

Electronic states of tellurium in 3d-transition-metal ditellurides

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The isomer shift S and quadrupole splitting Δ of the 35.5-keV ^{125}Te level in $M\text{Te}_2$ ($M = \text{Ti, V, Cr, Fe, Co, and Ni}$) were measured at 80 K. $M\text{Te}_2$ with pyrite- and marcasite-type structures exhibit a linear relationship between S and Δ , while those with CdI_2 -type structures show nearly vanishing Δ . Electronic populations of the $5s5p$ valence states of Te were approximately determined.

INTRODUCTION

The atomic ground state $5s^25p^4$ of tellurium allows a wide range of electronic states, yielding nominal valences between $2-$ and $6+$. In general the coordination number of Te in solids may vary between 2 and 6, but in some cases it is not well defined, for example, in some oxides or in Te-bearing glasses. Information on local Te bonding may be obtained from ^{125}Te hyperfine data, ^{125}Te being the only stable group-VI isotope which is accessible to nuclear γ -ray resonance.

γ -ray resonance of ^{125}Te ($E = 35.46$ keV) was observed first in the early sixties, using ^{125m}Te as source activated by neutron irradiation of ^{124}Te in matrices of TeO_2 (Ref. 1) PbTe (Ref. 2), or ^{125}Sb (Refs. 3 and 4) which decays to ^{125}Te via ^{125m}Te . The experimental widths of those sources, however, were commonly broadened and often not reproducible, i.e., not appropriate for the study of Te bonding in solids. Moreover, the sources had to be kept at 78 K or lower because of low recoilless fraction. ^{125}I was also employed as source,⁵ yielding similar results as ^{125}Sb . Many studies⁶ were made with ^{129m}Te as source which decays to ^{129}I ($E = 277.77$ keV). The half time of the first excited state of ^{129}I is 16.8 ns compared to 1.56 ns of that of ^{125}Te , yielding high resolution of the hyperfine interactions of ^{129}I . Although I and Te may have rather similar electronic states, the local fields of I at the Te site in the crystal are, at least in principle, not identical with those of Te.

Recently,^{7,8} the use of ^{125m}Te as source in Mg_3TeO_6 as matrix proved to yield experimental widths of 0.5 mm/s for Mg_3TeO_6 as absorber, i.e., only 4% more than the natural width ($2 \times 2.97 \times 10^{-7}$ eV or 5.02 mm/s) and quite acceptable for detailed bonding studies. Its recoilless fraction allows to keep the source at 295 K. In this paper, results on the Te bonding in 3d-transition-metal ditellurides obtained with that type of source are presented.

$M\text{Te}_2$ ($M = \text{Ti, V, Cr, Mn, Fe, Co, and Ni}$) form relatively simple crystal structures from a geometrical point of view. MnTe_2 (Ref. 9) is of the cubic pyrite type (space group $Pa\bar{3}$). FeTe_2 ($Pnnm$) (Ref. 10) and CoTe_2 ($Pnn2'$) (Refs. 10 and 11) are the orthorhombic marcasite type.

In pyrite, FeS_2 , S_2 pairs form a cubically close-packed arrangement, Fe filling the octahedral interstices (like NaCl type). In the marcasite modification of FeS_2 , the packing of S_2 is body centered, Fe being 8-fold coordinated (distorted CsCl type). In the structures of the pyrite type, the shortest S-S or Te-Te distances are shorter than the shortest M -S or M -Te distances. These structures may be considered to be composed of S_2^{2-} or Te_2^{2-} anions.

The ditellurides with $M = \text{V, Ti, Ni}$ crystallize with the structures of the hexagonal CdI_2 type (space group $C3m$ or lower)¹²⁻¹⁴ which consists of a hexagonal close-packed arrangement of I, M filling one half of the octahedral interstices. The type may be described as a layerlike structure, the small cations being nested between alternate layers of large anions. In pyrite, marcasite, and CdI_2 type structures, each S or Te has three M as nearest M neighbors.

EXPERIMENTAL

Samples of ditellurides were synthesized from high purity elements employing dry evacuated silica tube technique. All specimens were heated, quenched, reground, and annealed at 300°C for several weeks until complete equilibrium was attained. This was tested by x-ray diffraction. The ^{125}Te spectra were recorded at 80 K in a gas flow cryostat, the source being at 295 K. The absorbers contained 50 mg/cm² Te in natural abundance spread over an area of 0.40 cm². The source was prepared by activating 25 mg Mg_3TeO_6 enriched in ^{124}Te up to 90% in a beam of 10^{14} n/s cm² for 20 days in the Kernforschungszentrum Jülich. The final activity was measured to be 5.2 GBq.

