phys. stat. sol. 22, 517 (1967)

Subject classification: 18.4; 5; 22

Institute of Nuclear Research, Swierk/Otwock (a), and Institute of Structural Research, Polish Academy of Sciences, Wroclaw (b)

Neutron-Diffraction Study of Antiferromagnetism in USb_2 and UBi_2

By

J. LECIEJEWICZ (a), R. TROĆ (b), A. MURASIK (a), and A. ZYGMUNT (b)

The magnetic ordering in polycrystalline USb_2 and UBi_2 is studied by means of neutron diffraction. It is found, that the magnetic unit cell of USb_2 is twice the size of the chemical cell along the c-axis, with alternating ferromagnetic sheets in the sequence $+ - - + \cdots$. In the case of UBi_2 the magnetic and chemical unit cells are identical. The sequence of ferromagnetic sheets is $+ - + - \cdots$ in the direction of the c-axis. In both cases magnetic moments are parallel to the c-axis and their magnitudes are (0.94 ± 0.03) BM for USb_2 and (2.1 ± 0.1) BM for UBi_2.

Die magnetische Ordnung in polykristallinen USb_2 und UBi_2 wird durch Neutronenbeugung bestimmt. Die magnetische Einheitszelle in USb_2 hat die doppelte Größe der chemischen längs der c-Achse. Die ferromagnetischen Schichten sind entlang der c-Achse in der Folge $+ - - + \cdots$ gestapelt. In UBi_2 sind die magnetische und chemische Einheitszelle identisch. Die ferromagnetischen Schichten sind in der Folge $+ - + - \cdots$ entlang der c-Achse gestapelt. In beiden Verbindungen sind die magnetischen Momente von Uran parallel zur c-Achse. Ihre Größen sind: (0.94 ± 0.03) BM in USb_2 und (2.1 ± 0.1) BM in UBi_2.

1. Introduction

The magnetic properties of a number of UX_2 compounds (where X = P, As, Sb, or Bi) indicate antiferromagnetic ordering of the magnetic moments of uranium atoms [1, 2, 3]. This has been recently confirmed by neutron-diffraction studies of UP_2 [4] and UAs_2 [5], where a magnetic superstructure was found below corresponding Néel points. Now neutron-diffraction investigation has been extended to USb_2 and UBi_2.

The inverse magnetic susceptibility against temperature dependence for USb_2 shows that below 206 °K an antiferromagnetic ordering is present [2]. The Néel point for UBi_2 is at 183 °K [3]. The paramagnetic moments of USb_2 and UBi_2 are 3.04 and 3.40 BM, respectively. The corresponding Weiss constants as derived from the $1/\chi$ vs. T slopes are +18 °K for USb_2 and −54 °K for UBi_2.

The aim of the present neutron-diffraction study was the determination of the magnetic structure of USb_2 and UBi_2 in the antiferromagnetic state and the derivation of the magnetic moment of uranium. In the case of UBi_2 a clarification of its crystal structure seemed to be of interest because a neutron-diffraction study carried out in 1957 by Teitel [6] suggested a cubic structure with $a = 8.89$ Å.

2. Preparation of Samples

Both USb_2 and UBi_2 were prepared by direct reaction between the corresponding elements. Stoichiometric quantities of uranium powder (nuclear-grade purity) and lumps of antimony and bismuth (spectral purity) were sealed off in evacuated quartz tubes. The tubes were of special shape in order to separate the reacting elements, so that the reaction took place between the uranium powder and antimony (or bismuth) vapours. For this purpose the tubes were inserted into a furnace with a temperature gradient. The reaction temperature was 650 °C. After whole antimony (bismuth) reacted, as evidenced by visual inspection, the temperature was raised to 800 °C and held for one week. After that the samples were crushed and loaded into aluminium containers in a carefully controlled argon atmosphere. Serious difficulties were met in the case of UBi_2 because of its extremely high pyrophoric properties. All samples were controlled by X-rays using a standard powder camera. Only in the case of UBi_2 few weak lines due to Bi and UO_2 were identified.

