

The  $^{125}\text{Te}$  Mössbauer Effect in  $\text{FeTe}_2$ ,  $\text{CoTe}_2$ , and  $\text{RuTe}_2$ 

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$^{125}\text{Te}$  Mössbauer spectra of  $\text{FeTe}_2$ ,  $\text{CoTe}_2$ , and  $\text{RuTe}_2$  have been obtained at 4.2 K. These results, together with the literature data for  $\text{MnTe}_2$ , are discussed in terms of the structural properties of the compounds.

Mössbauer spectroscopy, using the 14.4 ( $3/2 \rightarrow 1/2$ ) and 37.2 keV ( $7/2 \rightarrow 5/2$ ) transitions in  $^{57}\text{Fe}$  and  $^{121}\text{Sb}$ , respectively, has previously been employed by the present authors<sup>1,2</sup> in studying the chemical bonding in ( $T\text{X}_2$ ) compounds with the pyrite ( $\text{FeS}_2$ -*p*), marcasite ( $\text{FeS}_2$ -*m*), and arsenopyrite ( $\text{FeAsS}$ ; binary prototype  $\text{CoSb}_2$ ) type crystal structures. We here report on the  $^{125}\text{Te}$  Mössbauer effect (*viz.* the 35.6 keV ( $3/2 \rightarrow 1/2$ ) transition) in the compounds  $\text{FeTe}_2$ ,  $\text{CoTe}_2$ , and  $\text{RuTe}_2$  which take the  $\text{FeS}_2$ -*m* or  $\text{FeS}_2$ -*p* type structure.

## EXPERIMENTAL

The stoichiometric  $\text{FeTe}_2$  and  $\text{CoTe}_2$  samples were prepared and characterized by Guinier photographic X-ray data as described previously.<sup>3</sup> A  $\text{RuTe}_2$  sample was prepared by heating a stoichiometric mixture of the elements in an evacuated, sealed quartz tube at 550°C for 14 days. The Guinier data of the product gave  $a = 6.3903(3)$  Å, in excellent agreement with the recent literature value of  $a = 6.3906(4)$  Å.<sup>4</sup>

The  $^{125}\text{Te}$  Mössbauer spectra were obtained at (P.C.M.U.,) Harwell, United Kingdom. The source ( $\text{Cu}^{125}\text{Te}$ , *viz.*  $^{125}\text{I}$  annealed into Cu) and absorber were maintained at 4.2 K. The preparation of absorbers and other experimental details, including the computational work, were performed as described previously.<sup>2</sup>

## RESULTS AND DISCUSSION

Fig. 1 shows the  $^{125}\text{Te}$  Mössbauer spectra of  $\text{FeTe}_2$ ,  $\text{CoTe}_2$ , and  $\text{RuTe}_2$  at 4.2 K. It can be seen that the chemical shifts ( $\delta$ ) and total line-widths of these spectra are equal within experimental error, although their maximum absorption effects differ. There are no resolved quadrupole or magnetic hyperfine interactions observed for any of the compounds. However, the peaks appear to be too broad to be accounted for by single lines and consequently they were computer fitted assuming quadrupole split lines of equal width and intensity.

