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Crystal Structure, Magnetic, and Mössbauer Studies of $Cu_6Fe_{0.9}V_6O_{19}$: A Compound with Relaxation Effect

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$Cu_6Fe_{0.9}V_6O_{19}$, grown by hydrothermal synthesis, crystallizes in the rhombohedral system, space group $R\bar{3}$, with $a = 12.9399(8)$Å, $c = 7.1275(3)$Å ($T = 293$ K), and $Z = 3$. The structure is related to that of so-called α-copper vanadate, $Cu_{6.78}V_6O_{18.78}$. Magnetic and Mössbauer studies were performed in order to characterize the physical properties of $Cu_6Fe_{0.9}V_6O_{19}$. The onset of magnetic ordering occurs close to 10 K and the iron in the trivalent state shows some relaxation effects.

Introduction

The investigation of the ternary system $CuO–Fe_2O_3–V_2O_5$ (*1*) evidenced two new compounds in the pseudo-binary system $Cu_3V_2O_8–FeVO_4$: $Cu_3Fe_4(VO_4)_6$, the structure of which is related to the mineral howardevansite (*2*), and $Cu_3Fe(VO_4)_3$. During the attempts to grow single crystals of $Cu_3Fe(VO_4)_3$ by hydrothermal synthesis at high temperature, reduction occurred to some extent due to the reducing medium and produced the compound described here.

Experimental and Results

Syntheses

The starting materials, $FeVO_4$ and $Cu_3V_2O_8$, were obtained by heating in air (1023 K, 7 days) a mixture of Fe_2O_3 or CuO with V_2O_5 in the ratios 1 : 1 and 3 : 1, respectively. After reaction, the X-ray powder diffraction patterns were recorded by step scan on a Siemens D501 diffractometer with Cu$K\alpha$ radiation (back graphite monochromator). The obtained diffractograms were compared to those of JCPDS files (*3*) Nos. 16-419 and 38-1372, respectively. The products were in this way identified as those expected and they were determined to be single-phased.

A mixture of the two samples in the ratio 1 : 1 was heated in air to 1023 K for 3 days to give $Cu_3Fe(VO_4)_3$. The black powder obtained was hydrothermally treated (973 K, 2000 bar, 3 days) in the presence of 1 ml water and a very small amount of NaF as mineralizer, in a sealed Pt-tube placed in a stainless steel autoclave.

The X-ray powder diffractogram recorded after the hydrothermal treatment corresponded to a mixture of α-Fe_2O_3, with small changes of the cell parameters, and an unknown phase. By studying the sample under the binocular it was found to contain

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three different types of crystals: a small amount of needle-shaped crystals and two sorts of blocks, of which one appeared to be magnetic at room temperature.

An energy dispersive X-ray analysis (EDX) performed by a JEOL 820 scanning electron microscope (SEM) equipped with a LINK energy dispersive X-ray spectrometer revealed that the chemical composition of the magnetic crystals essentially corresponded to Fe_2O_3. The mean composition of the second type of blocks (as obtained by investigation of >20 crystals) was $Cu_{7.8}FeV_{6.8}O_y$. The structure determination is in agreement with the composition $Cu_6Fe_{0.9}V_6O_{19}$ and isotypic with α-copper vanadate (*4*).

In order to obtain the same type of crystals, a second route of synthesis was followed by hydrothermal treatment (935 K, 1900 bar, 1 day) of a mixture of CuO, Fe_2O_3, Fe, and VO_2 in the ratio 18 : 1 : 1 : 18. The resulting sample contained two sorts of crystals: black platelets, too thin to be investigated by single crystal X-ray diffraction, and the same type of nonmagnetic blocks as described above.

For further magnetic purposes, attempts at cationic substitutions on the metallic network were also made. Substitution of Cu by Zn ($Zn_7V_6O_{19}$) would isolate the magnetic vanadium clusters, and Ti replacing V ($Cu_7Ti_6O_{19}$) would keep only the copper chains. However, both experiments failed: the former resulted in $Zn_3(VO_4)_2$ and the latter in a mixture of TiO_2 (rutile) and delafossite-related Cu_3TiO_4 (*5*).