3. Crystallographic Data

The crystal structures of both USb_2 and UBi_2 belong to the anti-Cu_2Sb type (C 38) [7, 8]. The space group is P4/nmm—D_{4h}^7[1]) (No. 129) with

2 uranium atoms in the (*c*) site: 1/4, 1/4, u; 3/4, 3/4, $\bar{u}$,
2 Sb I (Bi I) atoms in (*a*) site: 3/4, 1/4, 0; 1/4, 3/4, 0,
2 Sb II (Bi II) atoms in (*c*) site: 1/4, 1/4, z; 3/4, 3/4, $\bar{z}$
(the origin is taken at the centre of symmetry).

The u- and z-parameters as determined by the present neutron-diffraction study and X-rays determined lattice constants are listed in Table 1. The interatomic distances are listed in Table 2.

The coordination of Sb (Bi) atoms around an U atom is shown in Fig. 1. The coordination polyhedron of an U atom can be described as composed of two square pyramids with a common apex, at which an U atom is placed. At the corners of the lower pyramid the Sb I (Bi I) atoms are situated; the upper pyramid is formed by the Sb II (Bi II) atoms. In addition there is a ninth Sb II (Bi II) atom placed above the base of the upper pyramid.

A characteristic feature of the Sb I–Sb I (or Bi I–Bi I) distances within the lower square is that they approach closely the sum of the covalent radii of Sb or Bi, which is 2.82 and 3.04 Å respectively, suggesting in this way a strong atomic interaction. On the other hand the U–Sb I (Bi I) distance is longer than respective sums of covalent

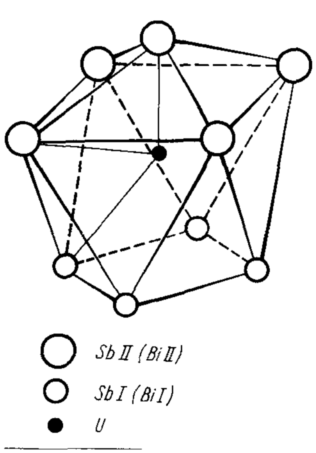

Fig. 1. Ninefold coordination of U in UX_2 compounds with the anti-Cu_2Sb type of crystal structure

[1]) Recently isostructural UP_2 has been studied by X-rays using single crystals. A different unit cell, however, related to the previous one has been discovered [9]. In the present study of polycrystalline USb_2 and UBi_2 no evidence of a different unit cell from that reported by Ferro [7, 8] was found.

Table 1

The *u*- and *z*-parameters
and the lattice constants for USb_2 and UBi_2

	u	*z*	*a* (Å)	*c* (Å)	*c*/*a*
USb_2	0.280	0.635	4.272	8.741	2.044
UBi_2	0.280	0.643	4.445	8.908	2.004

Table 2

Coordination and interatomic distances
in USb_2 and UBi_2

Atom	Neigh-bour	C.N.	Distance (Å) USb_2	Distance (Å) UBi_2
X I	X I	4	3.021	3.143
	X II	4	3.343	3.880
	U	4	3.248	3.340
X II	X I	4	3.343	3.880
	X II	4	4.272	4.455
	X II	4	3.833	4.046
	U	4	3.111	3.216
	U	1	3.103	3.234
U	X II	4	3.111	3.216
	X II	1	3.103	3.234
	X I	4	3.248	3.340

or ionic radii for U and Sb (or Bi). The U–Sb I (Bi I) bonds are in turn weaker than U–Sb II (Bi II) bonds, as can be concluded from the fact that the length of the latter is close to the sum of ionic radii U^{4+} and Sb^{3-} or Bi^{3-}. The above bonding scheme could explain the existence of a paramagnetic moment of U atoms in the UX_2 compounds in which the oxidation state of U^{+4} should be assumed.

