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^{125}Te MÖSSBAUER SPECTROSCOPIC STUDY OF LAYERED TRANSITION METAL DITELLURIDES WITH INTERLAYER COMMUNICATION

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The ^{125}Te Mössbauer spectroscopy of different 1T-transition metal ditellurides shows that the values of the isomer shift are dependent on the degree of the Te–Te interlayer interactions which decrease the 5*p* population by Te(*p*)–M(*d*) electron donation. The quadrupole splitting values are consistent with the departure from the ideal 1T-structure. For 2H–MoTe$_2$, the Mössbauer parameters are affected by the distortion in the environment of molybdenum atoms caused by extensive layer bending in the particles of this solid.

Keywords: Chalcogenides, Mössbauer spectroscopy, electron microscopy, superlattices.

SEVERAL AUTHORS have studied the electronic states of tellurium and bond ionicity in metal tellurides by using two alternative Mössbauer spectroscopy procedures. From the analysis of isomer shifts of ^{129}Te in Mössbauer emission spectroscopy, it was reported that the ionicity decreases with the transition metal content in different compounds of the Cr–Te [1] and V–Te [2] systems. More recently, ^{125}Te Mössbauer absorption spectroscopy was successfully applied to the study of 3d transition metal ditellurides by the use of ^{125m}Te sources in a Mg$_3$TeO$_6$ matrix. Thus, it was found that those solids with pyrite- and marcasite-type structures (CrTe$_2$, FeTe$_2$, and CoTe$_2$) exhibit a linear relationship between isomer shift and quadrupole splitting while those with layered structures (TiTe$_2$, VTe$_2$ and NiTe$_2$) showed nearly vanishing quadrupole splittings [3].

Group 5 transition metal ditellurides have attracted the interest of different research groups. The three compounds have a CdI$_2$-related structure, although a monoclinic distortion (*C*2/*m* s.g.) is well established [4, 5]. Recently, the electronic origin of this distortion was examined by the hidden 1-D band concept. The interlayer tellurium–tellurium interactions account for a fractional electron count in the transition metal ions. This in turn leads to intralayer metal–metal polymerizations which form the characteristic ribbon-chains of metal atoms running parallel to the layers [6, 7]. Moreover, the effects of alkali metal intercalation into these compounds have also been studied [8, 9].

In this paper the effects of the atomic interactions on the Mössbauer spectra of V, Nb, Ta ditellurides is studied. Additional insight is obtained by the comparison with other structurally more simple 1T- and 2H-systems, TiTe$_2$ and α-MoTe$_2$, respectively.

Powdered samples of MTe$_2$ (M: Ti, V, Nb, Mo, Ta) were obtained by direct synthesis from the elements in evacuated silica ampoules at 850°C (TiTe$_2$, VTe$_2$ and α-MoTe$_2$) and 1000°C (NbTe$_2$ and TaTe$_2$). The

