrupole splitting P(QS) for doublets and of magnetic hyperfine fields P(H) for sextets were first determined from the experimental spectra. In the second stage, these data were used to generate a model spectrum and then to fit the experimental spectra varying the full set of parameters. 41,42

**Magnetic Measurements.** The magnetization of vallerite samples was measured utilizing a superconducting quantum interference device (SQUID) magnetometer with a magnetic field H of 500 Oe (field-cooled [FC] and zero-field-cooled [ZFC], respectively) as the temperature varied from 4.2 to 290 K. The magnetic moment was also determined as a function of the magnetic field H in the range from −800 to 800 Oe at several temperatures. Magnetization in stronger fields was examined using a vibrating sample magnetometer with a Puzeys electromagnet in the temperature range of 78–300 K.

### RESULTS AND DISCUSSION

**X-ray Absorption Spectroscopy.** The Fe K- and Cu K-edge XANES spectra of vallerites are compared with the spectra of chalcopyrite (CuFeS₂) and bornite (Cu₅FeS₄) in Figure 2. The Fe K near-edge structures are distinct for the two vallerites due to various contents of iron- and oxygen-bearing substances. The main features in the spectra are the pre-edge peak A originating from electronic transitions from the core Fe 1s to vacant 3d states mixed with Fe 4p and S 3p or O 2p states, the white line B (7121 eV) attributed to the FeO₄ antifluorite-type subcells. The pre-edge peak A was further discussed of these spectra because of the multiphase composition of the samples. The Cu K-edge X-ray absorption spectra are more informative since vallerite is the only Cu-bearing phase in vallerite-1, and sample-2 contains comparable quantities of vallerite and chalcopyrite. The Cu K-edge XANES spectra of both vallerites resemble that of chalcopyrite with Cu⁺ in tetrahedral coordination with sulphide ions, 49–52 but not low bornite whose crystalline lattice consists of sphalerite-type and antifluorite-type subcells. The pre-edge peak A corresponds to transitions from Cu 1s to empty states having Cu 3d transitions to Fe 4p states hybridized with sulfur states in the valence band before the Cu 1s to vacant 3d states mixed with Fe 4p and S 3p or O 2p states.
In valleriites, feature A is widened and shifted to higher energy, similar to the spectrum of bornite, and the intensity of peak B at 8986.0 eV from 1s to 4p transition decreases in comparison with chalcopyrite. The changes in the position and intensity of the features can be interpreted in terms of disordering and a decrease of coordination number of Cu atoms and/or lowering the positive charge at Cu atoms relative to CuFeS₂. This concurs with the decrease of the leading peak at Cu L₃-edge at 932.6 eV attributed to Cu 2p₃/2. The post-edge maximum is widened and shifted to higher energy, which is expected to correspond with the decrease of the leading peak at Cu L₃-edge at 932.6 eV attributed to Cu 2p⁰. This is consistent with the decrease of coordination number of Cu atoms and/or lowering the positive charge at Cu atoms relative to CuFeS₂. This is particularly evident in valleriites in comparison with chalcopyrite. Also, EXAFS revealed a Cu−(Cu, Fe) bond length of 2.71 Å, which is absent in chalcopyrite but corroborates the Cu−(Cu, Fe) distance of 2.77 Å reported in ref 1. The bonds are also in agreement with those derived from the shape resonance positions in Cu K-XANES (Figure 2). A scheme illustrating the structure and bond lengths in sulfide layers of valleriite in comparison with chalcopyrite is given in Figure 4.

The Cu K-edge EXAFS results obtained for valleriites are presented in Figure 3a,b and Table S1 (Supporting Information) in comparison with chalcopyrite. The clear differences in the experimental data between the minerals are observed in the k range from 7 to 8 Å⁻¹. The model taking into account the two coordination shells of a central copper atom gives good fits of this and other features, while application of the three-shell model that includes longer Cu−S bonds does not improve the fitting. The simulation (Table S1) revealed Cu−S distances of 2.28−2.31 Å and a number Nₚ of 3.4 for the nearest S neighbors for both valleriites as compared with the values of 2.28 Å and 3.8, respectively, for chalcopyrite. The values are in reasonable agreement with the coordination numbers and interatomic distances derived from X-ray diffraction; particularly, Evans et al.¹ have found one apical (Fe, Cu)−S bond of 2.41 Å and three basal bonds of 2.30 Å for vallerite. Also, EXAFS revealed a Cu−(Cu, Fe) bond length of 2.71 Å, which is absent in chalcopyrite but corroborates the Cu−(Cu, Fe) distance of 2.77 Å reported in ref 1. The bonds are also in agreement with those derived from the shape resonance positions in Cu K-XANES (Figure 2). A scheme illustrating the structure and bond lengths in sulfide layers of valleriite in comparison with chalcopyrite is given in Figure 4.

