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## Metal Ordering in $(\text{Fe,V})_3\text{S}_4$

BY HIROMOTO NAKAZAWA

*National Institute for Research in Inorganic Materials, Namiki 1, Sakura-mura, Niihari-gun, Ibaraki 305, Japan*

KATSUHIRO TSUKIMURA

*Geological Survey of Japan, Namiki 3, Sakura-mura, Niihari-gun, Ibaraki 305, Japan*

HISAKO HIRAI

*Department of Geosciences, University of Tsukuba, Tennodai, Sakura-mura, Niihari-gun, Ibaraki 305, Japan*

AND HIROAKI WADA

*National Institute for Research in Inorganic Materials, Namiki 1, Sakura-mura, Niihari-gun, Ibaraki 305, Japan*

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### Abstract

The ordered arrangement of metals in  $(\text{Fe,V})_3\text{S}_4$  was determined by means of powder X-ray diffraction employing the anomalous dispersion of Cr  $K\alpha$  radiation for V and Fe atoms, although both atoms have similar atomic numbers. By comparison of the observed and calculated structure factors of  $\text{FeV}_2\text{S}_4$  and  $(\text{Fe}_2\text{V})_{2.88}\text{S}_4$  for Cr  $K\alpha$ , Fe  $K\alpha$  and Cu  $K\alpha$  radiations, it was concluded that Fe atoms occupy preferentially the  $M(1)$  site in the metal layer with vacancies, indicating that Fe atoms have a relatively stronger tendency to have neighbouring metal atoms along the  $c$  axis than do V atoms.

### Introduction

The transition-metal sulphides, commonly having the NiAs-type structure at high temperatures, undergo one or a series of phase transformations in which their ordered arrangements of vacancies change with decreasing temperature.  $\text{V}_3\text{S}_4$  is such an example and has a supercell of  $\sqrt{3}A \times A \times 2C$ , where  $A$  and  $C$  are the

cell edges of the NiAs-type fundamental cell. Its structure is the  $\text{Cr}_3\text{S}_4$  type at room temperature, consisting of two alternate metal layers with and without vacancies and of approximately hexagonal close-packed S layers (Fig. 1) (Kawada, Nakano-Onoda,

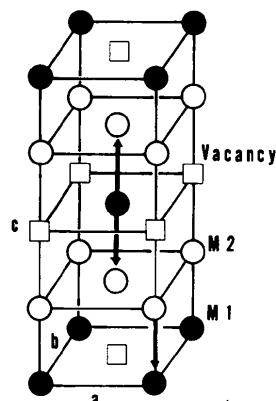


Fig. 1. Sublattice of metal atoms,  $M(1)$  and  $M(2)$ , and vacancies in the  $(\text{Fe,V})_3\text{S}_4$  structure. Arrows demonstrate the number of neighbouring metals around the  $M(1)$  and  $M(2)$  sites along the  $c$  axis.

Ishii, Saeki & Nakahira, 1975). There are two crystallographically distinct metal sites:  $M(1)$  0,0,0; and  $M(2)$   $\sim 0,0,\sim \frac{1}{4}$ .

From the systematic synthesis of crystals in the Fe–V–S system, it is known that Fe can easily replace V in  $V_3S_4$  and is stable over a wide range of composition up to  $Fe_2VS_4$  and also of temperature (Wada, 1978, 1980). The question arises, therefore, whether or not Fe and V atoms make an ordered arrangement.

Some indications of metal ordering can be perceived in previous reports: Wada (1979*a,b*), and Nozaki & Wada (1983) reported that only the  $c$  cell edge of  $(V,Fe)_3S_4$  decreased almost linearly with increasing mole fraction of replaced Fe atoms in the range from  $x = 0$  to 2 in  $Fe_xV_{3-x}S$ . This linear and one-dimensional shrinkage of the unit cell may be explained by assuming that bonding is present between the metals along the  $c$  axis, and that Fe atoms occupy the  $M(1)$  site preferentially, because the number of cation neighbours at the  $M(1)$  site is two times greater than that at the  $M(2)$  site (Fig. 1). These assumptions have previously been used to interpret certain magnetic behaviour, and Mössbauer and Raman spectroscopic data (Nozaki & Wada, 1983; Nozaki, Wada & Yamamura, 1982; Ishii, Wada, Nozaki & Kawada, 1982). A neutron diffraction study reported, however, that the metal ordering could only be observed in  $FeV_2S_4$  but was not evident in  $Fe_2VS_4$  (Kawada & Wada, 1981).