4. Neutron-Diffraction Measurements

Neutron-diffraction patterns of polycrystalline samples of USb_2 and UBi_2 both at the room and liquid nitrogen temperatures were obtained using 1.22 Å neutrons from the Swierk reactor EWA operating at the power of 4 MW. Each pattern was run twice at each temperature. Neutron measurements were made in the 2θ range between 5 and 32°. At the higher angles a considerable overlapping of the diffraction peaks with the reflections from the cryostat took place. Moreover in the case of UBi_2 peaks due to Bi and UO_2 phases were also present. In particular the (110) and (102) UBi_2 reflection turned out to be overlapping with the (111) UO_2. A peak due to Bi was clearly separated. Consequently for the determination of *u*- and *z*-parameters in UBi_2 the intensities of only 4 observable peaks were used. Observed relative intensities were derived in the usual way and compared with calculated values taking into account the *u*- and *z*-parameters reported by Ferro [7]. Using the trial and error procedure it was found that a very good fit is obtained adapting the parameters listed in Table 1. No temperature factor was allowed for.

5. Results

5.1 USb_2

On the neutron-diffraction pattern of USb_2 obtained at the liquid nitrogen temperature three distinct peaks of magnetic origin appeared (Fig. 2), which

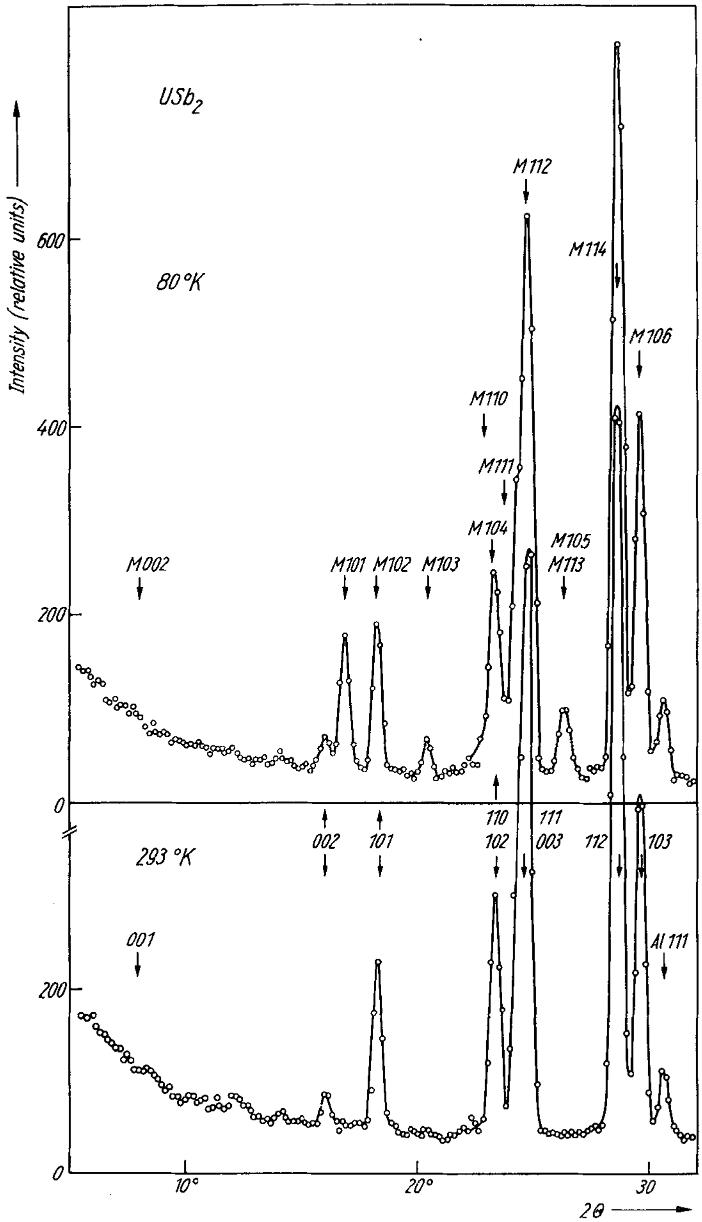

Fig. 2. Neutron-diffraction patterns of USb_2 at 293 and 80 °K. The $(j\,F^2)_{calc}$ values for $M(h\,k\,l)$ reflections with $l = 2\,n$ and the $M(h\,0\,l)$ reflections with $l = 2\,n$ are zero. Magnetic reflections $M(h\,k\,l)$ indexed on a c-doubled cell; nuclear reflections $h\,k\,l$ indexed on the chemical cell

