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Te^{125} MÖSSBAUER EFFECT STUDY OF NEUTRON CAPTURE EFFECTS IN PbTe, Te AND TeO_2*

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Abstract—The Mössbauer emission spectra of Te^{125} in PbTe, Te metal, and TeO_2 have been measured following neutron capture in Te^{124}. Mössbauer data for each sample were taken after the source irradiation and following thermal annealing. The irradiation conditions were chosen so that only the thermal neutron capture induced defects should have a significant effect on the environment of the Mössbauer emitting nuclei. Comparison of the data taken before and after the source annealing showed no differences in linewidth, isomer shift, quadrupole splitting, or resonance intensity within the standard deviations of the parameters. The results show that the thermal neutron capture process in Te^{124} does not affect the Te^{125} Mössbauer spectra. The possible reasons for this are discussed. The results also indicate that the anomalous isomer shift reported by Stepanov and Aleksandrov in a similar experiment on PbTe is probably caused by a high background of fast neutron induced displacements.

1. INTRODUCTION

CHANGES in the structure of Mössbauer emission spectra due to the presence of neutron capture induced displacements have been studied in processes involving both neutron activation of the first excited state of the Mössbauer nuclide[1–3] and neutron activation of an isomeric state parent[4, 5]. Because of the short lifetime of the first excited state of Mössbauer nuclides (10^{-10}–10^{-5} sec), the neutron activation of this state and the Mössbauer measurement must be done simultaneously. Thus, the first type of experiment must be done in a neutron beam. However, if the Mössbauer nuclide has a long-lived isomeric state, then the neutron activation and the Mössbauer measurement can be done at different times. In the second type of experiment the neutron irradiation can be done in-pile and the Mössbauer measurement can be made at leisure after the irradiation.

The principle advantage of the second type of experiment is that it avoids the usual problems of low neutron intensity and high background radiation associated with neutron beam experiments. There is one limitation, however, in the use of in-pile irradiations for investigating radiation effects; the measurements are restricted to materials with defect annealing temperatures greater than the reactor irradiation temperature (generally 50°C or higher). This severely limits the number of potential experiments. This, of course, is not true if low temperature irradiations are possible; however, low temperature irradiation facilities are not available at most reactors.

Sn^{119} and Te^{125} are two Mössbauer nuclides that offer favorable thermal neutron capture cross sections, isomeric state half-lives, and resonant gamma ray energies for use in the second type of experiment. Previous Mössbauer investigations of the effect of neutron irradiation on the resonant emission spectra of these nuclides have given some evidence of recoil induced changes in the electronic configuration about the emitting nuclei.

Hannaford *et al.*[4] found a small satellite peak in the emission spectrum of Sn^{119} in Mg_2SnO_4 following neutron activation. The

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intensity and isomer shift of the satellite peak indicated that approximately 25 per cent of the Sn atoms had suffered a recoil induced valency change. The valency change was clearly shown to be attributable to neutron capture induced displacements.

Stepanov and Aleksandrov[5] recently reported a Mössbauer measurement on Te^{125} in PbTe following neutron activation. The measurement showed an anomalous isomer shift. The PbTe source measured against a PbTe absorber had an isomer shift of 1·7 mm/sec (measured 20 days after the end of the irradiation) when, in fact, there should be no isomer shift if the source and absorber are chemically identical. The anomalous isomer shift indicated that the s-electron configuration of the PbTe source had been altered by the irradiation. The anomalous isomer shift was observed to decrease exponentially with time with a mean life of 10 ± 3 days. This indicated that the defect structure was annealed at room temperature.

The measurements reported in this paper were also done on Te^{125} following neutron activation. In addition to a measurement on PbTe, measurements were also made on Te metal and TeO_2. Mössbauer measurements were made on each of the three materials following the source irradiation and then following thermal annealing of the same source. The two spectra were then compared to see if there were any changes in the hyperfine spectra caused by neutron capture induced displacements.

Contrary to the results of Stepanov and Aleksandrov the Mössbauer spectrum for PbTe reported in this paper showed no anomalous isomer shift after the neutron irradiation. In fact, no changes were observed in the hyperfine spectra of any of the three materials.

The difference between these results for PbTe and those of Stepanov and Aleksandrov yields considerable insight into the defect mechanisms involved. The measurements reported in this paper were made with irradiation conditions chosen so that the Mössbauer spectra should only be affected by displacements caused by the thermal neutron capture process. The results indicate that the thermal neutron capture process in Te^{124} does not have an effect on the Mössbauer spectra of the Te^{125}. In conclusion, the anomaly observed by Stepanov and Aleksandrov in PbTe is probably the result of a high concentration of displacements induced by mechanisms other than thermal neutron capture. The most likely mechanism is fast neutron elastic scattering.