The resonant 35.5-keV γ -ray radiation was selected from the x-ray spectrum by use of a pure germanium detector operating at 78 K. The Mössbauer spectra were collected over 512 channels usually for two days, yielding a final statistics of 10^6 counts per channel (before folding). The experimental line width was determined from a Mg_3TeO_6 spectrum at 295 K containing 25 mg natural Te/cm² which corresponded to the effective absorber thickness $T_a = 1$. The measured full width (at half inten-

TABLE I. ^{125}Te hyperfine data, proposed electron configurations $5s^{2-a}5p^{2-b}$, and effective charges of Te of $M\text{Te}_2$ compounds. S and Δ of MnTe_2 are from Ref. 16; ST: structure type, *: assuming $b=0$ in C-type structures, the populations in $5s$ and $5p$ and the effective charges are, therefore, upper limits. The errors of S and Δ are 0.03 mm/s.

M	ST	S (mm/s)	Δ (mm/s)	$5s^{2-a}$	$5p^{2-b}$	Effective Te	charge M	Shortest distance	
								Te- M (Å)	Te-Te (Å)
Ti	CdI_2	1.21	<0.5	1.81*	6.00*	-1.81*	+3.62*	2.77	3.77 (Ref. 13)
V	CdI_2	1.26	<0.5	1.83*	6.00*	-1.83*	+3.66*	2.67	3.69 (Ref. 12)
Cr	?	1.14	6.87	1.70	5.42	-1.12	+2.24	?	?
Mn	pyrite	1.05	7.75	1.63	5.35	-0.98	+1.96	2.90	2.74 (Ref. 9)
Fe	marcasite	1.38	3.85	1.83	5.67	-1.50	+3.00	2.56	2.93 (Ref. 10)
Co	marcasite	1.45	3.09	1.87	5.74	-1.61	+3.22	2.58	2.91 (Ref. 11)
Ni	CdI_2	1.57	1.32	1.96*	6.00*	-1.96	+3.92	2.58	3.45 (Ref. 14)

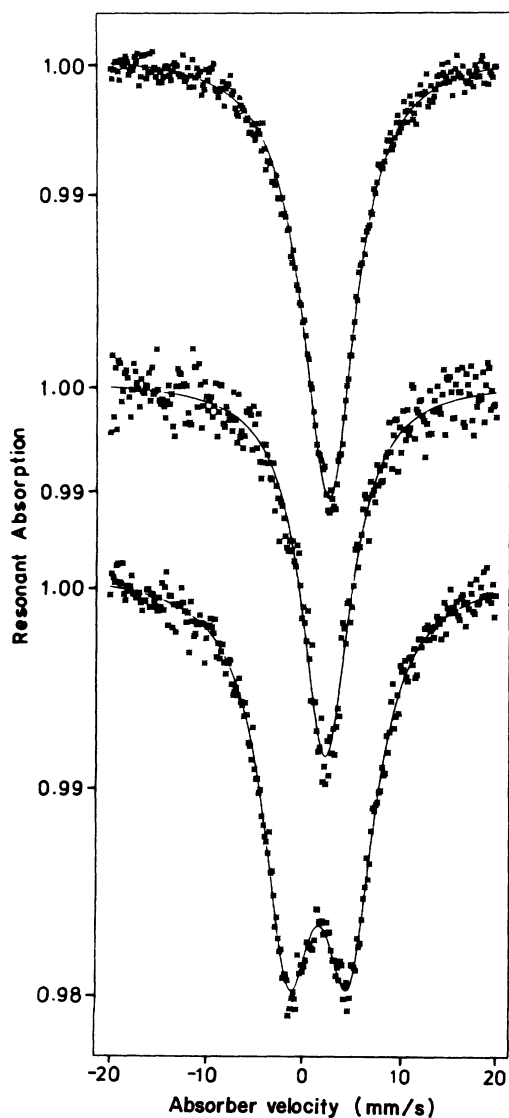


FIG. 1. ^{125}Te γ -ray spectrum of TiTe_2 (top), VTe_2 , and CrTe_2 (bottom); absorber 80 K, source 295 K.

sity) was 6.6 mm/s. The relative broadening of the line due to finite absorber thickness may be estimated¹⁵ as $0.27T_a=27\%$. Thus, the corrected experimental linewidth is 5.2 mm/s, i.e., very close to the natural linewidth of 5.02 mm/s. The velocity scale was determined from ^{57}Fe spectra of metallic iron. The isomer shifts are referred to Mg_3TeO_6 at 295 K.