X-Ray Data Collection and Characterization

Black metallic single crystals were selected from the first sample and their quality was checked by Laue photographs. The details of the data collection for one of the crystals on a Siemens AED2 four-circle diffractometer are summarized in Table 1. The cell parameters of $Cu_6Fe_{0.9}V_6O_{19}$ were determined from a long-exposure rotation photograph and then refined from 30 reflections by the double scan technique. All the calculations were performed with the SHELX-76 program (*6*). Atomic scattering factors and anomalous dispersion terms were taken from Ref. (*7*).

The unique condition for the observed reflections $hkil$, $-h + k + l = 3n$ led to the centrosymmetric space group $R\bar{3}$ (hexagonal axes) and the noncentric space group $R3$; all calculations were performed in the space group $R\bar{3}$. A starting model was obtained by the application of the direct methods (the TANG option of the program SHELX), showing the positions of the metal atoms Cu, Fe, and V. Refinement of these positions with isotropic thermal motion gave $R = 0.20$; four oxygen sites were located from a Fourier difference map. New refinements lowered the R value to 0.08 for the whole structure. After absorption correction and use of anisotropic thermal parameters, resulting in $R = 0.039$, the possibility of partial substitutions (random distribution over $3a$ and $18f$ sites for iron and vanadium) (see below) was explored. Such substitutions did not improve the final results, but increased the R value by 0.02–0.15 depending on the type of substitution considered. Moreover, attempts to refine the whole structure with Fe^{3+} at the $3a$ site combined with random distribution of V^{3+} and V^{4+} in the ratio 3 : 15 at the $18f$ site lead to the same R value as above (0.039). The same calculation with complete random distribution taking into account Fe^{2+}, Fe^{3+}, V^{3+}, and V^{4+} did not improve the results. When the above SEM analytical results are taken into account, partial occupancy of some sites could not be ruled out. The corresponding refinements showed that the occupancy factors of copper and vanadium were always equal to 1, but a significant improvement (>10%) of the R value (0.035 instead of 0.039) was obtained when the iron site was defective ($\tau = 0.90(1)$—too minute amounts of sample prevented our confirming this by chemical analysis). This means that the correct formula of the compound would be $Cu_6Fe_{0.9}V_6O_{19}$. As iron is present

TABLE I

CONDITIONS OF X-RAY DATA COLLECTION ON $Cu_6Fe_{0.9}V_6O_{19}$

Determination of cell parameters	Obtained from an oscillation photograph exposed for 12 hr 30 reflections
Space group	$R\bar{3}$ (No. 148—hexagonal axes)
Cell dimensions	a = 12.9399(8) Å c = 7.1275(3) Å
Volume/Z	1033.5 Å^3/Z = 3
Calculated density	3.02
Wavelength/monochromator	0.71069 Å (Mo$K\alpha$)/graphite
Temperature	293 K
Scan mode	ω-2θ
Step scan	$36 \leq N \leq 44$, every 0.035° and 4 s
Aperture	3.0 × 3.0 mm^2
Crystal dimensions	0.05 × 0.11 × 0.17 mm^3
Absorption corrections	Gaussian method
Transmission factors	T_{min} = 0.17 − T_{max} = 0.49
Absorption coefficient	μ = 139.69 cm^{-1}
Angular range of data collection	$2\theta \leq 75°$
Range of measured h,k,l	$-21 \leq h < 19$ $-22 \leq k \leq 22$ $-12 \leq l \leq 12$
Standard reflections (3)	(−1 −2 −5), (2 −7 3), (−7 5 3)
Measured every	60 min
Maximum intensity variation	1.7%
Measured reflections	2428
Unique reflections	1169
Independent ref. ($\|F\| > 6\sigma\|F\|$)	853
Number of refined parameters	51
Final Fourier residuals	−1.2 to 1.7 eÅ^{-3}
R/R_w	0.035/0.035

in the trivalent state (as shown below), electroneutrality implies that vanadium occurs in both the tri- and tetravalent states in the structure. Final parameters are reported in Table II; selected interatomic distances and bond angles are listed in Table III.

