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^{125}Te Mössbauer Spectra of the Intercalation Compound $(Te_2)_2(I_2)$

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Abstract

The quadrupole split asymmetric ^{125}Te Mössbauer spectrum recorded from the compound $(Te_2)_2(I_2)$, in which monomolecular planar layers of iodine molecules are intercalated between layers of tellurium, is a reflection of the distorted environment of tellurium atoms in a two-dimensional layered compound in which the elongated flat crystals are preferentially orientated. The differences between the Mössbauer parameters recorded from $(Te_2)_2(I_2)$ and those recorded from elemental tellurium and the tellurium(0) species in the compound Te_3Cl_2 are associated with small differences between the environments of tellurium in the three compounds. The Mössbauer spectra recorded from $(Te_2)_2(I_2)$ are consistent with a recently proposed model on which the electronic band structure of $(Te_2)_2(I_2)$ has been derived.

Introduction

A compound of formulation $^2_\infty(Te_2)_2(I_2)$ has recently been prepared and has been shown by X-ray crystallography to possess an unusual layer structure which can be described in terms of the intercalation of tellurium by elemental iodine [1]. Even more recently the electronic band structures of some inorganic solid compounds with layered structures, including $(Te_2)_2(I_2)$, have been calculated and related to the structural properties of the two-dimensional solids [2]. Given that ^{125}Te Mössbauer spectroscopy is well suited for the examination of bonding and stereochemistry about the tellurium atom in inorganic compounds, including the tellurium subhalides [3], we have examined the new iodine-intercalated tellurium phase by low-temperature Mössbauer spectroscopy and we report here on the interpretation of the results in terms of the crystallographic and electronic structure of the intercalate.

Experimental

The compound $(Te_2)_2(I_2)$ was prepared by hydrothermal synthesis in concentrated hydroiodic acid as previously described [1].

^{125}Te Mössbauer spectra were recorded with a microprocessor controlled Mössbauer spectrometer with both the ^{125}Sb/Rh source and the sample, which contained *ca.* 90 mg tellurium/cm^{-2}, being maintained at either 77 or 4 K. The drive velocity was calibrated with a ^{57}Co/Rh source and a natural iron foil. All spectra were computer fitted. The ^{125}Te chemical isomer shift data were calculated relative to ^{125}I/Cu by the subtraction of 0.22 mm s^{-1} from the δ value recorded relative to the ^{125}Sb/Rh source. The conversion factor has been derived from a comparison of the ^{125}Te Mössbauer parameters recorded from elemental tellurium with those reported in the literature.

Results and Discussion

The intercalation compound $(Te_2)_2(I_2)$ contains planar double layers of tellurium formed from Te_2 units which are arranged along the *c* axis [1] (Fig. 1). The tellurium atoms within the double layers exhibit a distorted tetragonal-pyramidal [1 + 4] coordination with each tellurium atom being involved in one short Te–Te bond (2.713(7) Å) in the Te_2 unit and in four longer Te–Te bonds (3.323(1) Å) between adjacent Te_2 units within a double layer. In contrast, trigonal elemental tellurium consists [4] of spiral chains of tellurium atoms (Fig. 2a) in which the tellurium atoms adopt distorted octahedral [2 + 4] coordination with short intrachain and longer interchain Te–Te distances of 2.835(2) and 3.495(4) Å respectively. The first sphere of coordination of each tellurium atom can be represented as ψ-tetrahedral, $[Te(Te)_2E_2]$, where E represents a non-bonding pair of electrons.

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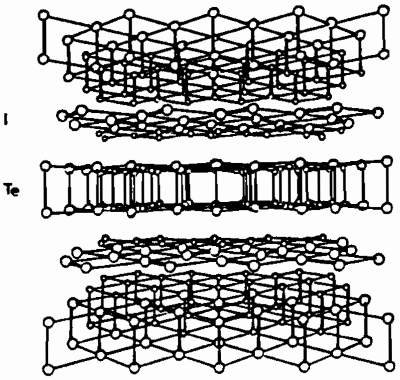

Fig. 1. Perspective representation of the layer sequence ([001]) in $(Te_2)_2(I_2)$. The Te_2 pairs and I_2 molecules are accentuated by bolder lines.

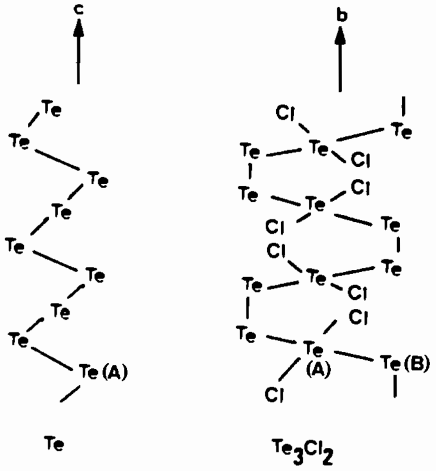

Fig. 2. Structural units of (a) elemental tellurium, (b) Te_3Cl_2.