Figure 3. (a, b) Cu K- and (c), (d) Fe K-edge EXAFS data for chalcopyrite (Cp) and the samples of vallerite-1 and 2 (val-1 and val-2): (a), (c) the k²-weighted experimental data (black lines) and the corresponding fit (red lines); (b), (d) Fourier transform magnitudes of these data and their fits in R-space (without phase corrections).

Figure 4. Fragments of a structure of vallerite in the crystallographic direction (120) and a lattice of chalcopyrite in the direction (021), and interatomic distances (Å) as determined from EXAFS. Right-hand panels show the sulfide fragments enlarged and slightly turned for clarity. S atoms are yellow, Cu atoms are blue and Fe atoms are brown. The ordered occupancy of Cu and Fe centers is conventionally shown in vallerite.

Figure 3c,d and Table S2 show the Fe K-edge EXAFS of valleriites and chalcopyrite. The substantially reduced numbers of neighboring S atoms are indicative of both Fe−S and some Fe−O bonding, especially in the case of vallerite-1 owing to oxidized pyrrhotite. The Fe−S distances are slightly shorter than those in chalcopyrite and the Cu−S ones in vallerite but, again, the Fe K-edge data are inconclusive because of the complex composition of the samples. It is noteworthy that Cu and Fe atoms have been suggested¹ to be statistically distributed in cationic positions of the sulfide structure of vallerite, in contrast to chalcopyrite; unfortunately, EXAFS fails to confirm any clustering of the metal atoms due to similar scattering of Cu and Fe.

**X-ray Photoelectron Spectroscopy.** The surface concentrations of elements derived from the XPS survey spectra (Figure 5) approximately agree with the compositions determined using EDX analysis and hard X-ray photoelectron spectroscopy (HAXPES) reported previously.¹ It is noteworthy that the contents of Mg, Al, and Si are notably higher than those of Cu, Fe, and S because ultrafine particles of aluminosilicates and especially serpentines tend to attach to the surfaces of vallerite and metal sulfides.³⁵ The high-resolution photoelectron spectra were collected from the ground vallerite samples with and without low-energy electron flooding in order to eliminate (inhomogeneous) electrostatic charging. The relative intensities of the components shifted to higher BEs owing to the charging without the flood gun applied were large for O, C, and Si spectra, less significant for Fe, Mg, and Al, and minimal for S and Cu. The findings
suggest the same small charging of 0.1−0.2 eV for the sulfide and brucite-like hydroxide layers, in contrast to iron oxy-hydroxides, silicates, and other gangue minerals. The quite narrow spectra of copper with the major Cu 2p3/2 peak at 932.2 ± 0.1 eV are characteristic of Cu+ bonded to S;37,38,56 Cu2+ species are negligible as the shake-up satellites in the spectral region of 940−944 eV are very weak if any. The Cu L3MM Auger peak is located at a kinetic energy of 917.6 ± 0.1 eV for both samples. This concurs with the spectra of sulfur with the major peak S 2p3/2 at 161.5 eV for valleriite-1 and 161.35 eV for valleriite-2, typical for monosulfide, along with minor di- (~162.5 eV), polysulfide (~163.6 eV), and sulfate (169 eV) signals, which arise upon surface oxidation of metal sulfides, including pyrrhotite and chalcopyrite.38 The Fe 2p spectra comprise contributions from both Fe3+-S (Fe 2p3/2 at about 708.0 eV), likely Fe2+-S (e.g., in pyrrhotite) and Fe3+-O species (BEs of 710 eV and higher). The latter exhibited a notable shift due to the electrostatic charging and can be largely related to admixture phases rather than Fe in hydroxide layers of vallerite. Fitting the Fe 2p spectra composed of several chemical species with their multiplet structures57 is not reliable and omitted here.

The results are in reasonable agreement with the X-ray absorption spectra (Figures 2 and 3) and the photoelectron spectra reported previously,3,4,31 although the earlier data are sometimes contradictory. For example, Li and Cui4 have reported the energies uncorrected for electrostatic charging, incomparable with those from other studies. The S 2p spectra of two synthetic samples studied by Hughes and co-workers3 were different, probably, because of essentially oxidized sulfide surfaces. Nonetheless, all of the XPS data are clearly indicative of Cu+, suggesting therefore predominant Fe3+ state in the sulfide sheets of vallerites.