RESULTS

All measured spectra consisted of a quadrupole-split doublet or an apparent single line broadened due to quadrupole interaction. The spectra of TiTe_2 , VTe_2 , and CrTe_2 are shown in Fig. 1 as example. The solid lines represent least squares fits assuming Lorentzian shape for resonant absorption. The hyperfine parameters such as isomer shift (S) and quadrupole splitting (Δ) are collected in Table I. The upper limits of Δ in VTe_2 and TiTe_2 arise from the single line broadening. Fits with assumed quadrupole doublet lead in these cases to unrealistically small line widths. The line widths varied between 7.3 and 7.8 mm/s. The data for MnTe_2 were taken from Ref. 16.

The S values plotted vs atomic number of the cation (Fig. 2) show a minimum electron density at the ^{125}Te nu-

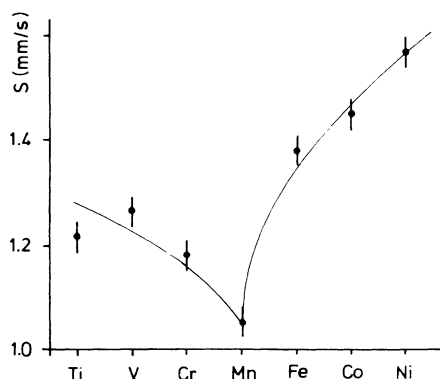


FIG. 2. ^{125}Te isomer shifts (S) of 3d-transition-metal ditellurides; source 295 K, absorbers 80 K.

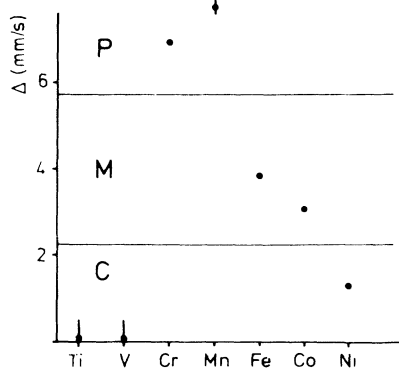


FIG. 3. ^{125}Te quadrupole splitting (Δ) of $3d$ -transition-metal ditellurides: source 295 K, absorbers 80 K; C: CdI_2 type; M: marcasite type; P: pyrite type and CrTe_2 (structure type not known).

cleus for MnTe_2 . The Δ values reflecting mainly the deviation of the Te $5p$ states from spherical symmetry are plotted vs atomic number of cations in Fig. 3. They may be divided into three groups: (i) $0 < \Delta < 2$ mm/s, i.e., ditellurides of the hexagonal CdI_2 type ($M = \text{Ti, V, Ni}$); (ii) $2 < \Delta < 6$ mm/s, i.e., ditellurides of the orthorhombic marcasite type ($M = \text{Fe, Co}$), and (iii) $\Delta > 6$, mm/s, i.e., ditellurides of the cubic pyrite type ($M = \text{Mn}$) and $M = \text{Cr}$ of which the crystal structure is still unknown.

DISCUSSION

Isomer shift (S)

The S of ^{125}Te is proportional to the electron density at the nucleus and determined mainly by the population of the $5s$ and $5p$ orbitals in the electronic $5s^{2-a}5p^{6-b}$ configuration of the Te valence shell, $a = b = 0$ representing the free Te^{2-} state. In tellurium compounds both $5s$ and $5p$ contribute to the effective bonding. From the extrapolation of ^{129}I data it was found that one $5s$ electron adds 2.4 mm/s to the S .¹⁷ Relating ^{125}Te γ -ray resonance and nuclear quadrupole resonance data of a series of tellurium hexahalides, it was also concluded that one $5p$ electron reduces the S by 0.4 mm/s due to enhanced shielding.¹⁸ Thus, it is not possible to determine the $5s5p$ configuration from the S alone.

The compound with the smallest S is MnTe_2 . In its cubic pyrite structure, six Te_2^{2-} pairs are nearest neighbors of the octahedrally coordinated Mn^{2+} which attains a "half-filled" $3d^5$ configuration.

