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Quadrupole interactions at ^{57}Fe in Te metal

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The quadrupole interaction frequency (QIF) of ^{57}Fe in tellurium is measured using ^{57}Fe Mössbauer spectroscopy in the temperature range 78–578 K. The value of QIF obtained at room temperature is 10.44(23) MHz. The QIF is found to follow the usual $T^{3/2}$ temperature dependence observed in most other cases. The results are discussed in view of the available theoretical and empirical models.

I. INTRODUCTION

There has been considerable recent interest in the study of the electric-field gradients (EFG's) and their temperature dependence in noncubic metals and alloys. Measurements on quadrupole interaction frequencies (QIF's) have been reported for many probes in a number of metal hosts.[1] On the theoretical side, Das and his group[2] reported the calculations for some cases using band theory approach. For the case of tellurium metal, Coker, Lee, and Das[3] calculated the EFG's using the extended Hückel approach. Recently, Bodenstedt and Perscheid[4] suggested that the conduction-electron charge shift is responsible at least to first order for the EFG's in hcp metals. In general, all these calculations seem to agree with the experimental measurements. However, there are many aspects of the electric-field gradients that are not well understood such as the relative magnitudes of the lattice and the electronic contributions and their probe and host dependences. Still less understood is the temperature variation of the EFG's from the microscopic point of view.

Considerable experimental data reported during recent years on the EFG's in metals and dilute alloys and the associated temperature variation enabled us to identify many interesting systematic trends leading to a better understanding of the origin of EFG's. It is quite clear that the lattice sum picture is not adequate and the contributions from the local and the conduction electrons are quite significant.[1] In spite of the expected complex nature of the electronic contributions, the observed simple relationship that the electronic contribution is about 2–4 times the lattice contributions is valid for most of the systems. This observation is both puzzling and interesting.[5] It is also surprising that most of the experimental data available on temperature variation follow a simple $T^{3/2}$ law.[6] In this paper, we report our measurements on the QIF at ^{57}Fe in tellurium metal in the temperature range 78–578 K. Tellurium is of trigonal structure. The crystal c axis is a threefold screw axis and atoms are situated on helical chains spiraling around the c axis, each passing through one of the three atoms in the unit cells. It is known that the covalent bondings between the different atoms play an important role in deciding the EFG asymmetry parameter, etc. It will be interesting to see if the general systematic trends observed for most of the other systems are applicable for tellurium also.

II. EXPERIMENTAL

A constant-acceleration Mössbauer spectrometer[7] and a ^{57}Co source in an Rh matrix were used. The linewidths for the inner peaks of the natural iron absorber were 0.28 mm/sec. A high-temperature vacuum furnace and a liquid-nitrogen Dewar were used for measurements above and below room temperature. The temperature is constant to within 1 K.

Tellurium of 99.999% purity and iron ($\sim$0.1 at.%) enriched to 91 at.% in ^{57}Fe were sealed in a quartz tube under high vacuum. The sealed samples were kept at 1100 K for about 10 days and were further annealed at 600 K for about 4 days and were used for the measurements. X-ray diffraction of pure tellurium metal and that of prepared alloy were taken and compared and the results show that iron has formed a solid solution and that no other Te-Fe phase is present.

During the course of the present measurements, the dependence of the Mössbauer parameters on the heat treatments given to the sample and possible hysteresis effects are also studied. Annealing at 600 K for about 4 days is sufficient to completely homogenize the alloy and further annealing has no detectable effects on the Mössbauer spectra. After this annealing, no hysteresis effects were observed. The observed linewidths are close to the expected values which ensure that iron atoms are occupying unique sites. Since the metallurgical data show that small quantitites of iron is soluble in tellurium[8] and our x-ray diffraction studies also confirm that iron ($\sim$0.1

at.%) is forming a solid solution in tellurium, one can be fairly certain that we are measuring the dilute impurity EFG at ^{57}Fe in the tellurium matrix.

An unrestricted nonlinear-least-squares-fit program was employed to analyze the data. Since the two components of the quadrupole doublet were well resolved, we find that this program is adequate to obtain the Mössbauer parameters.

III. RESULTS AND DISCUSSION

For pure electric quadrupole interactions, the energy splittings in the case of ^{57}Fe may be written as

$$E_Q = \frac{1}{2}e^2qQ\,(1+\frac{1}{3}\eta^2)^{1/2} \;, \qquad (1)$$

where eq is the electric-field gradient at the nuclear site and η is the asymmetry parameter. Values of eq and η cannot be determined separately from the ^{57}Fe Mössbauer spectra alone and therefore one has to obtain the value of η from some other experiments to obtain the magnitude of the electric-field gradient.