Because of the availability of a series of X-ray  $K\alpha$  and  $K\beta$  radiations from transition-metal targets, the determination of the crystal structure with atoms close to one another in atomic number is not difficult even with the usual powder X-ray diffraction technique. The  $K$  absorption edge of V lies at 2.27 Å, and that of Fe at 1.74 Å, while the wavelength of Cr  $K\alpha$  radiation is 2.29 Å, and so lies close to the V absorption edge. The scattering factor of each element will thus be considerably affected by anomalous dispersion. The values of  $f'$  are about  $-4.4$  for V and  $-1.6$  for Fe, so that the scattering factors of V and Fe for Cr  $K$  radiation will be sufficiently different (Templeton, 1962).

The determination of an ordered arrangement of V and Fe by means of X-ray powder diffraction employing the anomalous dispersion of Cr  $K\alpha$  radiation for V atoms is the primary objective of this paper.

### Experimental

Powdered samples of  $FeV_2S_4$  and  $(Fe_2V)_{2.88}S_4$  have previously been prepared for neutron diffraction experiments by heating the mechanical mixtures of reagent-grade  $VOSO_4 \cdot 3H_2O$  and  $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$  in an  $H_2S$  atmosphere at 1323 K for 4 h and annealing at 773 K for 1 month (Kawada & Wada, 1981). The metal/S ratios of the samples were determined by

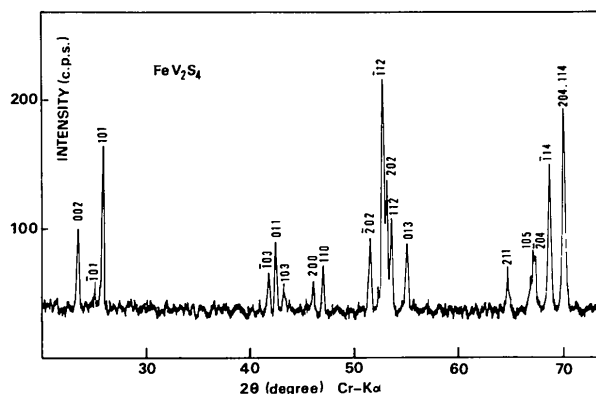


Fig. 2. Powder X-ray diffraction pattern of  $FeV_2S_4$  using Cr  $K\alpha$  radiation.

weighing the sulphides and their oxidation products. The Fe/V ratio is considered to be unchanged from that of the starting powdered mixture.

The integrated intensities of powder X-ray diffraction were measured by using a conventional powder X-ray diffractometer with Cr  $K\alpha$  radiation with a V filter as well as Fe  $K\alpha$  and Cu  $K\alpha$  radiations as references. The photon-counting instruments were commercial ones with a scintillation counter (Rigaku XGC-30), and no crystal monochromator was used.

The complete picture of the powder X-ray diffraction pattern is shown for  $FeV_2S_4$  in Fig. 2 as an example. In about 20 observable reflections, only seven peaks listed in Table 1 were adequate to measure their integrated intensities because they did not overlap with other peaks and were of sufficiently high intensity. The detailed profiles of the seven peaks were measured by step-counting for 10 s at every  $0.02^\circ$  of  $2\theta$  in the range of  $1.0^\circ$  centred on each reflection maximum. The contribution of background was evaluated by linear interpolation from both sides of the peak. Because of the fixed-time counting, the estimated error of the reflection intensities depends on intensities ranging from 2 to 10%.

### Results

The observed and calculated structure factors are listed for  $FeV_2S_4$  and  $(Fe_2V)_{2.88}S_4$  in Table 1. The known crystallographic data are as follows: the space group of  $(Fe,V)_3S_4$  is  $I2/m$  (No. 12) in the unreduced expression ( $C2/m$  is that of the reduced cell); lattice constants of  $FeV_2S_4$  are  $a = 5.872$  (2),  $b = 3.300$  (1),  $c = 11.294$  (6) Å and  $\beta = 92.12$  (2) $^\circ$  and those of  $(Fe_2V)_{2.88}S_4$  are  $a = 5.848$  (3),  $b = 3.301$  (1),  $c = 11.041$  (10) Å and  $\beta = 92.36$  (3) $^\circ$  (Kawada & Wada, 1981). The atomic coordinates for  $(Fe,V)_3S_4$  are assumed to be the same as those of  $V_3S_4$  as

Table 1. Comparison of the observed and calculated structure factors

$F_c(\text{NOA})$ : the calculated structure factors of the normally ordered model;  $F_c(\text{DOA})$ : those of the disordered model; and  $F_c(\text{IOA})$ : those of the inversely ordered model.