** Mössbauer Spectroscopy.** 57Fe Mössbauer spectra of the two vallerite samples are shown in Figure 6, and the fitting parameters are summarized in Tables S3 and S4; the probabilities of quadrupole splitting P(QS) for doublets and of internal hyperfine fields P(H) for sextets determined in the experimental spectra are presented in Figure S4 (Supporting Information). The room-temperature spectra of both samples are dominated by a central signal, whose relative intensities (60−75%) correlate with the share of iron in vallerites derived from XAFS, XRD, and EDX. The spectrum of valleriite-1 is fitted with a major doublet d1 with the isomer shift (IS) of 0.38 mm/s and QS of 0.64 mm/s, which is attributed to paramagnetic Fe3+ in tetrahedral coordination with S in the sulfide sheets of vallerite, in accordance with the previous studies,3,10,30,32−34 and three six-line Zeeman components with...
CuFe$_2$S$_4$\textsuperscript{54} despite a higher quadrupole splitting ($\sim$0.6 vs 0.22 mm/s in bornite) probably owing to the essentially distorted Fe–S coordination (Figure 3). So, the Mössbauer paramagnetic signal is due to predominant Fe$^{3+}$–S centers along with smaller contributions of other species, e.g., iron coordinated with hydroxide anions in brucite-like layers of valleriites.

The central doublets of both valleriites shift to a higher IS ($\sim$0.5 mm/s) as the temperature decreased to 78 K and their intensities decrease, especially at 4.2 K, while the lines of hyperfine magnetic structure emerge, or drastically increase, indicating ordering of Fe spins. For vallerite-1, the sextets of pyrrhotite probably incorporate some responses from vallerite at 78 K. When the temperature drops to 4.2 K, the spectrum of pyrrhotite can be approximated by one sextet s2 (IS = 0.65 mm/s and H = 333 kOe) with wide lines and a population of about 36\% (Table S3) as a result of the phase transition at 32 K.\textsuperscript{50,66–71} Two other sextets s1 and s3 that arise from the doublet of vallerite-1 reflect different distortions of the local environment (QS = 1.6 and $\sim$0.16 mm/s) and distinct magnetic interactions (H = 275 and 487 kOe) (Table S3) at iron sites in the vallerite layers.

The spectrum of vallerite-2 measured at 4.2 K also consists of a series of Zeeman sextets, with one of them (s3) clearly originating from chalcopyrite. The sextets s1 and s4 resemble those in vallerite-1, though somewhat differing in parameters and intensities (Table S4). The sextet s2 (IS = 0.54 mm/s, QS = 0.2 mm/s, and H = 310 kOe) can arise from vallerite too, taking in mind the complex nature of the broad doublet at RT. Alternatively, this feature may arise from chalcopyrite as the sextet s3 intensity is almost three times less than that at higher temperatures (Figure 6, Table S4). Since no significant changes in the spectra of chalcopyrite at low temperatures have been reported in the literature,\textsuperscript{13,54,72,73} we may suggest that Fe$^{3+}$ centers both in defective chalcopyrite (possibly, an intermediate product of its reaction with serpentine) and valleriite contribute to the sextet s3. The spectra of both samples measured at 4.2 K contain weak paramagnetic doublets with the Mössbauer parameters attributable both to sulphide and oxide local environment of Fe.

Although the accurate assignment of the hyperfine magnetic sextets, as well as the “residual” doublet, remains challenging, they definitely arise at the expense of the room-temperature paramagnetic signal of vallerite. A similar effect of temperature is well-known for bornite, in which the IS of the central doublet increases from 0.38 mm/s at room temperature to $\sim$0.5 mm/s at 70 K due to the second-order Doppler shift, and the QS almost does not change; that is typical for high-spin Fe$^{3+}$.\textsuperscript{54} The hyperfine structure arises in bornite at 65 K as three sextets with H of about 200 kOe and evolved at lower temperatures to a single six-line pattern with IS = 0.53 mm/s, QS $\sim$ 0, and H = 352 kOe. The Mössbauer spectra of vallerite having similar IS and H parameters agree with mainly Fe$^{3+}$ in the sulphide layers but QS is larger because of the lower coordination symmetry. The compositional and structural disorder in valleriites causes the appearance of several low-temperature hyperfine patterns.