Magnetic Studies

The problem of the oxidation state of the cations in this structure was difficult to solve; to approach it, we undertook magnetic susceptibility and Mössbauer measurements. Nonmagnetic crystals of $Cu_6Fe_{0.9}V_6O_{19}$ were separated from magnetic crystals of Fe_2O_3 by using a magnet at room temperature in order to obtain 60 mg of the compound. The magnetic susceptibility was measured by the Faraday method between 4.2 and 300 K and the resulting curve (χ^{-1} vs T) is presented in Fig. 1.

At T = 260(2) K the $\chi^{-1}(T)$ curve exhibits an accident which was assigned to the Morin transition of α-Fe_2O_3 (confirmed by a $\chi^{-1}(T)$ curve of pure α-Fe_2O_3). This means that, despite the careful separation mentioned above, our sample was contaminated with small amounts of magnetic α-Fe_2O_3 (see below the results of Mössbauer spectroscopy) and therefore no information could be extracted from the experimental value of the molar Curie constant (7.2). However, the most important feature of this study was the change in the slope of the $\chi^{-1}(T)$ curve close to 10(2) K, which seemed to indicate the onset of magnetic ordering at this temperature.

TABLE II

ATOMIC COORDINATES AND THERMAL PARAMETERS FOR $Cu_6Fe_{0.9}V_6O_{19}$

Atom	Site	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	B (Å^2)
Cu^{2+}	18f	0.0419(0)	0.7627(0)	0.0997(1)	164(2)	152(2)	189(2)	109(2)	−5(1)	0(1)	1.33
Fe^{3+}	3a	0	0	0	111(3)	111(3)	78(3)	55(1)	0	0	0.79
V^{4+}	18f	0.1552(0)	0.0204(0)	0.3292(1)	72(2)	91(2)	82(2)	43(1)	4(1)	1(1)	0.64
O1	18f	0.4801(2)	0.5768(2)	0.1699(3)	91(7)	106(7)	101(7)	68(6)	22(6)	18(6)	0.78
O2	18f	0.4566(2)	0.6837(2)	0.4823(3)	83(7)	96(7)	96(7)	40(6)	0(6)	−2(5)	0.70
O3	3b	0	0	1/2	79(10)	70(10)	81(15)	40(5)	0	0	0.63
O4	18f	0.5980(2)	0.7009(2)	0.8546(3)	111(8)	157(8)	91(7)	80(7)	15(6)	−5(6)	0.94

U_{ij} are $\times 10^4$

$B = 8\pi^2[(U_{11} + U_{22} + U_{33})/3]$

Note. Standard deviations in parentheses refer to the last digit.

Mössbauer Studies

^{57}Fe Mössbauer studies were performed at 300, 77, and 4.2 K by using the classical method with ^{57}Co source diffused into a rhodium matrix. The 60 mg of the sample previously used for the magnetic investigations was spread out in the sample holder with a surface of 3 cm^2; it appeared to contain about 1 mg of natural iron per cm^2. This low iron content can explain our difficulties in obtaining well resolved Mössbauer spectra. The data were refined using the MOSFIT program (*8*). (The corresponding results are included in the discussion below.)

Structural Details and Discussion

The structure of $Cu_6Fe_{0.9}V_6O_{19}$ is similar to that of the previously so-called α-copper vanadate $Cu_{6.78}V_6O_{18.78}$ (*4*), for which it was proposed, on R value considerations, that copper fully occupies the 18*f* and partially the 3*a* octahedral sites. The nonstoichiometry of the oxygen sublattice, which forms a cubic close packing, was deduced from valence considerations, but was not observed during the refinements within one standard deviation on the occupancy factor.

The structure contains blocks of six edge-sharing VO_6 octahedra. Within these octahedra, all V–O distances are characteristic for V^{4+}. The shortest one (1.673 Å) could be compared to the V=O bond distances within the vanadyl ion. In *trans* position to this short bond distance is a longer one (2.248 Å) to the oxygen in the center of the cluster. This central oxygen is octahedrally coordinated to six vanadium ions, where all V–O bonds are slightly too long to satisfy the valence bond rule (Table IV).

