A model for the reflectivity spectra of TmTe

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Abstract. A simple one dimensional diatomic chain model is proposed to explain the reflectivity spectra of TmTe as observed by Ward *et al*. It is suggested that the system undergoes a structural phase transition of order-disorder type at 4·2 K, where the new phase assumes an anti-ferroelectric type of arrangement of the atoms. The results, we obtained, agree well qualitatively with the experimental results.

Keywords. Lattice dynamics; reflectivity spectra; mixed valence system; structural phase transition; anti-ferroelectric order.

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1. Introduction

There exist a measurement of the infrared reflectivity study at different temperatures on the sample TmTe by Ward *et al* [1]. Their measurements of the reflectivity spectra at sample temperature 1·3 K show a single peak of optic frequency (ω_{TO}) at $115 + 2\,\mathrm{cm}^{-1}$. The increase of sample temperature to 4·2 K gives two additional reststrahlen peak at frequencies $173\,\mathrm{cm}^{-1}$ and $209\,\mathrm{cm}^{-1}$. When the temperature is increased further to 295 K, there is neither any change in the peak positions shown at 4·2 K nor appearance of new peaks except slightly broadening of the two peaks. Not only that, it appears to be the onset of a new structure with a dramatic 10^3 fold increase in the d.c. conductivity from $1·7 \times 10^{-5}\,(\Omega\text{-cm})^{-1}$ at 1·6 K to $2·5 \times 10^{-2}\,(\Omega\text{-cm})^{-1}$ at 7 K. They have accounted for this increased infrared reflectivity and the increased d.c. conductivity due to the existence of mixed valance state at 4 K, where some fractions of Tm ions are in the trivalent state. According to them, this fraction is very small, since the infrared reflectivity spectrum shows a little change from the basic reststrahlen spectrum. The additional structure has been explained qualitatively by considering the Tm^{3+} ion as defect bound to the rest of the lattice by the larger force constant appropriate to the trivalant state. The resonant frequency of the trivalent ion will thus be higher than the coresponding frequencies of the divalent lattice in accordance with the observation. The larger width of these resonances may be due to the strong coupling between the vibrational motion and the temporal fluctuation in valence.

In this paper, we explain the reflectivity spectrum of the system TmTe, assuming it a mixed valent one and suffers a structural phase transition of the order-disorder type, where the force constant plays the role of disordering species in the vibrating complex of the system, In most of the rare-earth compounds, it is seen that the lattice constant

can be given accurately by the sum of the ionic diameters of the constituent elements. Not only that, the ionic diameters of ions of these compounds are intimately related to their valencies i.e. the number of 4f electrons in the rare-earth ions. Smaller valence (larger number of 4f electrons), means larger ionic diameters or larger volume, Therefore, the fluctuating valence in a rare-earth ion, directly causes a fluctuation in the ionic diameter. The system TmTe, being a mixed valent one, the analysis of it can be done in a similar way as described above. From the electronic configuration of Tm atom, it is seen that, it exists in two valence states Tm^{+2} and Tm^{-3}, which are characterized by the states $(4f)^{13}$ and $(4f)^{12}$ respectively. This fluctuation in valence between 2 and 3, fluctuates the volume which ultimately changes the force constants.

To incorporate the above idea, we choose here a one dimensional diatomic lattice with one species occupying one of the two off-centre lattice sites. In an earlier paper, Subaswamy and Mills [2] considered such a system as a model to study structural phase transition of order-disorder type. Their analysis of the model has shown that the random force constant disorder result the ions of the system to rearrange themselves to form two types of arrangements (i) ferroelectric type where atoms of one sublattice move rigidly with that of the other and (ii) antiferroelectric type, with a particular species of alternate cells move in opposite directions with respect to the equilibrium positions. The analysis of the temperature dependent effective exchange interaction, shows that the antiferroelectric arrangement of atoms, have lower free energy compared to ferroelectric arrangement. We have used this finding to explain the reflectivity spectra of TmTe observed by Ward *et al*. In doing so, we assign the Te and Tm atoms to form the two units of the diatomic chain and for Tm we assume the existence of two off-centre sites. With this configuration, we have performed the lattice dynamical calculation of this mixed valance system and found to give the correct behaviour as seen in the above experiment.

The plan of this paper is as follows. In § 2, we discuss our model. The results have been discussed in § 3. Finally we conclude in § 4.