Typical Mössbauer spectra observed are given in Fig. 1 and the obtained parameters in Table I. The errors are given parenthetically. The isomer shift values are with respect to rhodium metal. Using the known quadrupole moment of the 14.4-keV state of ^{57}Fe, the experimental values of $eq\,(1+\frac{1}{3}\eta^2)^{1/2}$ were calculated at each temperature and are given in the fourth column of Table I.

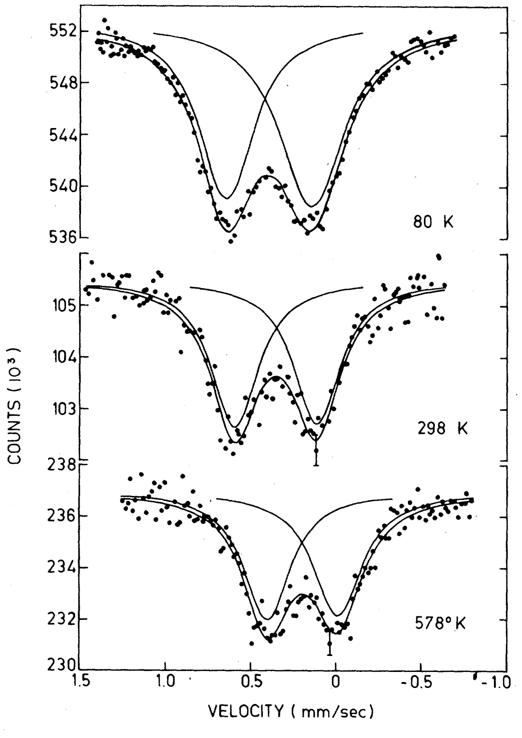

FIG. 1. Mössbauer spectra of Fe in ^{57}Fe*Te* system. The separated lines are shown slightly displaced.

TABLE I. Observed Mössbauer parameters for ^{57}Fe*Te* system.

Temperature (K)	Isomer shift (mm/sec)	Quadrupole splitting (mm/sec)	$eq_{\rm expt}(1+\frac{1}{3}\eta^2)^{1/2}$ (10^{17} V/cm^2)
577(1)	0.188(6)	0.412(8)	1.971(38)
486(1)	0.239(4)	0.436(6)	2.086(29)
395(1)	0.307(6)	0.458(8)	2.191(38)
298(1)	0.351(7)	0.481(10)	2.301(48)
78(1)	0.438(6)	0.504(6)	2.410(29)

In tellurium, the atoms form spiral chains. Three atoms per unit cell spiral about the *c* axis. The symmetry operations of the space group consist of a threefold screw axis parallel to the *c* axis and three twofold axes perpendicular to the *c* axis passing through each atom of the unit cell. The corresponding atoms of each spiral form a hexagonal net. The Te coordinations consist of two nearest-neighbor Te sites in the same chain, and four second-nearest neighbors in adjacent chains. The bonds between adjacent atoms on the same chain are covalent whereas between the chains, they are a weak mixture of electronic and van der Waals binding. Tellurium is a semimetal and one expects that it is somewhat similar to antimony and bismuth. However, the calculations of Hygh and Das[9] and Coker, Lee, and Das[3] show that unlike antimony, there is a strong directional character in the electronic distribution of tellurium probably due to its spiral and chain structure and therefore one should take account of the covalent binding between the individual atoms in obtaining the electron wave functions. This results in large EFG's in tellurium compared to antimony. The main difficulty in the study of the EFG's in tellurium host is to put the appropriate probe nuclei in the substitutional positions.

The earlier data on impurity location in tellurium show that ^{119}Sn is slightly shifted from its normal position,[10] ^{111}Cd occupies probably an interstitial position[11] and ^{181}Ta takes up two positions, one close to the substitutional site and the other an interstitial position.[12] However, the present data show that ^{57}Fe occupy unique positions and probably substitutional in tellurium.