At this point, it is of interest to note that electron densities at impurity (probe) isotopes (e.g., ^{197}Au , ^{57}Fe , ^{193}Ir , ^{99}Ru) in $3d^n$ metallic hosts increase with increasing atomic number of the host, reaching maximum in Mn ($n = 7$) or Cr ($n = 6$), and subsequently decrease again. This was explained as the results of the atomic volume effects and the host band structure.¹⁹ In the case of MTe_2 compounds the situation is just opposite: minimum electron density is observed for $M = \text{Mn}$, implying a charge transfer mechanism between metal and Te. The consecutively increasing densities at ^{125}Te in the cases of $3d^n$ cat-

ions, $n < 5$ as well as $n > 5$ (cf. Fig. 2), reflect the trends for reaching the half-filled $3d$ shell, $n = 5$ in the case of Mn^{2+} .

Quadrupole splitting (Δ)

For $I = 1/2, 3/2$ transitions, the Δ is

$$\Delta = \frac{1}{2}eQV_{zz} \left[1 + \frac{\eta^2}{3} \right]^{1/2},$$

where Q is the nuclear quadrupole moment of ^{125}Te , V the electrostatic potential at the nuclear position in the crystal. V_{zz} the second derivative of V in the principle axes system X, Y, Z , and $\eta = (V_{xx} - V_{yy})/V_{zz}$. Paramagnetic ^{125}Te spectra of polycrystalline samples do not supply any information of sign and direction of V_{zz} at the Te site in the crystal. The discussion of Δ for such cases is, therefore, based usually on structure-related assumptions. For MnTe_2 , a positive sign of V_{zz} was obtained from the mixed magnetic and electrostatic interaction of the magnetically ordered structure.¹⁶

The greatest Δ was observed for cubic MnTe_2 , whereas for hexagonal NiTe_2 , VTe_2 , and TiTe_2 , it apparently vanishes. In MnTe_2 , two adjacent Te atoms form a pair with an interatomic distance of 2.74 Å, the shortest Te-Te distance reported for the ditellurides of this study (cf. Table I). It is reasonable to assume that the Z direction of V_{zz} in MnTe_2 is about parallel to the Te-Te direction which represents a sigma bond, the positive V_{zz} being produced by an electron hole in the p_z orbital. This interpretation supports the point of view^{9,16} that in a first approximation, MnTe_2 may be considered as a basically ionic compound of close-packed M^{2+} cations and covalently bonded Te_2^{2-} molecular anions. The conception appears useful for explaining the trends in S and Δ of other ditellurides, especially those with marcasite-type structure such as FeTe_2 and CoTe_2 .

S - Δ relation

Δ values plotted vs S exhibit a simple linear relationship shown in Fig. 4. Exceptions are the values of TiTe_2 and VTe_2 (cf. discussion below). The linear dependence of the electron density at ^{125}Te on V_{zz} (assuming $\eta = 0$) may be interpreted in terms of a transfer of electronic charge from $5s^2$ and $5p^6$ of the ionic Te^{2-} state to the cation, causing a net decrease of the S (cf., Fig. 4, from right to left). At the same time, the Δ increases by enhancement of the hole in $5p_z$ as proposed in the previous section. This trend is expected to be associated with a shortening of the shortest Te-Te distance in the crystal structure, ending in the electronic configuration and geometry of MnTe_2 .

It appears interesting to estimate the $5s5p$ orbital populations of Te. Since the work of Townes and Dailey in 1949,²⁰ it is known that $5s5p$ compounds exhibit significant covalent bonding. The strength of this bonding may be estimated from Te- M bond-valence parameters of the structures in question.²¹ Application of that

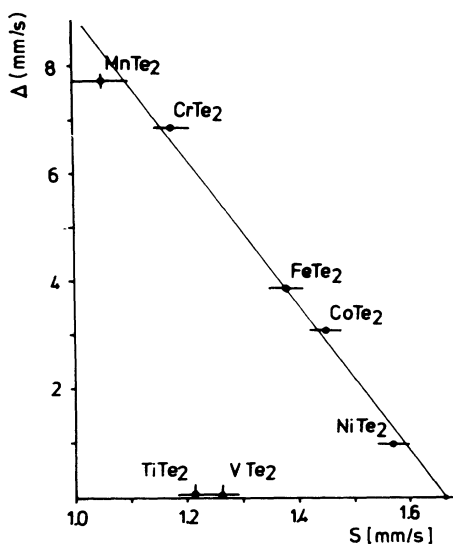


FIG. 4. S - Δ relationship of ^{125}Te in 3d-transition-metal ditellurides.

model to the series of crystal structures studied here shows that Te— M bond valences vary in a rather irregular way. The Te—Te bond, however, is related systematically to the structures. This allows the conclusion that the hyperfine parameters, S and Δ , are mainly determined by the Te-Te interactions, while the contribution of the Te— M bonding is rather invariable. Thus, only Te—Te bonding is discussed.