$$R = \sum |F_o - F_c| \times 100 / \sum F_o.$$

	<i>h</i>	<i>k</i>	<i>l</i>	2θ (°)	$F_o$	$F_c(\text{NOA})$	$F_c(\text{DOA})$	$F_c(\text{IOA})$
<b>FeV<sub>2</sub>S<sub>4</sub>, Cr Kα</b>								
	0	0	2	23.40	64.0	69.9	100.	129.
	1	0	1	25.80	134.	118.	107.	99.3
	2	0	0	45.90	106.	97.1	97.6	96.6
	1	1	0	46.90	93.5	92.9	95.1	94.9
	-2	0	2	51.40	176.	185.	157.	141.
	0	1	3	55.00	151.	137.	126.	118.
	-1	1	4	68.70	275.	285.	291.	291.
	R(%)					6.8	14.0	20.0
<b>Fe Kα</b>								
	0	0	2	19.80	87.7	102.	110.	114.
	1	0	1	21.80	117.	111.	109.	107.
	2	0	0	38.60	113.	112.	113.	112.
	1	1	0	39.35	113.	111.	112.	112.
	-2	0	2	43.10	154.	142.	135.	131.
	0	1	3	45.95	138.	126.	124.	122.
	-1	1	4	56.95	278.	287.	288.	288.
	R(%)					5.4	7.5	8.7
<b>Cu Kα</b>								
	0	0	2	15.70	79.9	99.7	112.	118.
	1	0	1	17.30	112.	116.	112.	110.
	2	0	0	30.40	107.	125.	125.	125.
	1	1	0	31.10	128.	126.	126.	126.
	-2	0	2	33.90	139.	132.	123.	119.
	0	1	3	36.20	133.	129.	125.	123.
	-1	1	4	44.60	300.	290.	291.	292.
	R(%)					6.5	8.5	9.9
<b>Fe<sub>2</sub>VS<sub>4</sub>, Cr Kα</b>								
	0	0	2	23.80	66.1	75.2	95.4	134.
	1	0	1	25.90	121.	123.	117.	103.
	2	0	0	46.00	112.	119.	120.	118.
	1	1	0	46.80	119.	117.	119.	119.
	-2	0	2	51.60	152.	154.	140.	108.
	0	1	3	55.50	142.	135.	130.	114.
	-1	1	4	69.40	289.	285.	288.	288.
	R(%)					3.3	6.6	16.0
<b>Fe Kα</b>								
	0	0	2	20.25	94.5	88.4	93.3	105.
	1	0	1	22.00	114.	117.	115.	112.
	2	0	0	38.70	123.	120.	120.	120.
	1	1	0	39.30	120.	119.	120.	120.
	-2	0	2	43.20	144.	136.	133.	126.
	0	1	3	46.40	133.	128.	127.	123.
	-1	1	4	57.55	272.	280.	281.	282.
	R(%)					3.5	3.4	5.4
<b>Cu Kα</b>								
	0	0	2	16.00	84.0	86.9	93.2	106.
	1	0	1	17.50	128.	119.	117.	113.
	2	0	0	30.60	130.	131.	131.	131.
	1	1	0	31.10	126.	132.	132.	133.
	-2	0	2	34.10	127.	123.	119.	110.
	0	1	3	36.60	127.	128.	126.	122.
	-1	1	4	45.10	277.	279.	280.	281.
	R(%)					2.4	4.0	7.0

refined previously by the single-crystal method (Kawada, Nakano-Onoda, Ishii, Saeki & Nakahira, 1975), *i.e.*  $M(1)$  at the  $2(a)$  position, 0,0,0;  $M(2)$  at  $4(i)$ , 0.54113 (18),  $\frac{1}{2}$ , 0.24362;  $S(1)$  at  $4(i)$ , 0.33862 (24), 0,0.36289 (13); and  $S(2)$  at  $4(i)$ , 0.66359 (25), 0,0.11246 (13), where  $M(1)$  and  $M(2)$

are metal sites in the metal-deficient and metal-full layers, respectively, and  $S(1)$  and  $S(2)$  are those of S atoms (Fig. 1).

To calculate the structure factors, there are three possible models of ordered and disordered arrangements of metal atoms. (1) The normal ordered arrangement (NOA), where Fe atoms occupy the  $M(1)$  site preferentially as assumed by consideration of the  $c$  cell-edge variation. In  $\text{FeV}_2\text{S}_4$ , the  $M(1)$  site is filled by Fe, and  $M(2)$  by V, and in  $\text{Fe}_2\text{VS}_4$ ,  $M(1)$  by Fe and  $M(2)$  by (Fe + V)/2. (2) The disordered arrangement (DOA), where Fe and V atoms are distributed randomly in both  $M(1)$  and  $M(2)$  sites, *i.e.* both metal sites are filled by (Fe + 2V)/3 in  $\text{FeV}_2\text{S}_4$  and by (2Fe + V)/3 in  $\text{Fe}_2\text{VS}_4$ . (3) The inversely ordered arrangement (IOA), where V atoms occupy the  $M(1)$  sites preferentially. In  $\text{FeV}_2\text{S}_4$ ,  $M(1)$  is filled by V and  $M(2)$  by (Fe + V)/2, and in  $\text{Fe}_2\text{VS}_4$ ,  $M(1)$  by V and  $M(2)$  by Fe.