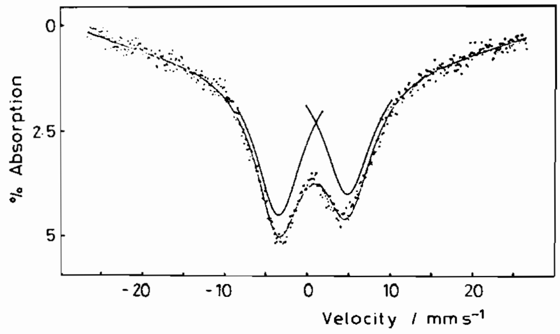

Fig. 3. ^{125}Te Mössbauer spectrum recorded from $(Te_2)_2(I_2)$ at 4 K.

TABLE I. ^{125}Te Mössbauer Parameters

Compound	$\delta^a \pm 0.05$ (mm s^{-1})	$\Delta \pm 0.1$ (mm s^{-1})	$\Gamma \pm 0.1$ (mm s^{-1})	Reference
Te	0.63	7.73	5.77	this work
$(Te_2)_2(I_2)$	0.70	8.33	7.18	this work
Te_3Cl_2	Te(A) 0.63(10)	11.0(8)	6.3	3
	Te(B) 0.78(12)	8.1(3)	6.5	

$^a\delta$ relative to $^{125}I/Cu$.

The compound Te_3Cl_2 consists (Fig. 2b) of an unlimited chain of tellurium atoms similar to that in elemental tellurium, and in which two tellurium(0) atoms (labelled B) are each coordinated by two other tellurium atoms with a ψ-tetrahedral $[Te(Te)_2E_2]$ local environment in a similar way to that in elemental tellurium, but in which every third tellurium(II) species (labelled A) is also bound to two chlorine atoms in axial positions [5]. The coordination of each Te(A) species is therefore ψ-trigonal-bipyramidal if the non-bonding pair of electrons E is included in the coordination scheme and can be represented as $[Te(Te)_2(Cl)_2E]$. The Te(B) site involving tellurium-(0) is therefore more analogous to that found in $(Te_2)_2(I_2)$. The Te–Te bond length in Te_3Cl_2 of 2.67 Å has been associated [5] with partial double bond character and is only slightly shorter than the short Te–Te bond length [1] in $(Te_2)_2(I_2)$. Hence the Te_2 units in $(Te_2)_2(I_2)$ have been envisaged as being stabilised by resonance

$$(:\dot{\underset{\cdot\cdot}{\mathrm{Te}}} - \dot{\underset{\cdot\cdot}{\mathrm{Te}}} \longleftrightarrow \dot{\underset{\cdot\cdot}{\mathrm{Te}}} = \dot{\underset{\cdot\cdot}{\mathrm{Te}}} \longleftrightarrow \dot{\underset{\cdot\cdot}{\mathrm{Te}}} - \dot{\underset{\cdot\cdot}{\mathrm{Te}}}:).$$

The ^{125}Te Mössbauer spectrum recorded from $(Te_2)_2(I_2)$ at 4 K (Fig. 3) was similar, but of superior quality, to that recorded at 77 K. The asymmetry in the spectrum is a result of the preferential orientation of the needle-like crystals. The ^{125}Te Mössbauer parameters, together with similar data recorded from elemental tellurium and the compound Te_3Cl_2, are collected in Table I.

The quadrupole splitting for tellurium in $(Te_2)_2(I_2)$ is larger than that recorded from the ψ-tetrahedrally coordinated tellurium atoms in elemental tellurium. The result reflects the more asymmetric environment of each distorted tetragonal pyramidal tellurium atom in $(Te_2)_2(I_2)$ which, although bonded to [1 + 4] tellurium atoms at distances of 2.713(7) and 3.323(1) Å (*vide supra*), is also 3.812(9) Å away from an iodine atom in an adjacent layer [1]. It is also relevant to note that the value of Δ for $(Te_2)_2(I_2)$ is more similar to that of the Te(B) atom in Te_3Cl_2 than to that of the tellurium atoms in the spiral chains of elemental tellurium. The difference between the values of Δ for Te(B) in Te_3Cl_2 and tellurium atoms in elemental tellurium may result from the electron withdrawing effect of chlorine atoms on the Te(A) species in Te_3Cl_2 which causes a small imbalance in the 5p orbital population of the adjacent Te(B) atom and which is reflected in a larger quadrupole splitting. In the respect it is interesting to note that the electronic band structure of $(Te_2)_2(I_2)$ has been derived from a model which permits the transfer of charge from tellurium to the more electronegative iodine [2]. The large ^{125}Te Mössbauer quadrupole splitting recorded from $(Te_2)_2(I_2)$ is consistent with such electron delocalisation from the tellurium 5p orbitals.

It is also pertinent to note that the chemical isomer shift recorded from $(Te_2)_2(I_2)$ is more positive than that recorded from elemental tellurium (Table I). The result also endorses the delocalisation of electrons from tellurium to iodine in $(Te_2)_2(I_2)$ since $\Delta R/R$ is positive for the ^{125}Te Mössbauer transition [6] and the removal of 5 p electrons from tellurium would be expected to increase the s electron density and give rise to a more positive chemical isomer shift. Although great caution must be exercised when interpreting ^{125}Te chemical isomer shift data, the coincidence in the differences between both Mössbauer parameters recorded from elemental tellurium on the one hand and $(Te_2)_2(I_2)$ on the other is quite consistent with the occurrence of tellurium–iodine charge transfer processes in $(Te_2)_2(I_2)$ and the model on which the electronic band structure has been derived [2].

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