Along the *c* axis, the blocks of VO_6-octahedra are connected, via edge-sharing, by an FeO_6-octahedron (Fig. 2). The infinite chains thus formed are, in the *a* and *b* directions, held together by chains of CuO_4 tetrahedra running in spirals along the *c* axis (see Fig. 3). This type of coordination around a Cu^{2+} is very exceptional but it has been found in a few cases (*12*).

The main difference between α-copper vanadate and our structure lies in the fact that the octahedra connecting the blocks of six VO_6 octahedra contain copper and iron, respectively. The Fe–O main distance within this octahedron (1.991 Å) (see Table III) is close to Fe^{3+}–O bond lengths with iron in the high spin state (2.025 Å) (from the sum of Shannon's ionic radii (*9*) with fourfold coordinated oxygen) or, improbably, to Fe^{2+}–O bond distances with Fe^{2+} in the low spin state (1.99 Å). Since crystallography and susceptibility measurements were unable to give any obvious solution as to whether the structure contains Fe^{2+} or

TABLE III

INTERATOMIC DISTANCES (Å) AND BOND ANGLES (°) IN $Cu_6Fe_{0.9}V_6O_{19}$

Cu polyhedron: tetrahedron

Cu	O1	O2	O4	O4
O1	**1.967(3)**	3.448(3)	3.251(3)	3.244(3)
O2	122.2(1)	**1.973(3)**	3.346(3)	3.168(2)
O4	108.4(1)	113.0(1)	**2.040(3)**	3.127(2)
O4	107.4(1)	103.6(1)	99.5(1)	**2.057(2)**

⟨Cu–O⟩ = 2.009 Å $d_{Shannon}$ = 1.935 Å (Ref. (*8*))

Fe polyhedron: octahedron

Fe	O2	O2	O2	O2	O2	O2
O2	**1.991(2)**	3.983(3)	2.592(2)	3.024(2)	2.592(3)	3.024(3)
O2	180.0(0)	**1.991(2)**	3.024(2)	2.592(2)	3.024(3)	2.592(3)
O2	81.2(1)	98.8(1)	**1.991(2)**	3.983(3)	2.592(2)	3.024(2)
O2	98.8(1)	81.2(1)	180.0(0)	**1.991(2)**	3.024(2)	2.592(2)
O2	81.2(1)	98.8(1)	81.2(1)	98.8(1)	**1.991(2)**	3.983(3)
O2	98.8(1)	81.2(1)	98.8(1)	81.2(1)	180.0(0)	**1.991(2)**

⟨Fe–O⟩ = 1.991 Å

V Polyhedron: octahedron

V	O4	O1	O1	O2	O2	O3
O4	**1.673(3)**	2.739(2)	2.762(2)	2.784(3)	2.810(2)	3.919(3)
O1	101.9(1)	**1.851(3)**	2.677(3)	2.770(3)	3.807(2)	2.677(2)
O1	102.4(1)	92.1(1)	**1.868(2)**	3.801(2)	2.718(3)	2.677(2)
O2	98.0(1)	91.8(1)	158.0(1)	**2.004(3)**	2.592(3)	2.702(2)
O2	98.6(1)	158.8(1)	88.6(1)	80.2(1)	**2.021(2)**	2.702(2)
O3	175.8(1)	80.9(1)	80.6(1)	78.7(1)	78.3(1)	**2.248(1)**

⟨V–O⟩ = 1.944 Å $d_{Shannon}$ = 1.953 Å

O1 polyhedron: roughly triangular

O1–V	1.851(3)
O1–V	1.868(2)
O1–Cu	1.967(3)

⟨O1–metal⟩ = 1.895 Å

O2 polyhedron: distorted terahedron

O2–Cu	1.973(3)
O2–Fe	1.991(2)
O2–V	2.004(3)
O2–V	2.021(2)

⟨O2–metal⟩ = 1.997 Å

O3 polyhedron: octahedron

O3–V	6 × 2.248(1)

⟨O3–metal⟩ = 2.248 Å

O4 polyhedron: triangular

O4–V	1.673(3)
O4–Cu	2.040(3)
O4–Cu	2.057(2)

⟨O4–metal⟩ = 1.923 Å

Note. The *M*–O distances are in bold characters. The O–O distances are given above the diagonal; the O–*M*–O angles below.