2. Model

The model, on which our analysis is based, is illustrated in figure 1. We consider a diatomic linear chain with masses M_1 and M_2 occurring alternately. We assume, each of the alternate site a double well potential symmetrically situated at its equilibrium position. We assign the $Tm(M_1)$ ions (because of both divalent and trivalent state) to occupy one of the equivalent site of the double well potential and the $Te(M_2)$ ions to occupy the single well potential sites of the unit cell. This is illustrated in figure 1(a).

We confine our discussion on the nearest neighbour interaction. Let the force constant be denoted by K. In the description of the lattice dynamical model, when the Tm ions occupy the right hand side of the equilibrium site of the double well potential, it couples to the right hand side Te ions with higher force constant than to that of the left. Since the double wells are symmetrically situated at the equilibrium sites, there appears a tightening or increase of the force constant towards right hand side and softening or decrease of same towards left side by an equal amount, say Δ with respect to original K. So occupying of Tm ions on right hand side correspond to the coupling of ions with force constant $K + \Delta$ on right hand side and $K - \Delta$ on left side respectively.
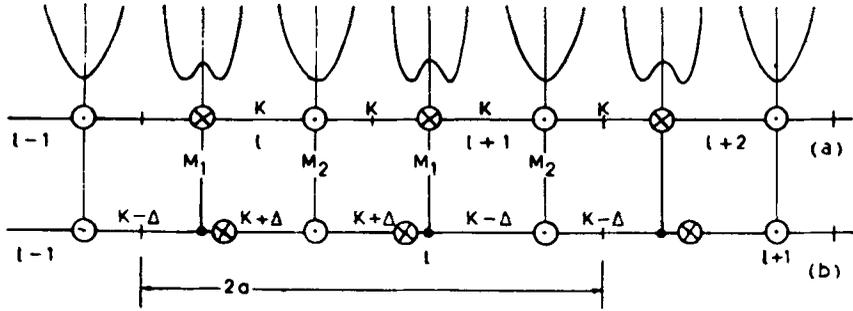
Figure 1. (a) The diatomic linear chain with single- and double-well potentials occurring alternately. The masses M_1 (Tm) is restricted to the double well and M_2(Te) to single well potentials. K is the nearest neighbour force constant. (b) In the changed phase at 4·2 K, diatomic linear chain model, with antiferroelectric arrangements became a four atomic linear chain. Δ is the force constant change.

Similarly, occupancy of Tm ions on left side corresponds to a coupling of $K + \Delta$ on left hand side and $K - \Delta$ on right side of Te ion. Moreover, the Tm ions have the equal probability of occupying any one of the equilibrium sites of the double well depending on the correlation that exist between different ions. Since the findings of Subaswamy and Mills [2] lead to an antiferroelectric arrangement of the atoms for a stable structure having lower energy compared to a ferroelectric arrangement, we assume here the system to suffer a phase transition at 4·2 K with ions to arrange themselves through an antiferroelectric way i.e. if ions of even cells move to right, say, then the masses of the odd cells move to the left without changing any lattice symmetry. With this arrangement, the diatomic system acquires a character of four atomic linear chain [Nayak [3] as depicted in figure 1(b)].

As in figure 1(b), the diatomic chain becomes a four atomic chain of mass say $M_{l\alpha}$ with nearest neighbours separated by a distance of $a/2$ where a is the lattice constant. Now it is straightforward to write the equations of motion. If $U_{l\alpha}$ be the displacement from the equilibrium of ions of masses $M_{l\alpha}$ on the sublattice a in the l th unit cell, the equations of motion is given by

$$M_{l\alpha}\omega^2 U_{l\alpha} = \sum_{l'\beta} A_{ll'\alpha\beta} U_{l'\beta}. \tag{1}$$

$A_{ll'\alpha\beta}$ is the force constant matrix and α, β takes values from 1 to 4. Defining $M_{l1} = M_{l3} = M_1$(mass of the Tm ion) and $M_{l2} = M_{l4} = M_2$ (mass of the Te ion) we can write the dispersion relation which is given by

$$(- M_1\omega^2 + 2K)^2(- M_2\omega^2 + 2v)(- M_2\omega^2 + 2v') - 2(- M_1\omega^2 + 2K)$$

$$\times [(- M_1\omega^2 + 2v)v'^2 + (- M_2\omega^2 + 2v')v^2] + 2v^2 v'^2(1 - \cos qa) = 0, \tag{2}$$

where $v = K + \Delta$ and $v' = K - \Delta$. Equation (2) is a quartic equation in ω^2 and gives the dispersion relation. For a general wave vector q, this equation can be solved numerically [4]. However, we shall examine the value for $q = 0$, i.e. in long wave length limit.

