Tellurium-125 Mössbauer Spectra of Gallium(II,III) Tellurohalides, Ga_3Te_3X, and Gallium(II) Telluride, GaTe

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Abstract

The mixed-valence gallium(II,III) tellurohalides of composition Ga_3Te_3X, where X is Cl, Br or I, and gallium(II) telluride, GaTe, have been examined by ^{125}Te Mössbauer spectroscopy. The chemical isomer shift data, which are insensitive to the nature of the halogen and mixed valence on the gallium site, are consistent with the presence of anionic tellurium in predominantly covalently bonded compounds. The small quadrupole splittings which characterise all the spectra are associated with the slightly distorted tetrahedral coordination around tellurium: $ETe(Ga^{II})_{3/3}$, $ETe(Ga^{II})_{2/3}(Ga^{III})_{1/3}$ and $ETe(Ga^{II})_{1/3}(Ga^{III})_{2/3}$ in the compounds Ga_3Te_3X; $ETe(Ga^{II})_{3/3}$ in the binary telluride GaTe where E is a lone pair of electrons.

Introduction

Novel mixed-valence gallium(II,III) tellurohalides of composition Ga_3Te_3X, where X is Cl, Br or I, have recently been synthesised and shown by X-ray structure analysis to adopt a one-dimensional structure containing $Ga_3Te_{3/3}X$ and $Ga_2Te_{6/3}$ units [1, 2]. As shown in Fig. 1, the macromolecules $^1_\infty[(Te_{3/3}(Ga^{II})_2Te_{3/3})(Te_{3/3}Ga^{III}X)]_2$ represent one-dimensional fragments of the GaTe structure. GaTe [3] is a pure gallium(II) compound which is built of layers of $^2_\infty[Te_{3/3}(Ga^{II})_2Te_{3/3}]$ units.

Given that ^{125}Te Mössbauer spectroscopy is well suited to the examination of the local environments of tellurium in inorganic solids [4], we have initiated a study of the gallium tellurohalides of composition Ga_3Te_3X, and of gallium telluride, GaTe, and report here on the interpretation of the data in terms of the structural and bonding properties of tellurium in these compounds.

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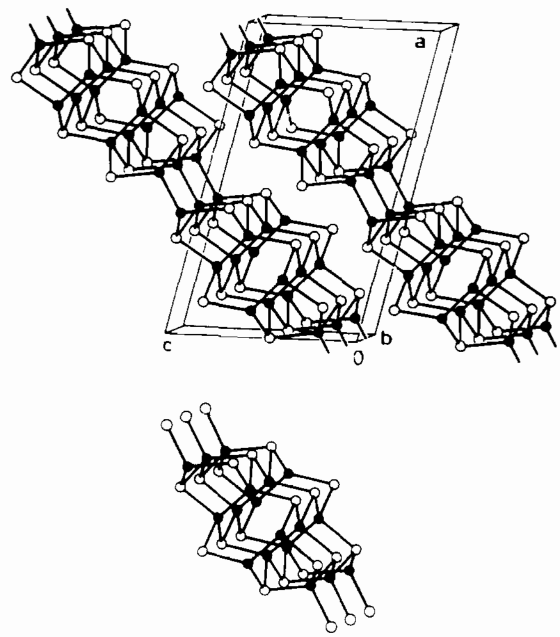

Fig. 1. One-dimensional macromolecules of Ga_3Te_3X (below) in terms of fragments of the GaTe layer structure (above). Black circles: Ga; open circles: Te and terminal halogen.

Experimental

The compounds were prepared by previously reported methods [1, 2]. They were ground and transferred into Pyrex cells in a nitrogen glove box.

The ^{125}Te Mössbauer spectra were recorded with a microprocessor controlled Mössbauer spectrometer using a ^{125}Sb/Rh source. The spectra were recorded with both the source and the samples, which contained *c.* 70 mg tellurium/cm^{-2}, at 77 K. The drive velocity was calibrated with a ^{57}Co/Rh source and a natural iron foil. All the 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 chemical isomer shift recorded relative to the ^{125}Sb/Rh source.

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Results and Discussion

The ^{125}Te Mössbauer spectra recorded from gallium(II) telluride and the gallium(II,III) tellurohalides were characterised by rather broad absorptions, Γ 6.77 to 7.92 mm s^{-1}, at δ *c.* 0.26 mm s^{-1}. All the spectra were amenable to fitting to a quadrupole split absorption without significant changes to the chemical isomer shift data. The ^{125}Te Mössbauer parameters are collected in Table 1 and a typical spectrum recorded at 77 K is shown in Fig. 2.