Boolchand *et al.*,[13] using the ^{125}Te Mössbauer effect in single crystals of Te, obtained $\eta = 0.64$ at 4.2 K. This is in good agreement with the calculated value of 0.65 obtained by Violet *et al.*[14] and 0.61 of

Coker *et al.*[3] However, Hamilton[15] deduced a value of $\eta = 0.17$ from his Mössbauer experiments on ^{125}Te in tellurium. Hamilton[16] tried to explain the relatively smaller value of η by taking account of the possible interactions between the different chains of atoms in the tellurium structure. The measured value of $\eta = 0.2$ for ^{111}Cd in Te obtained by Lis and Naumann[11] in their time-dependent perturbed-angular-correlation (TDPAC) experiments was interpreted by them in terms of suggested interstitial positions for ^{111}Cd probe atoms. For ^{129}I impurity in Te, the EFG is negative and $\eta = 0.73$.[17] At present, it seems reasonable that under the assumption of the probe occupying substitutional site, the asymmetry parameter may be taken to be 0.64. Thus we obtain $eq = 2.16 \times 10^{17}$ V/cm^2. The electric-field gradient in Te is reported to be negative by Boolchand *et al.*[18] and Langouche *et al.*[17] The theoretical calculations of Coker *et al.*[3] agree with this. However Kulessa[19] recently reported that the sign of the effecitve EFG on ^{111}Cd in tellurium is positive. At present, it appears to be difficult to comment on the sign of the EFG for ^{57}Fe in tellurium.

The lattice contribution to the EFG $eq_{\text{latt}} = -0.232 \times 10^{17}$ V/cm^2 (Ref. 5) and $(1-\gamma_\infty)$ for ^{57}Fe $= 10.14$ (Ref. 20) giving $eq_{\text{ion}} = eq_{\text{latt}}\,(1-\gamma_\infty) = -2.35 \times 10^{17}$ V/cm^2. Using this value we obtain $eq_{\text{el}} = 4.51 \times 10^{17}$ V/cm^2 if the sign of the EFG is positive and 0.19×10^{17} V/cm^2 if the sign of the EFG is negative.

Table II gives the quadrupole interaction frequencies for different probes in a tellurium host. For those cases, where the quadrupole moment and $(1-\gamma_\infty)$ for the probe atoms are known, eq_{ion} and eq_{el} are separated. It is seen that besides the ionic part the eq_{el} values are highly probe dependent. This is not unexpected because, as stated earlier, the covalent bonding between the atoms on the same chain play an important role in determining the EFG, and the bonding of the probe atom with nearest host atoms could change the EFG considerably. Therefore the EFG's on the probe nuclei could be highly probe dependent. In particular, the field gradient experienced by Te in Te is an order of magnitude larger than that experienced by other probes so far studied.

a. Correlation between eq_{el} and eq_{ion}. Raghavan *et al.*[5] pointed out an empirical correlation between eq_{ion} and eq_{el} given by

$$eq_{\text{el}} = -K eq_{\text{ion}} \ , \tag{2}$$

where K is a constant and is of the order of 3. The present data on tellurium seem to qualitatively support the suggested correlation if we assume that eq_{ion} and eq_{el} are of opposite sign. This assumption is in agreement with the observed systematics. However, one may add that an unambiguous determination of the sign of the EFG would enable us to check whether the Te-Fe system would follow the suggested correlation or not.

b. Temperature variation of QIF. The temperature dependence of the QIF's[21–23] may be expected from the changes in the lattice parameters, from the lattice vibrations, or possibly from the interactions of the neighboring quadrupoles. Perhaps the dominant contribution comes from the interaction of conduction electrons with the lattice. However, almost all the experimental data reported so far seem to follow the empirical law[6]

$$eq(T) = eq(0)(1 - BT^{3/2}) \ . \tag{3}$$

As seen from Fig. 2, the present measurements on the ^{57}Fe*Te* system seem to agree quite well with the above relationship. A least-squares fit to a straight line gives $eq(0) = 2.4 \times 10^{17}$ V/cm^2 and $B = 13.9$

TABLE II. The currently available data on quadrupole interactions for different probes in tellurium host. $eq^{\text{I}}_{\text{el}}$ and $eq^{\text{II}}_{\text{el}}$ are the calculated values assuming the total EFG to be positive and negative, respectively. All the values are taken from Ref. 1 except as noted. Values of γ_∞ are from Ref. 20.

Probe	eq_{expt}	eq_{ion}	eq^{I}_{el}	eq^{II}_{el}
^{111}Cd	2.97	−7.03	10.00	4.06
	+1.27	−7.03	8.30	
W	6.46	−12.92	19.38	6.46
Os	6.50	−10.90	17.40	4.40
Sm	1.75			
^{57}Fe	2.16[a]	−2.35	4.51	0.19
^{125}Te	−90.55	−4.48		−86.07
^{181}Ta	9[b]	−14.38	23	5
^{125}Te (calc)	−100.87[c]	−4.48		−96.39

[a] Present work. [b] Reference 12. [c] Reference 3.