The non-zero values in this limit give rise to optical phonon modes, which ultimately gives the strong reststrahlen absorption peak in the reflectivity spectra of the host crystal. In the limit $q = 0$ and using the notation

$$\frac{2K}{M_1} = X_1; \quad \frac{2K}{M_2} = X_2 \quad \text{and} \quad \omega^2 = X, \tag{3}$$

equation (2) takes the form of

$$\left(-\frac{X}{X_1} + 1\right)\left[\left(-\frac{X}{X_1} + 1\right)\left(-\frac{X}{X_2} + 1\right)^2 - \left(-\frac{X}{X_2} + 1\right)\left(1 + \left(\frac{\Delta}{K}\right)^2\right)\right.$$
$$\left. - 2\left(\frac{\Delta}{K}\right)^2 - \left(-\frac{X}{X_1} + 1\right)\left(\frac{\Delta}{K}\right)^2\right] = 0. \tag{4}$$

Equation (4) can be written in a more convenient form as

$$Y(Y - 1)(m^2 Y^2 - m(m + 2) Y + (1 + m)(1 - \eta^2)) = 0 \tag{5}$$

where

$$m = \frac{X_1}{X_2}, \quad Y = \frac{X}{X_1} \quad \text{and} \quad \eta = \frac{\Delta}{K}. \tag{6}$$

Equation (5) correspond to the solutions of

$$Y = 0$$

$$(Y - 1) = 0 \tag{7}$$

and

$$m^2 Y^2 - (m(m + 2)) Y + (1 + m)(1 - \eta^2) = 0. \tag{8}$$

Equation (7) gives two roots one at $Y = 0$ and other at $Y = 1$ which are independent of η, while (8), a quadratic equation give two η-dependent roots. Thus as expected, one of the two roots correspond to the acoustic mode as the frequency of it goes to zero at $q = 0$. The other three roots, which have finite values, correspond to the three optic mode and exhibit strong absorption in the reflectivity spectra.

3. Results and discussion

In the last section we obtained four solutions to the quartic equations (eqs 7 and 8) for the frequencies. Equation (7) gives two roots which are η-independent and the two roots of the quadratic equation (8) are η-dependent ones. One of the η-independent roots of (7) gives zero frequency at $q = 0$ which correspond to the acoustic mode. The other η-independent root i.e. $Y = 1$ correspond to a peak in the reflectivity spectra and appears at the same frequency for both $1\cdot3$ K and $4\cdot2$ K as observed in the experiment [1]. The additional two peaks which appear at phase transition temperature $4\cdot2$ K correspond to the two η-dependent roots obtained from (8). The values of the two roots are calculated for different values of η, which is the free parameter of the model. In doing so, we consider the quadratic equation (8) and evaluated the roots for different values of η from 0 to 1. These are assigned to be the roots 3 and 4. The roots 1 and 2 correspond to the solution obtained from (7). A few values of these roots for different values of η are

Table 1. Roots of the quartic equation.

Values of η	Root 1	Root 2	Root 3	Root 4
0·0	0	1	1·3239	2·3239
0·1	0	1	1·2940	2·3537
0·2	0	1	1·2131	2·4347
0·3	0	1	1·0980	2·5497
0·4	0	1	0·9623	2·6854

Table 2. Values of optic frequency at $q = 0$ for $\eta = 0$ and 0·1.

Frequency in cm^{-1}	$\eta = 0$		$\eta = 0·1$		Expt. values (cm^{-1})
	Values of roots	Calculated frequency	Values of root	Calculated frequency	
$\omega_1(\omega_{TO})$	1·0	115	1·0	115	115
ω_2	1·3239	152	1·2940	148	173
ω_3	2·3239	267	2·3537	270	209

tabluated in table 1. Assigning the frequency value $115\,cm^{-1}$, observed in the experiment, to the second root i.e. $Y = 1$ which appear at 1·3 K and 4·2 K, we evaluated the frequencies of the other two peaks. It is found that for small values of η between 0 and 0·1 the calculated values agree well with the observed values. These are given in table 2.

4. Conclusion

In this paper, we have used a simple one dimensional diatomic chain model to explain the observed reflectivity spectra of TmTe. This, we do essentially by assuming structural phase transition of order-disorder type at 4·2 K. The results so obtained agree well with the observed spectra. The discrepancy with the position of two peaks can be attributed to the fact that, the double well potential used for Tm, is more likely to have some asymmetry, which has not been considered here to avoid complications. However, we intend to explore this possibility in future.

References

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