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Three impurity cluster in a diatomic linear chain

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Abstract. The modes of vibration of a three impurity cluster in a diatomic linear chain is studied. The configuration of the three impurity atoms is such that two of these go into next nearest neighbour sites in one of the sub-lattices whereas the third occupies the central in between site in the other sub-lattice. New local, gap and inband modes are seen to exist, besides the ones corresponding to the impurity pairs. A new feature which appears is that the frequencies of some of the pair modes remain totally unaffected in the presence of the third impurity atom.

Keywords. Impurity clusters; impurity modes; lattice dynamics.

1. Introduction

In recent years, there is considerable amount of activity in studying the lattice vibrational modes due to impurity clusters in alkali halide crystals. Specially the impurity pair modes have been studied experimentally (see Barker and Sievers 1975 for a review) using infrared absorption and Raman scattering techniques. However, the extension of these measurements to a three impurity cluster of $H^- - Na^+ - H^-$ in KCl has been reported by Schneider (1973). For the above-mentioned system the impurity complex has a triangular configuration in the KCl lattice; and he has succeeded in observing all the five localized modes expected for this impurity cluster by infrared absorption. Out of these five local modes two are longitudinal and the rest transverse in character. Even though there exists a large variety of theoretical calculations to explain the impurity pair modes (Behera and Patnaik 1975), so far only one calculation by Gupta and Haridasan (1974) has been reported for the case of a three impurity cluster of $H^- - Na^+ - H^-$ in KCl. They have performed a Green's function calculation using a limited impurity space and succeeded in reproducing the five infrared active local modes, whose frequencies show only qualitative agreement with the corresponding experimental values. It has been shown earlier (Behera and Patnaik 1975, 1976) Patnaik and Behera 1976, that the diatomic linear chain model provides a good approximation for a qualitative understanding of the impurity pair modes for various systems. Hence in this paper we propose to extend this model to the case of a three impurity cluster. We shall show that there appears new modes characteristic of three impurities besides the pair modes. Strangely enough some of the pair modes do not get affected by the presence of a third impurity, whatever be the mass of the third impurity. This is a new feature which emerges out of the calculation. In section 2 we give a brief discussion of the model and the exact solutions in the various frequency regions. Section 3 is devoted to a discussion

of the results. In section 4 we conclude by briefly commenting on the comparison of our theory with the existing experimental data. We also comment on the possible consequences our results might bear on the experimental observation and identification of cluster modes in general.

2. Theory

We consider a diatomic linear chain with masses M_1 and M_2. When a cluster of three impurities are substituted, we assume that two of them with masses M'_2 and M''_2 being similar (either cation or anion type) occupy next-nearest-neighbour positions in the M_2 sublattice and the third one with mass M'_1 goes into the site in between the first two impurities in the M_1 sublattice. For convenience we assume that the impurity with mass M'_1 occupies the zeroth lattice site and the other two occupy the sites 1 and -1 respectively. Furthermore, we neglect the change in force constant on impurity atom substitution. The problem of the dynamics of this impurity cluster in diatomic linear chain can be solved exactly by using standard Green's function methods (see Maradudin *et al* 1971). The impurity modes, which can be calculated in inband, gap and outside band regions are obtained from the solutions of the following equations:

(i) The inband region $0 < x \leqslant (\omega_a^2/\omega_m^2)$ and $(\omega_0^2/\omega_m^2) \leqslant x < 1$

$$1-2\,\epsilon_1(\epsilon_2+\epsilon'_2)\,abx^2 - 8\epsilon_2\,\epsilon'_2\,b^2\,x^2\,y^{-1}(1-t) - 8\,\epsilon_1\,\epsilon_2\,\epsilon'_2\,ab^2\,x^3\,y^{-1/2}(1-t)^{1/2} = 0 \tag{1}$$