2. RADIATION EFFECTS

The Mössbauer isomeric state parent $Te^{125m}(58d)$ is produced by thermal neutron capture in Te^{124} (i.e. $Te^{124} + n_{th} \rightarrow Te^{125m} + \gamma$). The Te^{125m} nucleus can be introduced into the lattice as a defect if the recoil energy from the (n, γ)-reaction is greater than the minimum energy for displacement, E_d, which is typically of the order of 25 eV. The recoil energy arises from the emission of the 6·4 MeV of excitation energy of Te^{125} by 'prompt' gamma rays. By conservation of momentum the emitted gamma rays impart kinetic energy to the emitting nucleus.

A calculation of the mean recoil energy requires knowledge of the gamma rays emitted in the de-excitation process, including their energies, emission probabilities, and time and angular correlation. Unfortunatley the capture gamma ray energy spectrum has not been measured for neutron capture in Te^{124}; therefore the mean recoil energy cannot be accurately estimated.

In general the mean recoil energy for capture gamma ray emission is low (of the order of E_d). This means that the number of displaced atoms produced per thermal neutron captured is small; subsequently, the number of possible defect configuration is small. This is a particularly nice feature for Mössbauer measurements since the resultant Mössbauer spectrum is a weighted sum of the spectra characteristic of each defect configuration.

The isolation of displacements which are induced specifically by thermal neutrons is often very difficult when doing in-pile irradiations. This is due to the 'background' effects caused by displacements due to other recoil processes. All of the types of radiation present in a reactor (i.e. fast neutrons, gamma rays, etc.) can produce displacements through either scattering processes or nuclear reactions. For most elements the ratio of defects produced by thermal neutron capture to those produced by fast neutron scattering is less than one[6]. Thus, fast neutrons are usually responsible for most of the radiation effects observed with in-pile irradiations.

Under some conditions the Mössbauer effect measurement provides a means of separating displacements due to thermal neutron capture from those arising from fast neutrons and other sources. This is possible because the characteristic hyperfine interactions are, for the most part, only influenced by the 'local' electronic environment (atomic electrons and first few near neighbour atoms).

The fraction of the resonant emissions which have hyperfine structure characteristic of a defect environment is related to the probability that a defect is within the 'local' environment of an emitting nucleus. For defects produced by thermal neutron capture this probability should be nearly equal to 1 since the emitting nucleus itself is in a defect position. On the other hand, defects produced by other types of radiation are randomly located with respect to the emitting nuclei. Hence the probability that these defects are within the 'local' environment of an emitting nucleus is of the order of the ratio of the defect density to the appropriate atomic density.*

In order to minimize the effect of displacements caused by other types of radiation, the density of defects must be kept much less than the number density of atoms. Since the defect density is a linear function of the total radiation dose (in the absence of self annealing), it is possible to minimize the effect of undesirable displacements by proper choice of irradiation fluxes and times.

The measurements reported in this paper were carried out under conditions where the thermal neutron capture effects played a dominant role. Fast neutron scattering was the principal source of additional displacements; however, the estimated density of these displacements was $\sim 10^{-4}$–10^{-3} of the tellurium atom density. Thus, the fraction of Mössbauer emitting nuclei which are in close proximity to a fast neutron displaced atom is very small. The fast neutron induced displacements then should have little effect on the Mössbauer spectra.

3. EXPERIMENTAL PROCEDURE

(A) *Sources and absorbers*

The PbTe, Te metal and TeO_2 used in the measurements as sources were prepared from Te enriched to 94 per cent in Te^{124}. The PbTe† and Te metal powders were pressed into thin discs and then sintered in a hydrogen atmosphere at 550°C for 3 hr and 350°C for 6 hr, respectively. The TeO_2 was prepared from nitric acid solution following the procedure of Marshall[7]. This procedure results in TeO_2 with the tetragonal crystal structure. The structures of the materials were all verified by X-ray diffraction measurement.

The materials to be used as sources were irradiated in the Ford Nuclear Reactor. Samples were generally irradiated in fluxes of 10^{12}–10^{13} neutrons/cm^2-sec for periods of 10–15 days. The total thermal neutron doses for the PbTe, Te and TeO_2 samples reported on in this paper were 8×10^{17}, 9×10^{17} and 8×10^{18} neutron/cm^2, respectively. The fast neutron doses were a factor of 12 lower.