Fe^{3+}, a Mössbauer study of the compound was undertaken.

Mössbauer spectra obtained at 300, 77, and 4.2 K are presented in Fig. 4. All the spectra present a very well resolved, more or less asymmetric, doublet and an additional sextet corresponding to a magnetic phase. The doublet, which corresponds to the iron in $Cu_6Fe_{0.9}V_6O_{19}$, exhibits an increasing asymmetry with decreasing temperature. The magnetically ordered contribution can easily be identified as α-Fe_2O_3 (*13*) with a fitted hyperfine magnetic field of 543 kOe at 4.2 K ($H_f(0)$ = 544 kOe (*13*)).

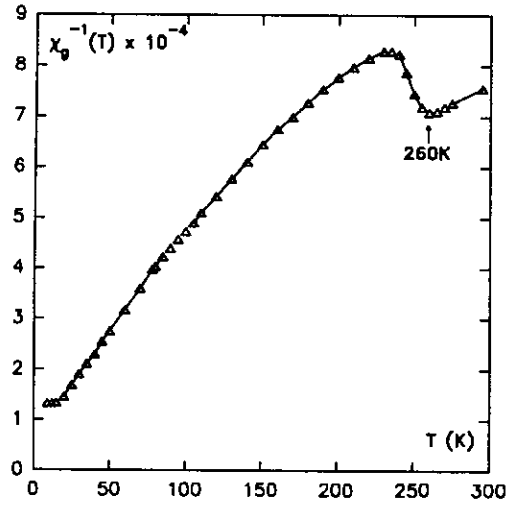

FIG. 1. Magnetic susceptibility curve indicating an onset of a magnetic ordering near 10 K. The curve also exhibits an accident at 260 K, which corresponds to the Morin transition of α-Fe_2O_3.

With all peaks fitted, the iron in our compound and the iron in the impurity were shown to contribute 50% each, which, after taking into account the respective amounts of iron in the two compounds, leads to about 6 wt% Fe_2O_3 in the sample.

The thermal evolution of the asymmetric doublet was considered as being due primarily to a mixture of Fe^{2+} and Fe^{3+} spread over all cationic sites in the structure, assuming that the hyperfine parameters would evolve differently with the temperature. The only possibility to fit the spectra at all three temperatures was the combination of a quadrupolar doublet and a single line with the hyperfine parameters Q.S. = 0 and I.S. = 0.9, where the isomer shift would be less dependent on the temperature. However, the fitted parameters of the single line were in agreement neither with the crystallographic results, nor with expected Mössbauer parameters: the value of I.S. was too

TABLE IV

VALENCE BOND CALCULATIONS FOR $Cu_6Fe_{0.9}V_6O_{19}$

	O1	O2	O3	O4	$\Sigma_{exp.}$	Σ_{theor}
Cu^{2+}	0.46	0.45		0.38		
				0.36	1.65	2
Fe^{3+}		0.53			3.18	3
V^{4+}	0.79	0.52	0.29	1.34		
	0.76	0.50			4.2	4
$\Sigma_{exp.}$	2.01	2.00	1.74	2.08		
$\Sigma_{th.}$	2	2	2	2		

Note. $s = \exp[(r_0 - r)/B]$ with $B = 0.37$ and $r_0 = 1.679$ for Cu^{2+}, $r_0 = 1.759$ for Fe^{3+} (from ref. *10*); $s = (R/R_0)^{-N}$ with $R_0 = 1.770$ and $N = 5.2$ for V^{4+} (from ref. *11*).