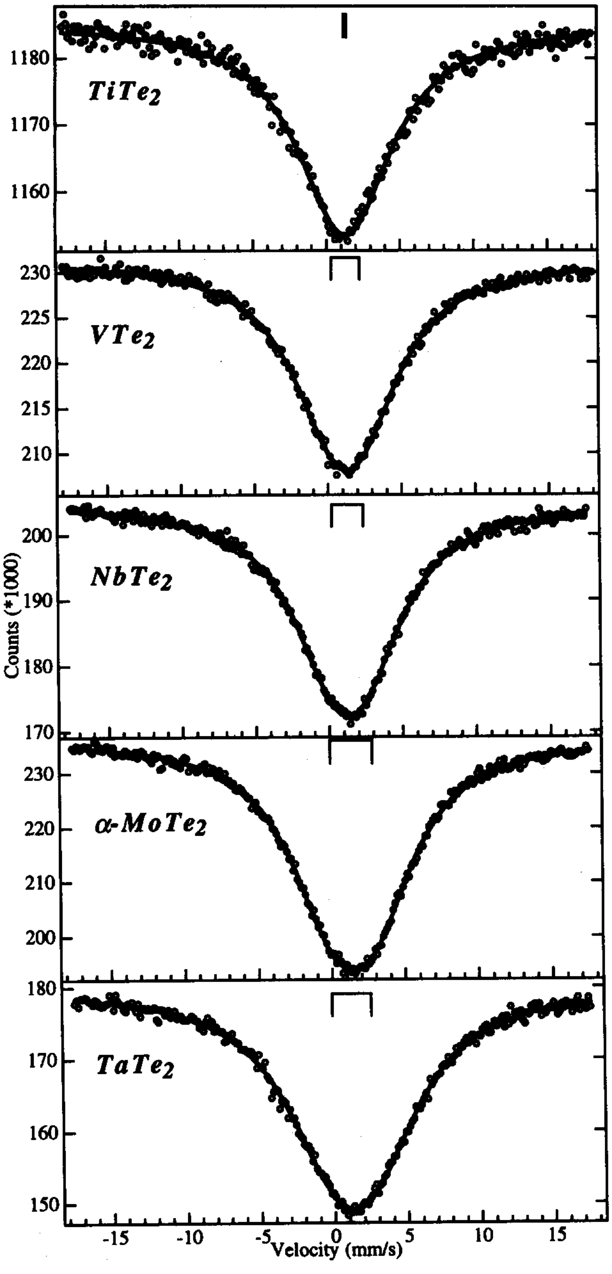

Fig. 1. ^{125}Te Mössbauer spectra recorded at 4.2 K.

^{125}Te Mössbauer spectra were recorded by using a $Mg_3^{125m}TeO_6$ source, prepared by activation of $Mg_3\,^{124}TeO_6$ under a flux of $3 \times 10^{14}\,n\,cm^{-2}\,s^{-1}$. Absorbers were prepared from powdered samples weighted to obtain a $1\,mg\,cm^{-2}$ ^{125}Te concentration. All the measurements were carried out at the Nuclear Radiation Physics Institute (IKS, Leuven, Belgium). Spectra were recorded using a Xe/CO_2 detector attached to a low-noise photomultiplier, with the escape peaks of the 35 KeV radiation. Both source and absorber were held at liquid helium temperature. The velocity calibration was obtained by a ^{57}Co(Cu) source and a ^{57}Fe enriched absorber. The zero-isomer shift was determined from the spectrum of Mg_3TeO_6 absorber recorded under the same experimental conditions. Electron microscopy studies were carried out in a JEOL 200CX apparatus.

Figure 1 shows the 4.2 K ^{125}Te Mössbauer absorption spectra of the different ditellurides. All spectra apparently consisted of a single line broadened by a quadrupole-split doublet. This is the expected behaviour for $TiTe_2$ and α-$MoTe_2$, as all tellurium atoms have an equivalent electronic state in each compound and are located in single sets of equivalent sites ($2d$ sites in the P-$3ml$ s.g. of the 1T-structure and $4f$ sites of the $P6_3/mmc$ s.g. of the 2H-structure, respectively). On the contrary, the ribbon chain modulation creates different Te environments in VTe_2, $NbTe_2$ and $TaTe_2$ (three different sets of $4i$ sites of the $C2/m$ s.g. for each compound) and this could lead to multiple components in each line. Nevertheless, due to the large natural linewidth of the ^{125}Te transition, $5.20 \pm 0.04\,mm\,s^{-1}$, the different components were not resolved. The precise parameters for the different sites are difficult to deduce from the single broadened line observed in the spectra of these distorted compounds. Thus, all spectra were fitted to a single Te resonance line with quadrupole splitting.