were readily indexed on the basis of a new c-doubled unit cell. The absence of the (001) and (002) magnetic reflections on the neutron pattern was an indication that the magnetic moments of uranium atoms are aligned along the fourfold axis. This implies two possible models of the magnetic structure: with the $+ - - +$ and $+ + - -$ sequences of the ferromagnetic layers built of uranium atoms stacked along the c-axis as it was found in UP_2 [4] and UOS [10], respectively. The relative intensities of magnetic reflections were calculated for both models. In the first case the space group P4/nmm can be retained. On the other hand the second case requires a space group of lower symmetry but with the same extinction rule (P4mm–C^1_{4v}, No. 99). A good fit between the observed and calculated intensities was found for the magnetic structure with the $+ - - +$ stacking of ferromagnetic sheets as discovered previously in UP_2 [4] and UAs_2 [5]. The magnetic moment of uranium was determined from the intensities of the three above-mentioned reflections adopting the space group P4/nmm with four U atoms in the magnetic unit cell in the (c) sites:

2 U in the (c) site; $u_1 = 0.140 \pm 0.001$,

2 U in the (c) site; $u_2 = 0.640 \pm 0.001$.

The magnetic form factor of uranium was taken as reported by Sidhu et al. [11] and the value of μ_B was found to be 0.94 ± 0.03 BM. A comparison of the observed and calculated neutron intensities for the 293 and 80 °K runs is presented in Table 3. The magnetic structure of USb_2 is shown in Fig. 3. Each uranium atom has four neighbours within the same layer and four in each of the two adjacent layers. The closest U–U distance within the layer is 4.272 Å. The shortest distance between the U atoms belonging to two layers in which the directions of the moments are the same is 5.693 Å, whereas the shortest U–U approach for the two adjacent antiferromagnetically coupled sheets is 4.909 Å.

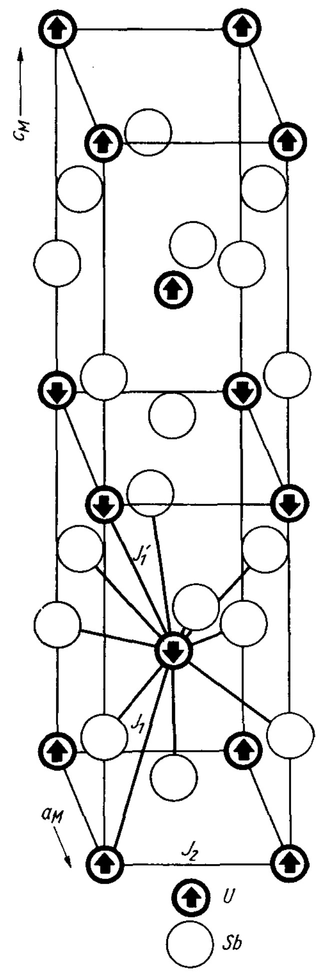

Fig. 3. The magnetic structure of USb_2. The uranium atom has been placed at the origin of the unit cell which is shifted by $-1/4$, $-1/4$, $\bar{u}$ from the centre of symmetry

Table 3

Observed and calculated neutron intensities for USb_2 at room temperature and liquid nitrogen temperature. Magnetic reflections $M(h\,k\,l)$ indexed on the c-axis-doubled cell. Nuclear reflections are indexed on the chemical cell