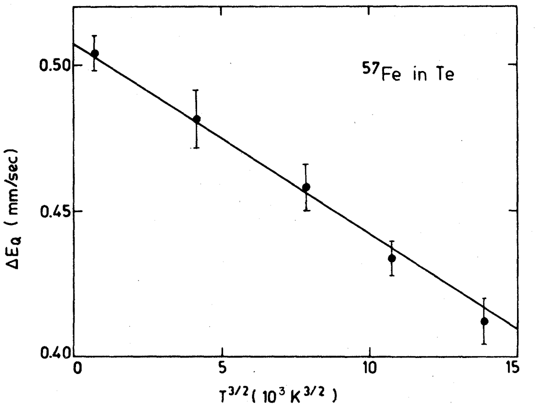

FIG. 2. Temperature variation of the electric-field gradient on ^{57}Fe in tellurium. The data are fitted to the usual $T^{3/2}$ law.

$\times 10^{-6}/T^{3/2}$. The slope parameter B is positive as found in all cases excepting ^{181}Ta*Be*.[24] It is believed that the slope parameter B will have a large positive value when the QIF is smaller and vice versa. This does not seem to be valid for the ^{57}Fe*Te* system. Since the temperature dependence of the asymmetry parameter η is not known, we are not able to correct the observed splittings to obtain the exact electric-field gradients. Calculations similar to those done by Violet *et al.*[14] result in a value of 0.60 for the value of η at 4 K. Therefore, the asymmetry parameter η varies by about 1% in the temperature range 4–300 K. As the thermal expansions for the lattice are smooth and monotonic, we do not expect any large variation of the asymmetry parameter in the presently studied temperature range 78–578 K. Therefore one may infer that the $T^{3/2}$ law is valid for the EFG in a Te matrix which has a complicated spiral structure and where the covalent bonding between the chains of atoms are expected to play an important role on the electric-field gradients.

c. Systematics of the EFG's in 5 sp metal hosts. For *sp* host as we increase the number of *p* electrons, we increase the nonspherically-distributed valence electron density and this may be expected to increase the EFG on a given probe as we increase the *sp* electrons of the host. This is expected because the EFG on the probe ion is known to have a constant relationship to eq_{latt}. Figure 3 shows the variation of eq for different probes as one goes from the indium to the tellurium host. The data on iodine are not yet available. This new systematic trend is quite striking and this shows that as the number of *p* electrons increase, the quadrupole interaction increases because the *p* electrons contribute to the EFG at the nuclear site through their contribution to the conduction band. It is seen from the figure that for any particular probe, the field gradient for the Sn host is indeed larger by a factor of about 1.7 than that for the In host. The field gradient seems to have a maximum value at Sn for ^{67}Ge and ^{69}Ge probes and at Sb for ^{111}Cd probe. If these systematic trends are valid, then one expects that the values on Fe in the Sn host are likely to be larger than for the In and smaller than that for the Sb host. Further experimental data would verify whether this trend is valid or not. It also appears that for any particular probe, the QIF reaches a maximum value somewhere near the middle of the band, This behavior is not unexpected because electrons and holes are expected to behave similarly. However, more experimental data would be helpful to study these systematic trends further.

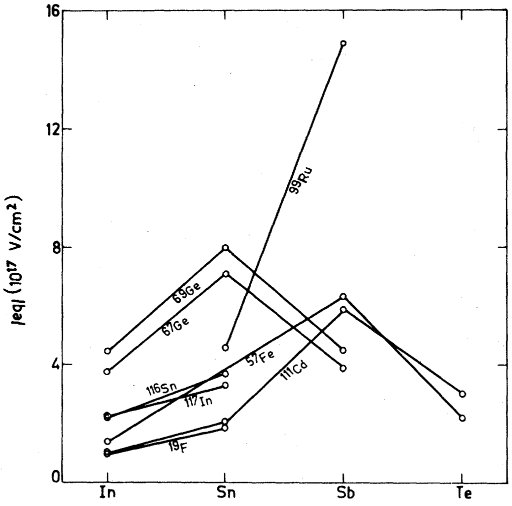

FIG. 3. Systematics of the electric-field gradients in 5 *sp* metal hosts. Most of the data are taken from Ref. 1 excepting the present work and the data on ^{57}Fe*Sb* (the data on ^{57}Fe*Sb* are planned to be published soon).

IV. CONCLUSIONS

We conclude that the EFG on ^{57}Fe in tellurium essentially obeys the well-known systematic trends observed for other systems, and the complicated spiral structure and the known strong covalent bonding in tellurium does not seem to affect the general systematic trends.

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