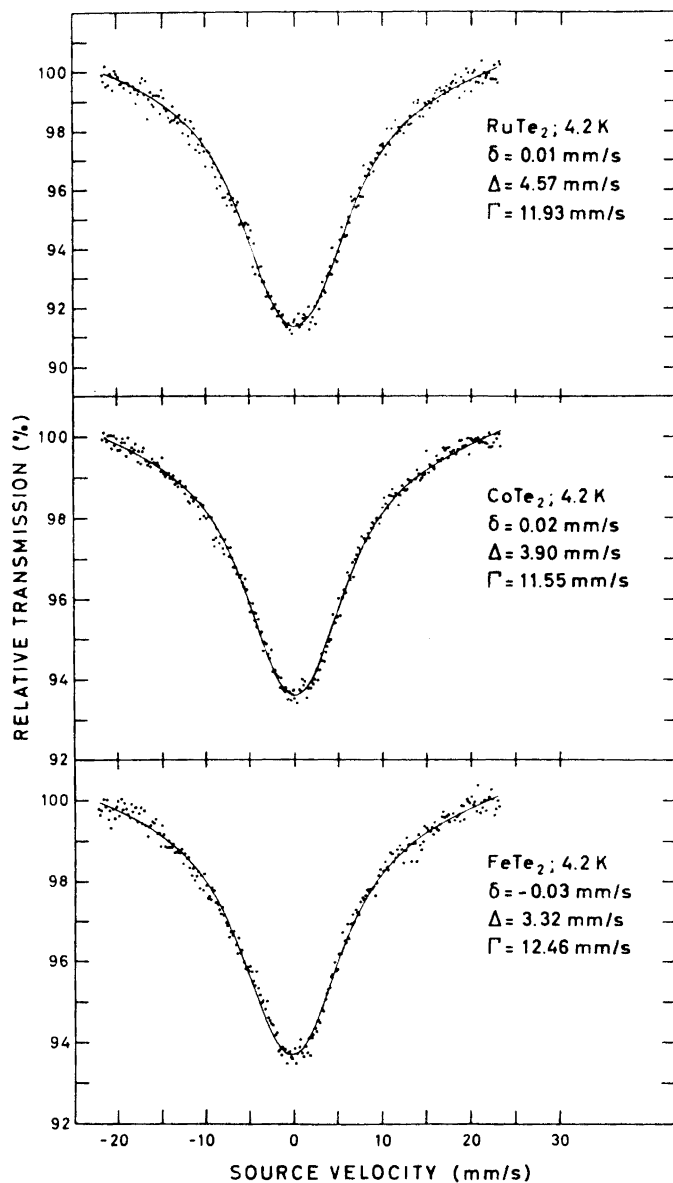


Fig. 1. <sup>125</sup>Te Mössbauer spectra for FeTe<sub>2</sub>, CoTe<sub>2</sub>, and RuTe<sub>2</sub> at 4.2 K. The curves show the computer fitting to the experimental points.

The resulting values for the parameters  $\delta$ ,  $\Delta (= \frac{1}{2} |eQV_{zz}|)$ , and  $\Gamma$  are indicated on the diagram. RuTe<sub>2</sub> is diamagnetic,<sup>5</sup> which immediately excludes the possibility of a magnetic exchange interaction in this compound. The almost

identical appearance of the three spectra (Fig. 1) consequently suggests that magnetic exchange interactions are also absent in  $\text{FeTe}_2$  and  $\text{CoTe}_2$  at 4.2 K. Certain indications from magnetic susceptibility data<sup>6-10</sup> appear to suggest cooperative magnetic phenomena in  $\text{FeTe}_2$  and  $\text{CoTe}_2$  and this has been positively claimed in the case of  $\text{FeTe}_2$  which is said to be antiferromagnetic below a Néel temperature of 83–85 K.<sup>7,8</sup> On the other hand, the present finding concerning  $\text{FeTe}_2$  is consistent with its  $^{57}\text{Fe}$  Mössbauer spectrum at 81 K in which a magnetic hyperfine interaction is not apparent.<sup>11</sup>

It is interesting to compare these observations with those reported by Pasternak and Spijkervet<sup>12</sup> for  $\text{MnTe}_2$  ( $\text{FeS}_2$ -*p* type structure). Their  $^{125}\text{Te}$  Mössbauer spectra above and below the Néel temperature of 83.8 K exhibit resolved quadrupole splittings giving a temperature independent value  $eQV_{zz} = -15.5$  mm/s for the quadrupole coupling constant. In addition, the spectra recorded for the antiferromagnetic state of  $\text{MnTe}_2$  show significant changes in spectral shape and line width from those recorded for the paramagnetic state. The internal magnetic field induced at the Te nuclei takes a constant value of  $114 \pm 7$  kOe between 4.2 and 20.3 K, decreasing to  $55 \pm 3$  kOe at 77.3 K. None of these features are detected in the spectra of  $\text{FeTe}_2$ ,  $\text{CoTe}_2$ , and  $\text{RuTe}_2$ .