$h\,k\,l$	293 °K		80 °K	
	$j\,F^2$ (obs.)	$j\,F^2$ (calc.)	$j\,F^2$ (obs.)	$j\,F^2$ (calc.)
0 0 1	not observed	0.00	not observed	0.00
0 0 2	0.65	0.94	0.90	0.94
M(101)	not observed	—	3.8	3.80
1 0 1	5.1	6.30	4.5	6.30
M(103)	not observed	—	1.1	1.00
1 1 0, 1 0 2, M(111)	15.4	13.16	16.1	15.68
0 0 3, 1 1 1	51.8	52.30	52.0	52.30
M(105), M(113)	not observed	—	5.6	5.60
1 1 2	64.0	62.32	64.3	62.62
1 0 3	31.7	33.36	30.4	33.36

5.2 UBi_2

Like in USb_2 the magnetic (001) reflection is absent on the neutron diagram of UBi_2 obtained at the liquid nitrogen temperature, thus indicating the same direction of magnetic moments as it was found in USb_2. However, no superstructure peaks similar to those observed in USb_2 are present. Only one reflection of pure magnetic origin appears. It was indexed as (100) on the basis of the chemical cell. This implies an antiparallel alignment of the magnetic moments of the two uranium atoms in the unit cell. In this way the magnetic structure of UBi_2 consists of a succession of ferromagnetic sheets of U atoms piled up in the direction of the c-axis. The sequence of sheets is $+ - + -$, etc. The symmetry of the magnetic unit cell is P4mm with two atoms in the following sites:

$$1\ \mathrm{U\ in}\ (b)\ \mathrm{site:}\quad 1/2,\ 1/2,\ u_1;\quad u_1 = 0.280 \pm 0.001\ ,$$

$$1\ \mathrm{U\ in}\ (a)\ \mathrm{site:}\quad 0,\ 0,\ u_2;\quad u_2 = 0.720 \pm 0.001\ .$$

A similar magnetic structure was discovered in UOTe [12]. The determination of the magnetic moment in UBi_2 was less reliable since in fact only one pure magnetic peak was at disposal. The value of $\mu_B = 2.1 \pm 0.1$ BM was found taking into account the above atomic parameters and the magnetic form factor as for USb_2. A comparison of the observed and calculated intensities at 80 °K is shown in Table 4. Each uranium atom is surrounded by 8 uranium atoms with antiparallel moment orientation: four of them at 4.820 Å and four at 5.895 Å. The observed values of μ_B for USb_2 and UBi_2 are compared with the previously found ones in the other members of the UX_2 series what is shown in Table 5.

Table 4

Observed and calculated neutron intensities for UBi_2 at liquid nitrogen temperature

h k l	$j\,F^2$ (obs.)	$j\,F^2$ (calc.)
0 0 1	not observed	0.22
0 0 2 *M*(100)	4.69	4.62
1 0 1 *M*(101)	2.78	1.05
1 1 0 1 0 2 *M*(102)	contaminated by UO_2(111) reflection	20.53
0 0 3 1 1 1 *M*(111)	117.5	119.74
1 1 2 *M*(112)	108.2	109.91
1 0 3 *M*(103)	40.0	38.00

Table 5

A comparison of the μ_B-values in Bohr magnetons (BM) for UX_2 compounds in their paramagnetic and antiferromagnetic states

Compound	Sequence	Magnetic moment		Reference
		paramagn.	antiferromagn.	
UP_2	+ − − +	2.50	1.0 ± 0.1	[1, 4]
UAs_2	+ − − +	2.94	1.61 ± 0.01 *)	[2, 5]
USb_2	+ − − +	3.04	0.94 ± 0.03	[2], present study
UBi_2	+ − · · ·	3.40	2.1 ± 0.1	[3], present study

*) Except for UAs_2 the μ_B-values are measured at 80 °K.

The systematic increase of the paramagnetic moment in these series would suggest that the same should be observed also in the ordered state. However, this is not the case (see USb_2). To clarify this point neutron-diffraction measurements should be made at 4 °K.

6. Magnetic Interactions

As it was originally shown by Bertaut [13, 14] for a given crystallographic symmetry the possible moment configurations can be evaluated on the basis of a Hermitian matrix $\xi(k)$, the eigenvectors and eigenvalues of which are directly related to the magnetic-moment configuration and exchange energy.