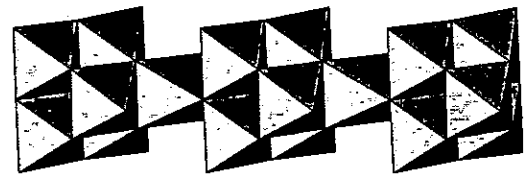

FIG. 2. A fraction of the structure of $Cu_6Fe_{0.9}V_6O_{19}$ showing the connection along the c axis of the blocks of six VO_6-octahedra via an FeO_6-octahedron.

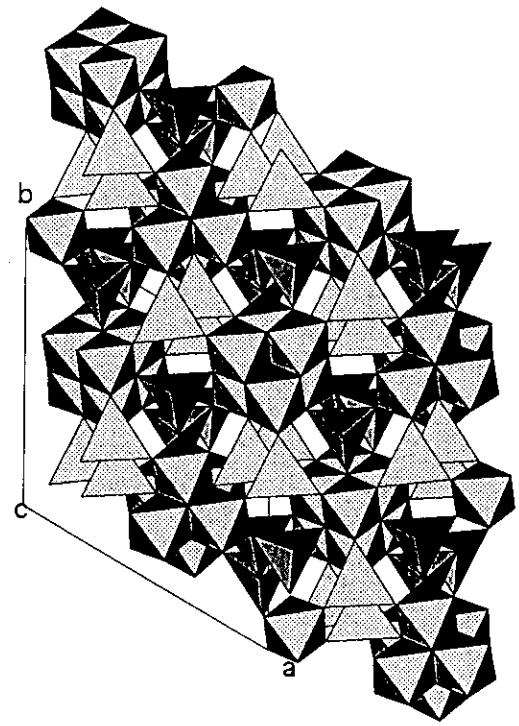

FIG. 3. Ideal structure model $Cu_6Fe_{0.9}V_6O_{19}$ seen along [001].