The values of isomer shift δ collected in Table 1 were used to study the different degree of interaction between tellurium atoms in each compound. In fact, the electron density at the nucleus is mainly dependent on the population of the valence shell orbitals, which

Table 1. Mössbauer parameters recorded at 4.2 K. *Spectra are fitted in the hypothesis of a single* Te *resonance line width quadrupole splitting*

Compound	δ ($mm\,s^{-1}$)	Δ ($mm\,s^{-1}$)	Γ ($mm\,s^{-1}$)	X^2
$TiTe_2$	1.32(2)	<0.44	7.83	1.129
VTe_2	1.30(1)	1.9(1)	7.2(1)	0.957
$NbTe_2$	1.38(1)	2.1(1)	7.1(1)	1.923
$MoTe_2$	1.66(9)	2.85(5)	7.13(8)	1.992
$TaTe_2$	1.36(1)	2.6(1)	8.4(1)	2.113

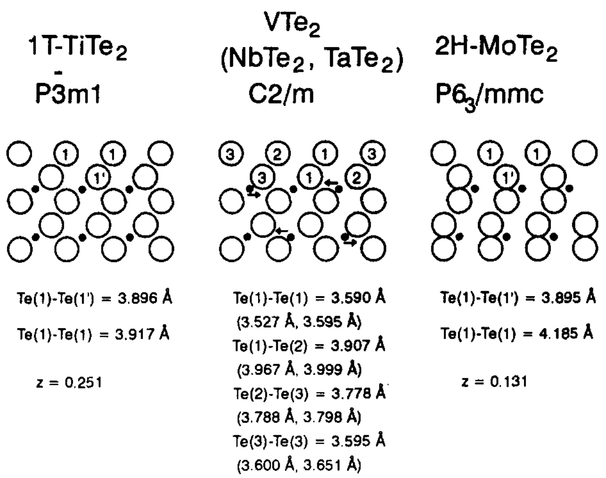

Fig. 2. Schematic (1 1 0) projection of undistorted 1T–TiTe$_2$, monoclinic VTe$_2$, NbTe$_2$ and TaTe$_2$, and 2H-MoTe$_2$.

may differ from that of the hypothetical Te^{2-} ion by covalent interactions. According to the results in [3], the δ values for compounds having Te–Te covalent bonds show a linear relationship with Δ while the δ values for CdI$_2$-related structures are similar. For the studied compounds, Fig. 2 shows that the interlayer Te–Te distances are always shorter than the distances measured parallel to the layers, irrespective of the distortion present in group 5 compounds. Nevertheless, the existence of a true covalent dimer Te$_2$ cannot be derived in these compounds. Thus, similar δ values are expected, the differences being mainly related to the strongest interlayer Te–Te interactions. However, the observed δ value for MoTe$_2$ is particularly large while Te–Te distances are similar. This effect shall be discussed in the light of the quadrupole splitting parameters.

On the other hand, it has been demonstrated that the presence of interlayer Te–Te interactions increase the p-block band energies, thereby leading to partial electron transfer from the top portion of the Te p-block bands to the d-block bands of the metals [6, 7]. An indirect measurement of these interactions comes from the particularly short interlayer Te–Te distances found in group 5 transition metal ditellurides. The shorter the distance, the larger the rise in energy of the p-block bands, and the larger the electron donation. This in turn should be reflected in a larger deficit in $5p$ orbital population near the nucleus which increases the δ values according to the following expression [3]:

$$\delta(\mathrm{mm\,s^{-1}}) = \delta_0 - 2.4a + 0.4b,$$

where δ_0 is the isomer shift of the hypothetical Te^{2-} anion and a and b are the deficits in $5s$ and $5p$ populations in the true electronic structure of tellurium atoms ($5s^{2-a}5p^{6-b}$). If we take into account that the shortest interlayer Te–Te distance is observed for NbTe$_2$ (3.527 Å [4]) as compared with VTe$_2$ (3.590 Å [5]) and TaTe$_2$ (3.595 Å [4]) (see Fig. 2) the largest isomer shift in this group 5 metal ditelluride is consistent with the above interpretation. Moreover, the interlayer Te–Te distance in TiTe$_2$ (3.896 Å for $a = 3.766$ Å, $c = 6.491$ Å and $z_{\mathrm{Te}} = 0.251$ [10]) is intermediate between these values and the maximum interlayer Te–Te distance between closest neighbors in V, Nb and Ta ditellurides, in agreement with the experimental δ value.