The quadrupole coupling which is present in  $\text{FeTe}_2$ ,  $\text{CoTe}_2$ , and  $\text{RuTe}_2$ , as a consequence of the distortion from  $T_d$  symmetry of the coordination polyhedra around Te, is only resolved by resorting to computer fitting. A measure of the angular part of the distortion from cubic symmetry is given by the average deviation ( $\xi$ ) of the bond angles from the tetrahedral value of  $109.5^\circ$ , as described in a preceding paper.<sup>2</sup> The values of  $\xi$  (ranging from  $8.3^\circ$  for  $\text{AuSb}_2$  to  $13.6^\circ$  for  $\text{FeSb}_2$ ) have been found to correlate well with the quadrupole coupling constants obtained from the  $^{121}\text{Sb}$  Mössbauer spectra of  $T\text{Sb}_2$  compounds with the  $\text{FeS}_2$ -*p*,  $\text{FeS}_2$ -*m*, and  $\text{CoSb}_2$  type structures.<sup>2</sup> (The  $\xi$  values for  $\text{MnTe}_2$ ,  $\text{FeTe}_2$ ,  $\text{CoTe}_2$ , and  $\text{RuTe}_2$  are 6.3, 10.1, 9.9, and  $8.9^\circ$ , respectively.) A corresponding relationship between  $\xi$  and  $eQV_{zz}$  should also be valid among the ditellurides provided the bonding characteristics of the *T* atoms are similar within the series under consideration. In  $\text{MnTe}_2$  there is a high spin  $d^5$  ( $t_{2g}^3 e_g^{*2}$ ) configuration associated with the Mn atoms.<sup>13</sup> This gives rise to longer and weaker Te–Mn bonds and shorter, stronger Te–Te bonds.<sup>1</sup> Hence, the values for  $\xi$  and  $eQV_{zz}$  for this compound are likely to deviate from the relationship which may be devised for the corresponding parameters of the (low spin) compounds  $\text{FeTe}_2$ ,  $\text{CoTe}_2$ , and  $\text{RuTe}_2$ . The fact that, for the  $T\text{Te}_2$  compounds, there does appear to be some correlation between  $\xi$  and  $|A|$  may well be fortuitous in view of the undetermined sign of  $A$  for  $\text{FeTe}_2$ ,  $\text{CoTe}_2$ , and  $\text{RuTe}_2$ .

The positive sign for  $V_{zz}$  in  $\text{MnTe}_2$  distinguishes this compound from the ten  $T\text{Sb}_2$  compounds discussed previously,<sup>2</sup> which consistently have a negative sign for  $V_{zz}$ . In the latter series of compounds the negative sign has been interpreted on the basis of an anisotropic expansion of the Sb  $5p$  orbitals into the bonding orbitals. This implies that there is a net excess of electron density localized in the Sb  $5p_z$  orbitals, the *z* direction defined as being along the *X*–*X* pair, cf. Ref. 2. For  $\text{MnTe}_2$  where the Te–Mn bonds are weakened the major residual  $5p$  population is localized in the  $5p_x$  and  $5p_y$  Te atomic orbitals. The smaller quadrupole interactions in  $\text{FeTe}_2$ ,  $\text{CoTe}_2$ , and  $\text{RuTe}_2$  are consistent with this interpretation since an increase in the delocalization of the  $5p_x$  and

$5p_y$  electron density into the (stronger) bonding  $Te-T$  orbitals would reduce the quadrupole coupling constant compared with the value observed for  $MnTe_2$ .

An analysis of the structural data for compounds with the  $FeS_2-p$ ,  $FeS_2-m$ , and  $CoSb_2$  type structures suggests that the bonding in these compounds is of a predominantly covalent nature.<sup>1</sup> The  $T-X$  bond lengths in the high spin manganese dichalcogenides are considerably longer than those for the other  $3d$  transition metal dichalcogenides. As mentioned above the elongation of the  $Mn-X$  bond length is attributed to the influence of the half filled  $e_g^*$  orbitals. Since this is a crucial point of the model it is gratifying to note that this view is supported by the recent  $^{57}Fe$  Mössbauer data of Bargeron *et al.*<sup>14</sup> These authors substituted 2%  $^{57}Fe$  into samples of  $MnS_2$ ,  $MnSe_2$ , and  $MnTe_2$  and found that at atmospheric pressure the quadrupole interaction is characteristic of high spin Fe. This should be compared with the situation which prevails in the low spin compounds  $FeS_2$ ,  $FeSe_2$ , and  $FeTe_2$ . There is accordingly a definite correspondence between the  $T-X$  bond length and  $e_g^*$  population. In fact, the high spin situation which prevails in  $MnX_2$  can be converted to low spin by squeezing the atoms together under the application of high pressure.

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