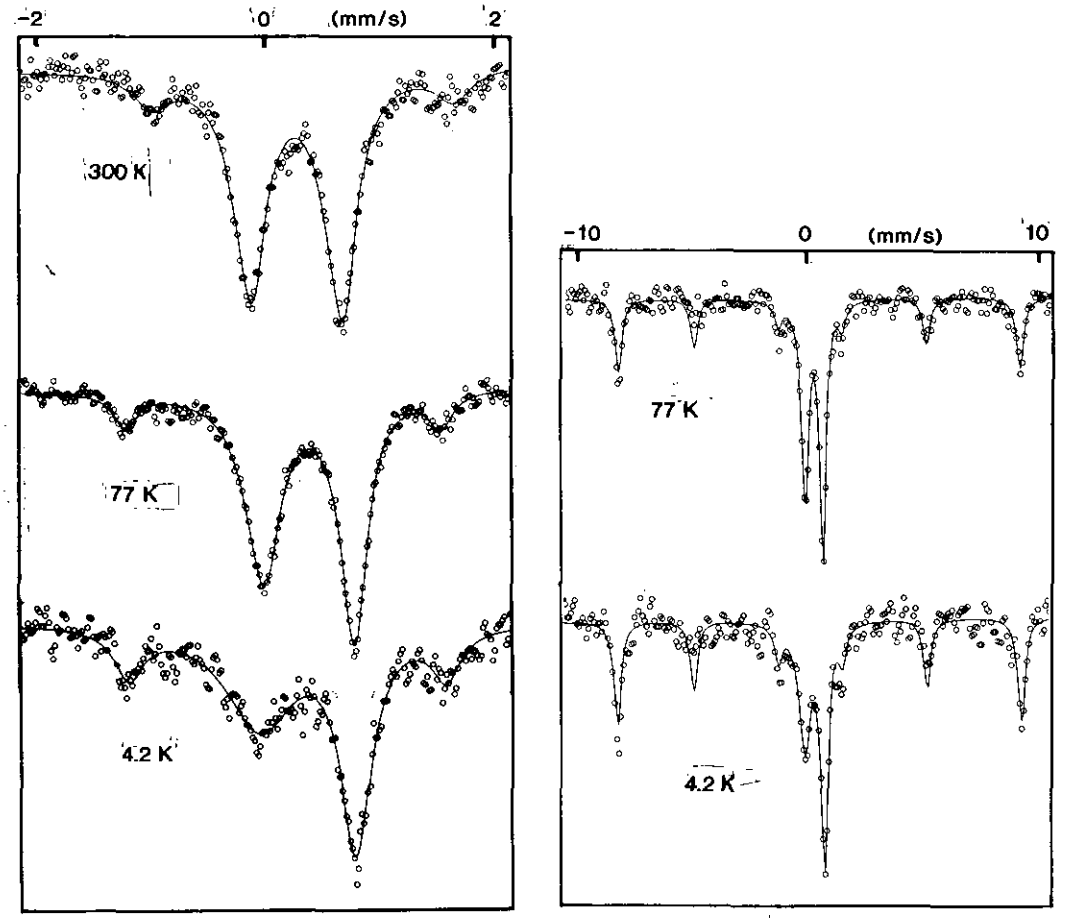

FIG. 4. Mössbauer spectra recorded at 300, 77, and 4.2 K and at $v = 2$ and 10 mm/s, respectively.

high for Fe^{3+}, the presence of Fe^{2+} at a noncubic site in an oxide would give an important quadrupolar splitting, and, finally, the second order Doppler effect would be large.

However, an asymmetric quadrupole pattern of a polycrystalline, isotropic absorber can also be fitted by presuming two lines. The observed asymmetry could then arise from three different causes: (i) a preferential orientation of the crystallites in the powder, i.e., a texture effect (analogous with the effects observed for an oriented single crystal (*14*) with a temperature independent asymmetry (*15*)), (ii) a Goldanskii–Karyagin effect due to an anisotropy of the Debye–Waller factor, giving lines with identical shapes and different intensities and an asymmetry increasing with temperature (*16*), and (iii) a relaxation effect, which would lead to lines with different widths but equal intensities (*17*). The asymmetrical lines reflect in the third case the fact that the corresponding low- and high-velocity transitions relax with different frequencies.

The data for the hypothesis with two different lines are given in Table V. The spectra were fitted with two Lorentzian lines of different widths, Γ_1 and Γ_2. The fitted values of the linewidths are different, but the line intensities remain equal, and the difference, $\Delta\Gamma$, increases with decreasing temperature. These results are in agreement with a relaxation effect, which has already been ob-

TABLE V

MÖSSBAUER DATA ON $Cu_6Fe_{0.9}V_6O_{19}$

T (K)	I. S. (mm/s)	Q. S. (mm/s)	Γ_1 (mm/s)	Γ_2 (mm/s)	S_1/S_2
300	0.378	0.795	0.34	0.33	0.96
77	0.475	0.800	0.37	0.29	1.00
4.2	0.47	0.84	0.60	0.33	1.05

Note. I. S.: Isomer shift relative to iron metal at 300 K. Q. S.: Quadrupolar splitting. Γ_1, Γ_2, and S_1/S_2: Linewidths and amplitude ratio for the lines 1 and 2.

served for other Fe^{3+} compounds (*18*), and they show that the relaxation time increases with decreasing temperature, as usually observed for spin–lattice relaxations (*19*).

The isomer shift relative to iron metal, I.S. = 0.38 mm/s at room temperature, is characteristic of a Fe^{3+} high-spin ion in oxides and the quadrupolar splitting, ΔE_Q = 0.80 mm/s, being independent of the temperature is typical for an Fe^{3+} ion in an octahedral site (*14, 20, 21*). This indicates thus that the final formula of our compound would be $Cu_6^{2+}Fe_{0.9}^{3+}[V_{0.7}^{3+}V_{5.3}^{4+}]O_{19}$.

The S_1/S_2 surface ratios are close to 1 whatever the temperature. At 4.2 K, the linewidth of the low-velocity component of the doublet becomes important. We consider that the important broadening of the left line in the doublet at this temperature could be attributed to the beginning of a magnetic ordering of the iron, where the two lines would collapse before the appearance of the magnetic sextet. These results are in agreement with the change of slope of the $\chi^{-1}(T)$ curve near 10 K. Experiments under applied magnetic field are currently in progress.

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