On the other hand, the Δ values in Table 1 give information about the average deviation of the electronic states of tellurium from spherical symmetry. In undistorted 1T and 2H transition metal dichalcogenides, each chalcogen atom is surrounded by six in-plane equidistant chalcogen atoms, three equidistant metal atoms belonging to the same sandwich layer and three equidistant chalcogen atoms from the adjacent layer. As a result, a $3m$ site symmetry is found for the chalcogen sites in both structural variants and low but signficant Δ values are expected in these compounds. In contrast, the number of different interatomic distances increases dramatically with the monoclinic distortion in group 5 transition metal ditellurides (see Fig. 2) and site symmetry now decreases to m. Particularly large Δ values are expected as a result of the marked departure from the spherical symmetry. From the comparison of Δ values of undistorted 1T-TiTe$_2$ with those of VTe$_2$, NbTe$_2$ and TaTe$_2$ (Table 1) a good correspondence with the expected behaviour is patent. However, it should be noted that the Δ value found for monoclinic VTe$_2$ contrasts with the low value reported by Stanek *et al.* [3] from ^{125}Te Mössbauer spectra of CdI$_2$-related VTe$_2$ recorded at 80 K. This difference may be indicative of an undistorted phase, probably as a result of the different synthesis temperature (300°C) used in [3] as compared with this study (850°C). In this way, Ohtani *et al.* [10] have reported a phase transition from the monoclinic superstructure to the undistorted Cd(OH)$_2$-type structure in the 390–474 K temperature interval.

On the other hand, the expected trend in Δ values is not followed by α-MoTe$_2$. It is usually assumed that this solid has an undistorted 2H structure similar to the common α form of MoS$_2$ [11]. However, electron micrographs of the α-MoTe$_2$ particles, obtained with the incident electron beam lying parallel to [0 0 1] (Fig. 3) show a complex texture and bent lattice fringes in extended regions near the edges of the platelike particles. Electron diffraction patterns of