For calculations of structure factors of all these models, the atomic scattering factors were corrected for anomalous dispersion by using Tables 3.3.2A and B for Cr  $K\alpha$  and Cu  $K\alpha$  radiation of Templeton (1962), and Hönl's formula for Fe  $K\alpha$  radiation. The non-stoichiometry in metal/S ratio was also corrected on the assumption that the additional vacancies in the form of  $(\text{Fe,V})_{2.88}\square_{0.12}\text{S}_4$  were distributed preferentially in  $M(1)$  sites, because the NiAs-CdI<sub>2</sub>-type structure consists of two alternate metal layers with and without vacancies. The reliability factors are listed for each model and for X-ray intensity data measured by Cr  $K\alpha$ , Fe  $K\alpha$  and Cu  $K\alpha$  radiations (Table 1).

## Discussion

Comparison of observed and calculated structure factors indicates obviously that Fe and V atoms are present in an ordered arrangement, and that Fe atoms occupy preferentially the  $M(1)$  site in the metal layer 'with' vacancies (Table 1). The Fe atom tends, therefore, to prefer strongly the  $M(1)$  site where the number of neighbouring metal atoms along the  $c$  axis is two times greater than that of the  $M(2)$  site. In other words, Fe may more strongly tend to couple with metal atoms than does V. This is consistent with the fact that the  $c$  cell edge is reduced by increasing the Fe content.

In other transition-metal sulphides, similar structures are commonly known to have the NiAs-CdI<sub>2</sub>-type fundamental structure and to form a solid solution with the second transition metal such as Fe in  $\text{V}_3\text{S}_4$ . The determination of metal ordering in such a series of structures may indicate which element couples more strongly with vacancies. In turn, this preference to couple with vacancies may help to elucidate the stabilization mechanism of those structures which are characterized by a wide range of non-stoichiometry.

The second point demonstrated by the present experiments is that the determination of transition-metal ordering is not difficult using only powder X-ray diffraction techniques. In the present calculation, the fixed atomic parameters and  $B$  factors of  $V_3S_4$  were used, because the number of reflections sufficient to measure the accurate intensity was limited to seven, and was thus much less than the number of parameters to be determined. Even so, the reliability of the NOA model can obviously be recognized in the differences in  $R$  values (Table 1), and in the match of  $F_o$  and  $F_c$ , especially for reflections 002, 101, 202 and 013, the structure factors of which are dominantly contributed to by the difference in the atomic scattering factors allocated to  $M(1)$  and  $M(2)$ . This easy recognition of metal ordering suggests the possibility of investigating the behaviour of metal ordering 'at high temperatures'. This may elucidate the question of whether vacancy ordering and different metal ordering are coupled or are independent, because the *in situ* X-ray diffraction experiments at high temperature have so far concerned only vacancy ordering (e.g. Nakazawa, Saeki & Nakahira, 1975; Nakazawa, 1979; Wada, 1979a,b). The use of synchrotron-radiation X-rays may be particularly helpful in this context, because of tunability for a given wavelength and the intense flux.

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## Experimental Charge Density Study of Dicobalt Octacarbonyl\* and Comparison with Theory

BY P. C. LEUNG AND P. COPPENS

*Department of Chemistry, State University of New York at Buffalo, Buffalo, NY 14214, USA*

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### Abstract

The structure of dicobalt octacarbonyl,  $Co_2(CO)_8$ , has been redetermined at low temperature. Cell dimensions at 100 K are:  $a = 6.503$  (1),  $b = 15.445$  (2),  $c = 11.121$  (1) Å and  $\beta = 90.57$  (2)°. A significant difference between axial and equatorial Co–C bond lengths is observed which could not be seen at room temperature. The data have been refined with the aspherical-atom multipole formalism. Model maps based on the refinement results show the extension of the bridging C atom's lone-pair density in the plane containing the two Co atoms, in agreement with

theoretical results predicting metal–metal bonding through the bridging ligand.  $d$ -Orbital populations derived from the refinement results agree well with theoretical values. The splitting of the ' $e_g$ -type' levels is evident when the refinement is performed in a coordinate system fitted to the local pseudo octahedral symmetry.

### Introduction

The structure determination of dicobalt octacarbonyl by Sumner, Klug & Alexander (1964) ended much speculation about the molecular geometry of this compound and showed that in the solid state two of the

\* Di- $\mu$ -carbonyl-bis(tricarbonylcobalt).