To apply this method to the case of uranium compounds with the anti-Cu_2Sb or PbFCl types of crystal structures we must first of all analyse the environment of magnetic atoms. Great care should be taken, so that no essential interaction is left out.

In both cases of USb_2 and UBi_2 there are two Bravais lattices composed of uranium atoms with the origins in U I (1/4, 1/4, u) and U II (3/4, 3/4, $\bar{u}$) (see Section 3). Each uranium atom of one lattice is surrounded by eight uranium atoms belonging to the other lattice. As it was shown in the last section they are not at the same distance. Consequently they must be distinguished by respective exchange integrals. For example the U atom has neighbours at $-1/4$, $-1/4$, $\bar{u}$; 3/4, $-1/4$, $\bar{u}$; $-1/4$, 3/4, $\bar{u}$; 3/4, 3/4, $\bar{u}$ with a corresponding exchange integral denoted by J_1. In addition there are four neighbours in the positions $-1/4$, $-1/4$, $1-u$; 3/4, $-1/4$, $1-u$; $-1/4$, 3/4, $1-u$; 3/4, 3/4, $1-u$ with an exchange integral denoted by J_1. Moreover four uranium atoms of the parent Bravais lattice are in the same plane at 1/4, 5/4, u; 5/4, 1/4, u; 1/4, $-3/4$, u; $-3/4$, 1/4, u, with a corresponding exchange integral denoted by J_2.

In the frame of above three exchange interactions only indirect character of exchange may be considered because the distances between respective uranium atoms are too large. The matrix problem is of the order two and the matrix $\xi(k)$ takes the form

$$\xi(k) = \begin{pmatrix} \xi_{11} & \xi_{12} \\ \xi_{21} & \xi_{22} \end{pmatrix}.$$

In the general form the elements ξ_{ij} of the matrix $\xi(k)$ are defined as

$$\xi_{ij}(k) = \sum_{R_j'} J_{R_i R_j'} \exp\ 2\pi i \hat{k}\ (\hat{R}_i - \hat{R}_j'),$$

where summation is carried out over all equivalent neighbours of R_i belonging to the lattice j.

In the case of USb_2 and UBi_2 the matrix elements ξ_{ij} take the form:

$$\xi_{11} = \xi_{22} = 2 J_2 (\cos X + \cos Y),$$

$$\xi_{12} = 4 \left(J_1 + J_1' \exp(i Z)\right) \exp(-i 2 Z u) \cos \frac{1}{2} X \cos \frac{1}{2} Y,$$

$$\xi_{21} = \xi_{12}^*;$$

$$X = 2\pi h, \quad Y = 2\pi k, \quad Z = 2\pi l.$$

Hence the eigenvalues are given by

$$\lambda = 2 J_2 (\cos X + \cos Y) \pm 4 (J_1^2 + J_1'^2 + 2 J_1 J_1' \cos Z)^{1/2} \cos \frac{1}{2} Y \cos \frac{1}{2} X.$$

If we restrict ourselves to a collinear-moment arrangement then from the above relation three antiferromagnetic (a), b), c)) and one ferromagnetic (d)) modes can be deduced:

a) [0, 0, 1/2]	$\lambda = 4 J_2 - 4 (J_1 - J_1')$;	observed in UOS [10],
b) [0, 0, 1/2]	$\lambda = 4 J_2 + 4 (J_1 - J_1')$;	found in UP_2 [4] and UAs_2 [5],
c) [0, 0, 0]	$\lambda = 4 J_2 - 4 (J_1 + J_1')$;	observed in UOTe [12],
d) [0, 0, 0]	$\lambda = 4 J_2 + 4 (J_1 + J_1')$;	hitherto unobserved.