*The atomic density used here must take into account the range of the hyperfine interactions (referred to as the 'local' environment). This density will be smaller than the number density of atoms for long range interactions and will approach the number density for short range interactions (hyperfine interactions affected only by the atomic electrons).

†Prepared by New England Nuclear Corp., Boston, Mass.

The sample temperatures during the irradiation were measured to be ~45°C.

After the Mössbauer measurement was made following the source irradiation, the sources were all annealed to restore any displaced atoms to normal lattice sites. The PbTe and Te sources were annealed in a hydrogen atmosphere at 400°C for 11 hr and 350°C for 12 hr, respectively. The TeO_2 was dissolved in HNO_3 and recrystallized following the procedure in the initial preparation.

The Mössbauer measurements for PbTe and Te were made using a single line absorber of PbTe (17·5 mg/cm²) enriched to 95 per cent in Te^{125}. The measurements for TeO_2 were made using a single line absorber of $Te(OH)_6$ (39 mg/cm²) with a natural abundance of Te^{125} (7 per cent).

(B) Apparatus

The Mössbauer measurements were made using the 35·6 keV gamma ray resonance in Te^{125}. Details of the decay scheme and the relevant Mössbauer parameters have previously been reported [8].

The 35·6 keV gamma rays were detected using a xenon–nitrogen filled proportional counter. With this detector the 35·6 keV gamma ray is only partially resolved from the intense background due to the Te K_α and K_β X-rays at 27·4 and 31·2 keV. The gamma ray can best be discriminated by using the escape peak at 7·0 keV. All measurements were made with the single channel analyzer set at the escape peak energy.

The signal-to-noise ratio of the escape peak was further improved by using a 5 mil copper (113 mg/cm²) absorber to reduce the X-ray intensity. This increased the signal-to-noise ratio by a factor of 3·5 with only a factor of 0·33 reduction in the count rate. The 8·0 keV copper X-rays which are generated in this absorber are almost completely absorbed in the 20 mil aluminum window on the proportional counter.

The resonant absorption spectra were taken using a time mode Mössbauer spectrometer. The multichannel analyzer was calibrated using the magnetic hyperfine spectrum of Fe^{57} in iron metal. Calibration runs were made before and after each Te run to check the constancy of the equipment.

The source and absorber were both cooled to liquid nitrogen temperature in a styrofoam insulated dewar similar to the one described by DeWaard *et al.*[9]. The source and absorber temperatures were not externally controlled and were generally ~ 82°K.

4. RESULTS

The results of the measurements on PbTe, Te and TeO_2 are shown in Fig. 1. The data points shown are those taken in the Mössbauer measurements immediately following the

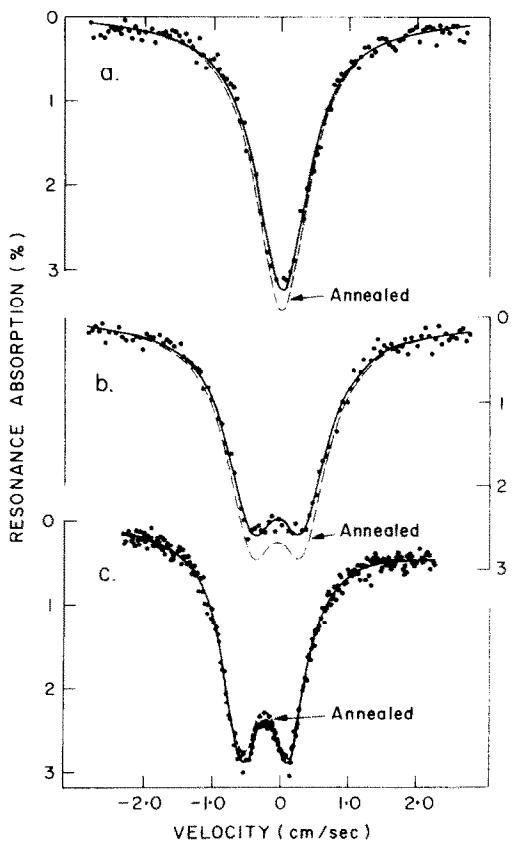

Fig. 1. Resonance absorption spectra taken before and after source annealing for: (a) PbTe; (b) Te metal; (c) TeO_2.

irradiations. The solid line is the least squares fit to the data with an assumed spectral shape. A single line of Lorentzian shape was fit to the PbTe spectrum and two lines of Lorentzian shape (quadrupole split) were fit to the Te and TeO_2 spectra.