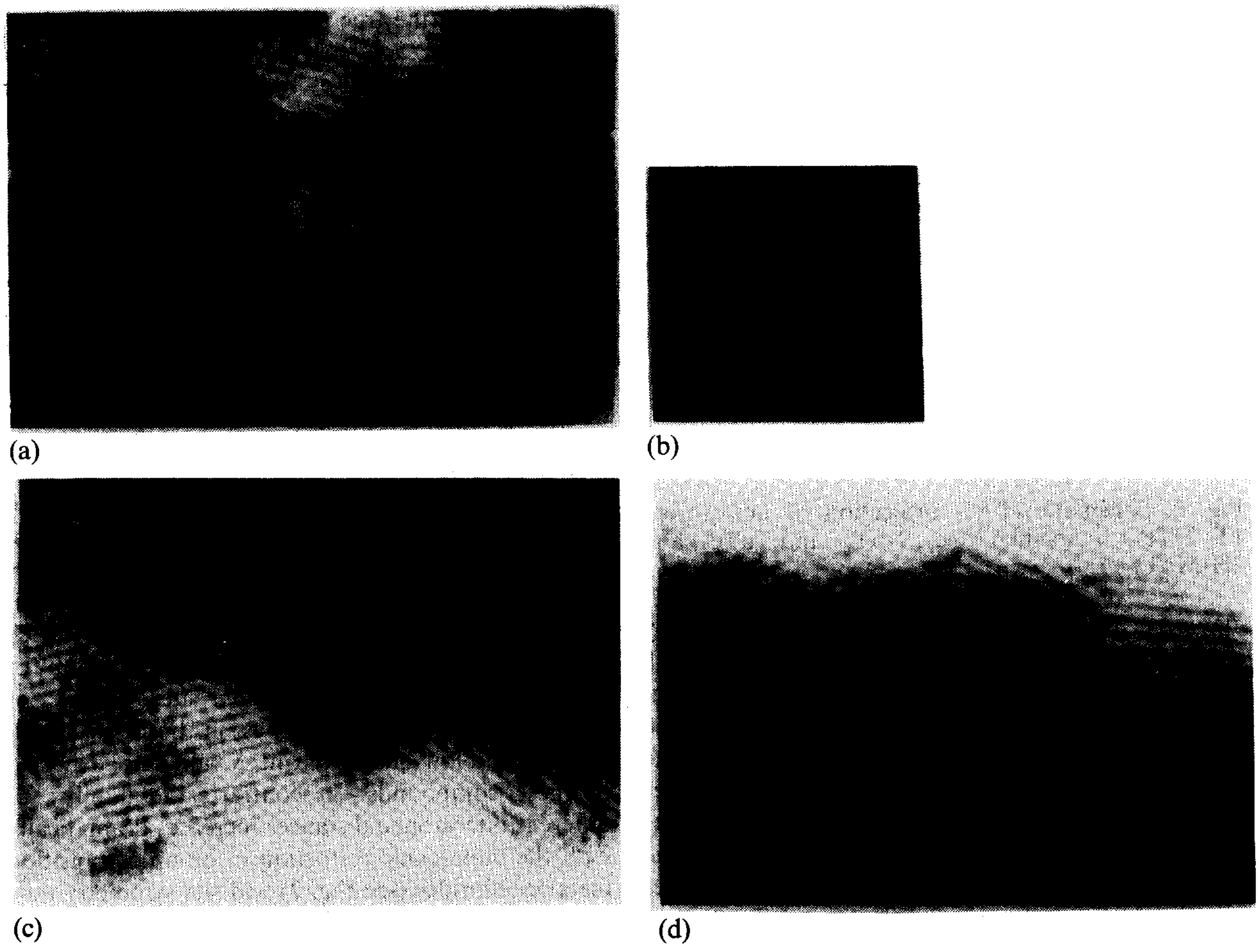

Fig. 3. Electron micrographs of layer bending in crystals of α-MoTe$_2$: (a) extended region; (b) corresponding electron diffraction pattern; (c) surface region; (d) twinning preventing closure. The spacing between fringes agrees with the distance between consecutive Mo atoms along [0 0 1] ($c/2$).

these zones evidence rotation of different sets of $\{hk0\}$ spots. It should be noted that transition metal dichalcogenides with 2H structures and d^2 electron count provide different examples of layer curling [12], tubular crystals and polyhedral crystals [13]. Layer bending has marked effects on the interatomic distances and site symmetry of metal atoms in the structure of MoTe$_2$. The resulting distortion of the environment of tellurium atoms may be responsible for the large Δ values observed in the Mössbauer spectra. This in turn may condition large Te–Te interactions that may be responsible for the large δ values shown above.

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REFERENCES

1. J. Granot & S. Bukshpan, *J. Phys. C: Solid State Phys.* **8,** 1435 (1975).
2. T. Ohtani & H. Sakai, *Solid State Commun.* **57,** 81 (1986).
3. J. Stanek, A.M. Khasanov & S.S. Hafner, *Phys. Rev.* **45,** 56 (1992).
4. B.E. Brown, *Acta Cryst.* **20,** 264 (1966).
5. K.D. Bronsema, G.W. Bus & G.A. Wiegers, *J. Solid State Chem.* **53,** 415 (1984).
6. E. Canadell, S. Jobic, R. Brec, J. Rouxel & M.H. Whangbo, *J. Solid State Chem.* **99,** 189 (1992).
7. M.H. Whangbo & E. Canadell, *J. Am. Chem. Soc.* **14,** 9587 (1992).
8. R. Guzmán, J. Morales & J.L. Tirado, *J. Mater. Chem.* **3,** 1271 (1993).
9. R. Guzmán, J. Morales & J.L. Tirado, *Inorg. Chem.* **33,** 3164 (1994).
10. T. Ohtani, K. Hayashi, M. Nakahiri & H. Nozaki, *Solid State Commun.* **40,** 629 (1981).
11. S.N. Magonov & M.H. Whangbo, *Adv. Mater.* **6,** 355 (1994).
12. J. Moser, H. Liao & F. Lévy, *J. Phys. D: Appl. Phys.* **23,** 624 (1990).
13. R. Tenne, L. Margulis & G. Hodes, *Adv. Mater.* **5,** 386 (1993).