The lack of sensitivity of the chemical isomer shift data to the nature of the halogen is a striking feature of the data. Indeed, the data contrast with those recorded from inorganic tellurium halides of composition TeX_6^{2-} [5] and $M_2TeX_4Y_2$ [6] (X, Y = Cl, Br or I) which have demonstrated a clear dependence of the chemical isomer shift on the electronegativity of the halogen. The insensitivity of the chemical isomer shift data to the nature of the halogen in compounds of composition Ga_3Te_3X reflects the separation of the tellurium and halogen by at least one gallium atom in all the compounds as is shown in Fig. 1. The similarity between the chemical isomer shifts of the gallium tellurohalides and that of gallium(II) telluride illustrates the extent to which the gallium atoms in Ga_3Te_3X insulate the electronic environment about tellurium from the electron withdrawing effects of the halogen. The observed similarity between δ in the gallium tellurohalides and gallium(II) telluride also demonstrates that mixed valence on the gallium sites has little influence on the electronic environment of the nearest neighbour tellurium species. The small positive chemical isomer shift which characterises all the compounds is indicative of the presence of electron-rich anionic tellurium in predominantly covalently bonded compounds.

TABLE 1. ^{125}Te Mössbauer parameters recorded from gallium telluride, GaTe, and gallium tellurohalides, Ga_3Te_3X

Compound	$\delta^{a} \pm 0.15$ (mm s^{-1})	$\Delta \pm 0.3$ (mm s^{-1})	$\Gamma \pm 0.1$ (mm s^{-1})
GaTe	0.27	2.22	6.17
Ga_3Te_3Cl	0.22	2.10	6.53
Ga_3Te_3Br	0.26	2.38	6.64
Ga_3Te_3I	0.27	1.64	6.13

^{a}δ relative to ^{125}I/Cu.

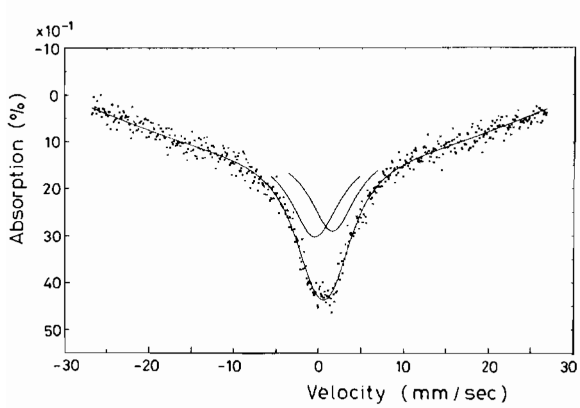

Fig. 2. ^{125}Te Mössbauer spectrum recorded at 77 K from Ga_3Te_3Cl.

The small quadrupole splittings recorded from the covalently bonded compounds is unusual since covalently bonded tellurium atoms usually exhibit large quadrupole splittings. The small quadrupole splittings observed here may be associated with the distorted tetrahedral environment about the tellurium atom in both the gallium tellurohalides and gallium(II) telluride. In all these compounds the tellurium atom may be envisaged as being coordinated by three covalently bonded gallium atoms with Ga–Te–Ga bond angles of 90–103° (Ga–Te: 2.523–2.689 Å), and a stereochemically active lone pair of electrons (Ga_3Te_3X:$ETe(Ga^{II})_{3/3}$, $ETe(Ga^{II})_{2/3}(Ga^{III})_{1/3}$ and $ETe(Ga^{II})_{1/3}(Ga^{III})_{2/3}$; GaTe:$ETe(Ga^{II})_{3/3}$) where E represents the lone pair. The arrangement presumably gives rise to a small electric field gradient at the tellurium nucleus and consequently to a small quadrupole splitting. Indeed the small quadrupole splittings resemble those recorded [7] from compounds of the type Te_2X [8], where X is Br or I, in which tellurium experiences a similar distorted environment.

Hence the ^{125}Te Mössbauer chemical isomer shift and quadrupole splitting data show that the mixed-valence gallium(II,III) tellurohalides and gallium(II) telluride may be considered as predominantly covalently bonded materials in which the anionic tellurium species enjoy slightly distorted tetrahedral coordination.

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