The spectra characteristic of the normal lattices were obtained after treating the sources to restore any displaced atoms to normal lattice sites. The results of the curve fitting to the Mössbauer spectra taken after annealing are shown in Fig. 1. by the dashed lines.

The parameters obtained from the least squares fit to the spectra taken before and after annealing are listed in Table 1. The standard deviations of the parameters listed in the table are calculated from the error matrix generated in the final iteration of the least squares fitting routine. It is apparent from this tabulation that the linewidth, the isomer shift and the quadrupole splitting for the three materials are identical in the two runs within the standard deviations of the parameters.

The only parameter which shows a significant variation between runs is the resonance intensity. In all cases the variation in resonance intensity (3–11 per cent) is greater than the standard deviation in the intensity parameter (1–2 per cent). However, this standard deviation reflects only the statistical uncertainty in the fitting and does not include a contribution due to variations in experimental conditions. Several experimental factors can have a significant effect on the measured resonance intensity. These include the detector signal-to-noise ratio, the source and absorber temperature, and the experimental geometry. An accurate comparison of resonance intensities for two different runs requires that these factors not only remain stable during the course of each run but be exactly reproducible for each run. In both respects the conditions for our experiments were not the most desirable. Runs were generally of the order of 4–5 days in duration; this, of course, put a limitation on the temperature and electronic stability. In addition, the samples had to be removed between runs for annealing; this made exact reproducibility of all conditions difficult. A careful analysis of the stability and reproducibility of all the previously mentioned factors for our measurements indicates that the experimental uncertainty in the resonance intensity amounts to about 10 per cent.

As a result, the observed variations in the resonance intensity are only of the order of the uncertainty in the measured intensity. To see if the variations in resonance intensity for each material were reproducible, the sets of measurements were repeated using new sources. This second set of measurements for each material (only the measurements with the best statistics are reported in this paper)

Table 1. *Parameters obtained from the least squares fit to the data of Fig.* 1

Source		Linewidth (mm/sec)	Isomer shift* (mm/sec)	Quadrupole splitting (mm/sec)	Resonance intensity†
PbTe	– Pre-anneal	9·60 ± 0·23	0·07 ± 0·05	0	0·0324 ± 0·0003
	Post-anneal	9·58 ± 0·22	0·03 ± 0·04	0	0·0351 ± 0·0003
Te	– Pre-anneal	9·07 ± 0·24	−0·44 ± 0·08	7·51 ± 0·14	0·0197 ± 0·0004
	Post-anneal	8·83 ± 0·26	−0·41 ± 0·09	7·35 ± 0·15	0·0221 ± 0·0005
TeO_2	– Pre-anneal	6·42 ± 0·12	−1·98 ± 0·04	6·72 ± 0·11	0·0226 ± 0·0002
	Post-anneal	6·49 ± 0·12	−1·99 ± 0·04	6·89 ± 0·11	0·0219 ± 0·0002

*Shift relative to PbTe for the PbTe and Te source and $Te(OH)_6$ for the TeO_2 source.
†Maximum resonance intensity uncorrected for background.

did not show the same variation in resonance intensity as the first set. In all cases the magnitude of the change was different and in one case even the direction of the change was different. Again, as in the first set of measurements, the resonance intensity changes ranged up to about 10 per cent.

From this evidence we conclude that if there are any f value changes in any of the materials due to the source irradiation, the change is certainly less than 10 per cent of the normal f value. To determine whether or not there indeed is a real f value change would require that the experimental conditions be much better controlled than in our measurements.

The quadrupole splittings for Te and TeO_2 obtained in our measurements are in agreement with previously reported values. All previous results, except for a recent measurement by Pasternak and Bukshpan[10], are summarized in a paper by Violet and Booth [11]. For comparison with previous results, the values obtained for the quadrupole splitting in our measurements are $0{\cdot}75 \pm 0{\cdot}01$ cm/sec and $0{\cdot}69 \pm 0{\cdot}01$ cm/sec* for Te metal and TeO_2, respectively.

To compare isomer shifts with the values tabulated by Violet and Booth, our values have all been referred to a Te source. With respect to a Te source, the isomer shifts are $-0{\cdot}04 \pm 0{\cdot}01$ cm/sec and $+0{\cdot}02 \pm 0{\cdot}01$ cm/sec for PbTe and TeO_2†, respectively. The isomer shift for TeO_2 agrees with the value obtained by Violet and Booth; however the isomer shift for PbTe is less than the value reported by Stepanov *et al.*[12].