The deficit b in $5p_z$ population, assuming that $5p_x$ and $5p_y$ remain fully populated, may be calculated as

$$b = \Delta / \Delta_0, \quad (1)$$

where $\Delta_0 = 12$ mm/s is the quadrupole splitting produced by one electron hole in the $5p_z$ orbital.²² Moreover, it is possible to estimate the population a of the $5s$ state. The S is mainly

$$S \text{ (mm/s)} = S_0 - 2.4a + 0.4b, \quad (2)$$

where S_0 is the isomer shift of the hypothetical Te^{2-} anion with $5s^2 5p^6$ configuration in 3d-transition-metal ditellurides, and a is the population deficit in the $5s$ orbital. $S_0 = 1.66$ mm/s may be derived by extrapolating the apparently linear relation as shown in Fig. 4 to $\Delta = 0$.

a and b values calculated by use of Eqs. (1) and (2) are presented in Table I. This simple approximation is expected to become less significant with increasing ratio of the shortest distances, $d_{\text{Te-Te}}/d_{M-\text{Te}}$. In fact, TiTe_2 and VTe_2 ($\Delta = 0$) do not follow the linear S - Δ relation. According to the model above, $\Delta = 0$ implies a completely filled $5p$ state. The apparently vanishing Δ in the structures of the CdI_2 type may be due to the high Te-Te coordination number of this type which approaches 12, resulting in about equal population of $5p_x$, $5p_y$, and $5p_z$.

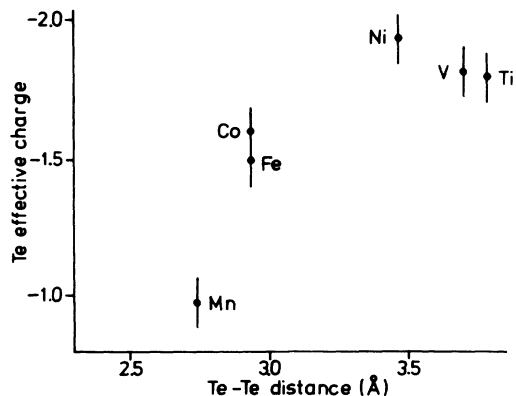


FIG. 5. Effective charges of Te in 3d-transition-metal ditellurides concluded from ^{125}Te γ -ray resonance.

The S in those cases, however, are indicative of substantial deficits in $5s$ population and, therefore, considerable charge transfer from Te to M .

Effective charges

From the electronic orbital populations above, effective charges $q = -2 + a + b$ may be computed for Te (Table I). The systematic increase of the net charge with increasing nearest Te-Te distance (cf. Fig. 5) appears reasonable. It should be noted that the nominal charge -1 of Te postulated for MnTe_2 (Ref. 23) is confirmed by the present model.

The effective charges of Te imply correlated cationic charges as shown in Table I. Each of these are possible formally. Some of them, however, may be up for further discussion. FeTe_2 , for example, has been described generally as low spin Fe^{II} (Refs. 19 and 24) although $S = 0.47$ mm/s and $\Delta = 0.52$ mm/s are rather typical for high spin Fe^{3+} . The problem was discussed in the past using MO theory, but with an *a priori* assumed Fe^{II} state.¹⁹ Compounds with quadrivalent Ni are rare. Yet diatomic Ni^{4+} complexes with sulfur ligands are known, e.g., $(\text{C}_5\text{H}_5)_2\text{Ni}_5\text{Si}_6$.²⁵

The net cationic charge appears to have structural consequences in that the shortest Te-Te distances increase more or less accordingly. This leads to a transformation from the pyrite type ($M = \text{Mn}$), through the marcasite type ($M = \text{Fe}, \text{Co}$) to the CdI_2 type ($M = \text{Ti}, \text{V}, \text{Ni}$).

CONCLUSION

The hyperfine parameters S and Δ properly reflect the Te local symmetry within the investigated series. The data may be affected, however, first, by the uncertainty of some scaling factors such as contributions to the S and Δ by $5s$ and $5p$ electrons. Second, the arbitrary neglect of covalency effects in M —Te bonding leads to overestimation of the $5s$ and $5p$ orbital population and consequently of the net charges of the cations. The concluded Mn^{2+} state for MnTe_2 , which is widely accepted, may nevertheless be used as an argument for the model.

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