**Magnetic Properties.** Figure 7 shows the temperature dependences of magnetization of vallerite samples and the hysteresis loop for vallerite-1 at 4.2 K. The magnetization of vallerite-2 is rather simple, exhibiting a linear dependency of magnetization vs field H, which is due to the antiferromagnetic phase of chalcopyrite\textsuperscript{6,72–74} and paramagnetic character of

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**Figure 6.** $^{57}$Fe Mössbauer absorption spectra (dots) of vallerite-1 (Val-1) and vallerite-2 (Val-2) samples measured at different temperatures and the results of fitting (color lines) summarized in Tables S3 and S4 (Supporting Information); smaller dots are differences between experimental spectra and fits.
valleriite. The plots of reciprocal magnetic susceptibility $\chi$ versus temperature are linear until about 30 K, and the slope increases at lower temperatures (Figure 7f) due to a contribution of antiferromagnetic chalcopyrite.53,54,73

The magnetization of valleriite-1 can be described as a sum of ferromagnetic, antiferromagnetic, and paramagnetic components, which are often difficult to separate in complex mineral systems.37,76 A minor amount of ferromagnetic phase (e.g., monoclinic pyrrhotite), magnetite Fe$_3$O$_4$ and/or some others seem to be responsible for the hysteresis loop.76,77 Both pyrrhotite and magnetite have the phase transition nearby 130 K.68−71,76,77 Magnetization below 30 K can be related to a growing paramagnetic component; the effect is observable in the strong field of 14 kOe starting from ~150 K. On the other hand, such a behavior may be due to short-range antiferromagnetic interactions.24 No clear signs of super-paramagnetic blocking and (super)spin-glass freezing in valleriite, which are typical for magnetic nanoparticles and layered structures, for example,78−81 were found. At any cost, no paramagnetic-to-antiferromagnetic state transitions were observed in both valleriites, in contrast to bornite with a Néel temperature of 65 K.35,44,82,83

**Chemical Bonding in Sulfide Sheets and Implications for the Formation of Valleriite.** The combination of element-sensitive Cu K- and Fe K-edge X-ray absorption spectroscopy together with previous soft XANES studies (Cu L$_2$, Fe L$_2$ and others),34 XPS, and Mössbauer spectroscopy allow us to shed new light onto the chemical states of copper and iron. All of the methods support the main oxidation states as Cu$^+$ and Fe$^{3+}$, despite some uncertainty in the interpretation of Mössbauer spectra. The Cu K-edge absorption spectra demonstrate that valleriites are closer to chalcopyrite than bornite Cu$_x$FeS$_2$. However, the local positive charges at Cu and probably Fe sites in the sulfide layers are lower while the electron density at S atoms is insignificantly higher than in chalcopyrite. This may be explained in terms of either specific chemical bonding in the two-dimensional structures or negative charging of the layers stacked between the hydroxide layers bearing a positive charge.1 It is noteworthy that the electrostatic charging of both layers is equal and low under the XPS experiment conditions, implying a kind of electronic equilibrium in the nanocomposite and delocalization of electrons over the sulfide sheets.

There are some compositional and structural differences between valleriite-1 and valleriite-2. The first valleriite sample is not associated with chalcopyrite and contains a higher amount of Fe and lower amounts of Cu and Al. The additional iron is mainly associated with pyrrhotite (Figures 1, S2) but one can expect that the phase interactions under geological conditions result in substitution of some Cu and Al (Mg) by Fe both in sulfide and brucite-like layers of valleriite. Nevertheless, Mössbauer spectra indicate that the Fe positions in valleriite-1 are more ordered. Vallerite in sample-2 closely intergrown with CuFeS$_2$ and serpentine is the product of an incomplete reaction between these minerals. Some signs, particularly Cu K post-edge features almost identical for valleriite-1 and valleriite-2 and tentative splitting of the Mössbauer signal of chalcopyrite in valleriite-2 at 4.2 K, infer certain changes of intrinsic chalcopyrite during the reaction. For example, the near-surface regions of the “reacted” chalcopyrite can have partially disordered or and nanoparticulate structures.35−57,84−86 These mechanisms, which are important for understanding the formation of such unusual 2D composites and the mineral processing performance, require further investigation.

**Magnetism in Vallerites.** Mössbauer spectra of valleriites exposing Zeeman splitting due to internal magnetic fields at low temperatures were compared with that of bornite, Cu$_x$FeS$_2$. Meanwhile, the nature of the high-temperature disorder (caused by a partial disordering of the Fe$^{3+}$ and Cu$^+$ in

![Image](https://dx.doi.org/10.1021/acsomega.0c06052)