5. DISCUSSION

Our measurements show no clearly resolved changes in the Mössbauer hyperfine spectra of Te^{125} which could be attributed to neutron capture induced recoils. There are several possible explanations for the lack of any observable effects; however, it is difficult to establish any conclusive explanation due to the lack of supplemental information.

First, the changes in the hyperfine structure may be too small to be resolved. The broad lines of the Te^{125} resonance, of course, make observation of small changes in the hyperfine spectra very difficult. It is also very difficult to theoretically predict the isomer shift and electric quadrupole splitting that might occur for various possible defect configurations.

Second, there may be insufficient recoil energy on the average to displace the atoms from their normal lattice sites.

Third, defect annealing may occur at the reactor irradiation temperature of 45°C. Previous measurements indicate that such annealing probably does occur in Te metal, but definitely not in PbTe. A study of electron bombardment effects on Te metal showed that the defects anneal fairly rapidly even at room temperature[13]. Rather extensive measurements of the Hall coefficient, the Seebeck coefficient, the electrical resistivity and the thermal conductivity of PbTe both during and following thermal and fast neutron irradiation show little annealing below temperatures $\sim$ 150°C[14, 15]. There are no previous measurements of radiation effects in TeO_2.

It is quite clear from our results that the thermal neutron capture process in Te^{124} does not lead to any significant changes in the Mössbauer hyperfine spectra. The PbTe data, in particular, give evidence that the isomer shift anomaly observed by Stepanov and Aleksandrov is probably caused by displacements induced by other types of reactor radiation. All the measurements reported in this paper were made within approximately three weeks after the end of the irradiation. Using Stepanov and Aleksandrov's annealing curve, an isomer shift of at least 1·5 mm/sec should have been observed if the anomaly was

*The values quoted here are the average values obtained from several runs.

†The TeO_2 isomer shift was obtained by combining the results reported in this paper with an additional measurement with a PbTe source and Te(OH)6 absorber which showed an isomer shift of $-0{\cdot}13 \pm 0{\cdot}01$ cm/sec.

caused by neutron capture induced recoils.

The most likely cause of the isomer shift anomaly observed by Stepanov and Aleksandrov is fast neutron induced displacements. No information is given on the fast neutron flux used in their irradiation; however, if it is assumed that the fast flux is $\frac{1}{10}$ the magnitude of the thermal flux quoted in their paper and that there is no saturation of defects, the Te defect density could be as large as $\frac{1}{5}$ the Te atomic density. Thus the Stepanov and Aleksandrov measurement seems to have been carried out under irradiation conditions where 'background' displacements have a high enough density to significantly affect the Mössbauer spectrum.

REFERENCES

1. HAFEMEISTER D. W. and SHERA E. B., *Phys. Rev. Lett.* **14**, 593 (1965).
2. FINK J. and KIENLE P., *Phys. Lett.* **17**, 326 (1965).
3. BERGER W. G., FINK J. and OBENSHAIN F. E., *Phys. Lett.* **25A**, 466 (1967).
4. HANNAFORD F., HOWARD C. J. and WIGNALL J. W. G., *Phys. Lett.* **19**, 257 (1965).
5. STEPANOV E. P. and ALEKSANDROV A. YU., *JETP Lett.* **5**, 83 (1967).
6. WALKER R. M., *J. nucl. Mater.* **2**, 147 (1960).
7. MARSHALL H., In *Inorganic Syntheses* (Edited by L. F. Audrieth), Vol. 3. McGraw-Hill, New York (1950).
8. See *Mössbauer Effect Data Index* (Compiled by A. H. Muir Jr., K. J. Ando and H. M. Coogan). Interscience, New York (1966).
9. DeWAARD H., DEPASQUALI G. and HAFEMEISTER D., *Phys. Lett.* **5**, 217 (1963).
10. PASTERNAK M. and BUKSHPAN S., *Phys. Rev.* **163**, 297 (1967).
11. VIOLET C. E. and BOOTH R., *Phys. Rev.* **144**, 225 (1966).
12. STEPANOV E. P., ALESHIN K. P., MANAPOV R. A., SAMOILOV B. N., SKLYAREVSKY V. V. and STANKEVICH V. G., *Phys. Lett.* **6**, 155 (1963).
13. VAN LINT V. A. J., WIKNER E. G. and MILLER P. H., Jr., Rep. No. GA-1513 (1960).
14. DANKO J. C., KILP G. R. and MITCHELL P. V., *Adv. Energy Conversion* **2**, 79 (1962).
15. FROST R. T., CORELLI J. C. and BALICKI M., *Adv. Energy Conversion* **2**, 77 (1962).