The modes a) and c) correspond to the observed antiferromagnetic arrangements in USb_2 and UBi_2 respectively. For these two modes the stability conditions from the requirement that λ must be maximum leads to the following inequalities:

$$USb_2: \quad J_1 > 0\,, \qquad J_1' < 0\,, \qquad 2\,J_2 + J_1 - J_1' > 0\,;$$

$$UBi_2: \quad J_1 < 0\,, \qquad J_1' < 0\,, \qquad 2\,J_2 - J_1 - J_1' > 0\,.$$

The change of magnetic ordering observed in UBi_2 could be related to its large negative Weiss constant as compared to the positive value exhibited by remaining members of UX_2 series. The positive sign of the Weiss constant suggests some ferromagnetic interaction in UP_2, UAs_2, and USb_2 in agreement with the stability conditions of their magnetic structures given above.

It is of interest to consider the prevailing interaction mechanism leading to magnetic ordering in these compounds.

Recently the electric conductivity and thermo-e.m.f. measurements have been carried out for UP_2 and UAs_2, using single-crystal samples [15]. The results show metallic-type conductivity with $\varrho_{293\,°K} = 1.83 \times 10^{-4}$ and $1.95 \times \times 10^{-4}\ \Omega$cm for UP_2 and UAs_2, respectively. A similar type of conductivity could be assumed for USb_2, and UBi_2.

These facts could suggest that the exchange interaction via conductivity electrons plays a significant role in UX_2-type compounds similarly as it was recently proposed for some of the rare-earth alloys with bismuth [16].

Considering low values of the magnetic moment of uranium in both USb_2 and UBi_2 in their antiferromagnetic state the crystalline field splitting should be undoubtedly taken into account.

Calculations for the ordered state have been hitherto made for UO_2 only [17], where the lower value of $\mu_B = 1.80$ BM [18] as compared for the free ion U^{4+} (3.20 BM) has been quantitatively explained by the effect of the crystal field.

Acknowledgements

The authors would like to express their thanks to Prof. W. Trzebiatowski and Prof. B. Buras for their kind interest in this study.

References

[1] W. Trzebiatowski and R. Troć, Bull. Acad. polon. Sci., Sér. sci. chim. **11**, 661 (1963).
[2] W. Trzebiatowski, A. Sępichowska, and A. Zygmunt, Bull. Acad. polon. Sci., Sér. sci. chim. **10**, 687 (1964).
[3] W. Trzebiatowski and A. Zygmunt, Bull. Acad. polon. Sci., Sér. sci. chim. **14**, 495 (1966).
[4] R. Troć, J. Leciejewicz, and R. Ciszewski, phys. stat. sol. **15**, 515 (1966).
[5] A. Oleś, J. Phys. Radium **26**, 561 (1965).
[6] R. J. Teitel, J. Metals **9**, 131 (1957).
[7] R. Ferro, Atti Accad. naz. Lincei, Rend., Cl. Sci. fis., mat. nat. **14**, 89 (1953).
[8] R. Ferro, Atti Accad. naz. Lincei, Rend., Cl. Sci. fis., mat. nat. **13**, 53 (1952).
[9] K. Łukasziewicz, private communication.
[10] R. Ballestracci, E. F. Bertaut, and R. Pauthenet, J. Phys. Chem. Solids **24**, 487 (1963).
[11] S. S. Sidhu, W. Vogelssang, and K. D. Anderson, J. Phys. Chem. Solids **27**, 1197 (1966).
[12] A. Murasik and J. Niemiec, Bull. Acad. polon. Sci., Sér. sci. chim. **13**, 291 (1965).
[13] E. F. Bertaut, Magnetism, Ed. G. T. Rado and H. Suhl, Vol. 3, Academic Press, New York/London 1963 (p. 149).

[14] E. F. BERTAUT, Advanced Course on Magnetic Exchange Interactions in Transition Metal Compounds, Institutt for Atomenergi, Kjeller, Sept. 1964.
[15] W. TRZEBIATOWSKI and Z. HENKIE, private communication.
[16] T. TSICHIDA and W. E. WALLACE, J. chem. Phys. **43**, 2087 (1965).
[17] H. U. RAHMAN and W. A. RUNCIMAN, J. Phys. Chem. Solids **27**, 1833 (1966).
[18] B. C. FRAZER, G. SHIRANE, and D. E. COX, Phys. Rev. **140**, A1449 (1965).

(Received May 3, 1967)