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the considered sites, or a partial charge transfer between Fe$^{3+}$
and Cu$^+\) and the paramagnetic-to-antiferromagnetic transition
at 65 K, which can be ascribed either to a structural
transformation (the reduction of lattice symmetry) or electron
spin ordering in bornite, are still disputable.\textsuperscript{53,54,82} The
hyperfine magnetic interactions are more nontrivial in
valleriites as occurring in the two-dimensional Fe–Cu sulﬁde
sheets and, possibly, dielectric (Mg, Al, Fe) hydroxide quasi-
monolayers coupled by the opposite electric charges. The
similarity between valleriite-1 and valleriite-2 means that the
effects do take place in the composites but not in impurity
phases, and the multiplicity of the hyperﬁne sextets implies
several distinct spin-ordering patterns, comparable but not
identical in the two valleriites. In contrast to chalcopyrite and
bornite, valleriites did not show antiferromagnetic character.
Magnetic effects in valleriites can be modiﬁed via a number of
factors, for example, compositions of sulﬁde (Fe, Cu)$_2$S$_2$
and hydroxide (Mg, Al, Fe)(OH)$_2$ layers and their electrical
charges, a number of the atomic layers, external electric and
magnetic ﬁelds, and so on. Moreover, the composition of
valleriite-like materials can be changed in a very wide range as
there exist minerals in which magnesium is replaced by iron in
hydroxide layers (\textit{"ferro)valleriite})\textsuperscript{27,89} or iron is substituted by
chromium in sulﬁde sheets,\textsuperscript{91} or mackinawite-type iron
sulﬁde layers with no copper in tochilinite or ferrotochilin-
ite.\textsuperscript{32,33,90–92} In addition to the magnetic properties,
superconductivity has been reported in such iron chalcogenide
layers.\textsuperscript{35} Consequently, valleriite emerges as a platform for
numerous two-dimensional composite materials, exhibiting
very special and tunable properties for various applications.
Further studies should be focused on the preparation and
characterization of pure synthetic analogues with well-
controlled composition and structure, as well as on detailed
examination of natural samples.

\section*{CONCLUSIONS}

Two mineral assemblies from Noril’sk ore deposition containing
about 50\% of valleriite composed of stacked 2D
sulﬁde (Cu, Fe)$_2$S$_2$ and brucite-like (Mg, Al, Fe)(OH)$_2$
quasi-
monolayers were examined. The ﬁrst valleriite was associated
mainly with pyrrhotite Fe$_7$S$_{10}$. The second one accompanied
by chalcopyrite and serpentine was the product of the
incomplete reaction between them. The X-ray Cu K-edge
absorption spectra (XANES and EXAFS) collected in the
ﬂuorescence mode are close for both valleriites and somewhat
different from chalcopyrite, showing a less positive charge
localized at Cu$^+$ centers and additional Cu-(Cu, Fe) distances
of about 2.7 Å, while some other bonds did not manifest
themselves in EXAFS and in XANES (as post-edge shape
resonances). These ﬁndings agree with the crystal structure of
valleriites and possibly hint at some changes occurring in the
near-surface layers of chalcopyrite as intermediate of the
reaction. The Fe K-edge XAFS showed signiﬁcant contributions
of surface products of oxidation of sulﬁdes and was insufﬁciently informative in terms of chemical bonding in
valleriites. The XPS data conﬁrmed the Cu$^+$ and Fe$^{3+}$
state in the sulﬁde part of valleriites and suggested that the sulﬁde and
(Mg, Al) hydroxide layers are in a sort of electron equilibrium.
It was discovered by $^{57}$Fe Mössbauer spectroscopy that the
central signals attributed to paramagnetic Fe$^{3+}$\textsuperscript{37} in valleriites and
dominated the spectra at room temperature decrease at 78 K
and almost disappear at 4.2 K. Instead, a series of Zeeman
sextets similar but not identical for valleriite-1 and valleriite-2
arise, indicating internal hyperﬁne magnetic ﬁelds in the 2D
layers. Magnetic measurements revealed the paramagnetic
behavior of valleriites to be different for the two samples but
antiferromagnetic transitions, which can be expected by
analogy with bornite and chalcopyrite, are absent. The unusual
structure and properties of valleriite that can be widely tuned
via its composition and other parameters, including the electric
charge of the layers, make it a promising prototype for a family
of composites of transition metal sulﬁde and hydroxide
(mono)layers. The new insights are also important for understanding the formation and processing of valleriite-
containing ores.

\section*{ASSOCIATED CONTENT}

\section*{Supporting Information}

The Supporting Information is available free of charge at
https://pubs.acs.org/doi/10.1021/acsomega.0c06052.

- SEM, EDX, element mapping (Figures S1, S2); X-ray
diffraction (Figure S3); EXAFS ﬁtting results (Tables S1
and S2); probabilities of quadruple splitting and
hyperfine internal magnetic ﬁeld for Mössbauer spectra
(Figure S4); and parameters of the spectra ﬁts (Tables
S3, S4) (PDF)

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Notes
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