(ii) The gap region $(\omega_0^2/\omega_m^2) < x < (\omega_0^2/\omega_m^2)$

$$1 + (\epsilon_2+\epsilon'_2)\,bx\,(y')^{-1/2}t^{-1/2} - \epsilon_1\,ax\,(y')^{1/2}\,t^{-1/2} - 2\epsilon_1(\epsilon_2+\epsilon'_2)\,abx^2\,[1-(1-t^{-1})^{1/2}] - 4\,\epsilon_2\,\epsilon'_2\,\times b^2\,x^2\,(y')^{-1}\,[2(t-1)+2(t(t-1))^{1/2}-(1-t^{-1})^{1/2}] - \epsilon_1\,\epsilon_2\,\epsilon_2'\,ab^2\,x^3\,(y')^{-1/2}\{t^{-3/2}+4t^{-1/2}\,[1-(1-t^{-1})^{1/2}]^2\,\times [t+(t(t-1))^{1/2}]-t^{-1/2}\,[2t^{1/2}-t^{-1/2}+2(t-1)^{1/2}]^2\} = 0 \tag{2}$$

(iii) The outside band region $x>1$

$$1 + (\epsilon_2-\epsilon'_2)\,bxy^{-1/2}(-t)^{-1/2} + \epsilon_1\,axy^{1/2}(-t)^{-1/2} - \epsilon_1(\epsilon_2+\epsilon'_2)\,x^2\,ab\,[2-2(1-t^{-1})^{1/2}] - 4\,\epsilon_2\,\epsilon'_2\,\times x^2\,b^2\,y^{-1}\,[2(1-t)-(1-t^{-1})^{1/2}-2(t(t-1))^{1/2}] - \epsilon_1\,\epsilon_2\,\epsilon'_2\,\times ab^2x^3y^{-1/2}\{t^{-1}(-t)^{-1/2}+4(-t)^{-1/2}\,[(1-t^{-1})^{1/2}-1]^2[t+(-t)^{1/2}\,\times (1-t)^{1/2}]+(-t)^{-1/2}\,[2(-t)^{1/2}+(-t)^{-1/2}-2(1-t)^{1/2}]^2\} = 0 \tag{3}$$

In eqs (1)–(3),

$$x = \omega^2/\omega_m{}^2;\ a = 1 + M_1/M_2,\ b = 1 + M_2/M_1 \tag{4a}$$

$$\epsilon_1 = (M'_1 - M_1)/M_1,\ \epsilon_2 = (M'_2 - M_2)/M_2,\ \epsilon'_2 = (M''_2 - M_2)/M_2 \tag{4b}$$

$$y = (1 - bx)/(1 - ax);\ (y')^{1/2} = \mp\,(-y)^{1/2},\ t = abx\,(1 - x) \tag{4c}$$

and ω_a, ω_o and ω_m are respectively the zone boundary acoustic, optic and the maximum optic mode frequencies. Solution of eqs (1)–(3) give respectively, the frequencies of the local, gap and inband resonant modes for the three impurity cluster. It can be easily verified that if we put ϵ_1 equal to zero in eqs (1)–(3) then these reduce eqs (1)*–(3) of Behera and Patnaik (1975) corresponding to the case of next-nearest-neighbour impurity pair modes. On the other hand, if we put either ϵ_2 or ϵ'_2 equal to zero in eqs (1)–(3), these reproduce eqs (1)-(3) of Behera and Patnaik (1976) corresponding to the nearest neighbour impurity pair case.

3. Results and discussion

We solved eqs (1)–(3) numerically to determine the local, gap and resonant modes. In doing so we have chosen the parameters of the perfect diatomic linear chain to be those corresponding to the KI host crystal (Behera and Patnaik (1975)) which is known to have a wide gap. In performing the numerical calculations to study the behaviour of impurity modes the following possibilities of impurity substitution and variation is taken into account. (i) A pair of similar impurities are substituted into the light mass (K^+) sub-lattice and the variation of impurity modes on varying the mass of the impurity substituted into the heavy (I^-) sublattice is studied. (ii) The same study as in (i) but with the pair of similar impurities substituted into the heavy mass sublattice and the third impurity whose mass is varied is substituted into the light mass sublattice. (iii) A pair of dissimilar impurities occupying nearest-neighbour positions one substituted into the light mass sublattice and the other into the heavy mass sublattice and the third impurity atom whose mass is varied is substituted into the heavy mass sublattice. The results of all these studies are depicted respectively in figures (1) to (3). In all these cases the mass of the single impurity atom is allowed to vary from the limiting case of ($\epsilon=-1$) a vacancy to $5M$ ($\epsilon=4$) a heavy impurity. Moreover, wherever possible the impurity atoms whose masses are kept fixed are chosen to be either alkali metal atoms or halogen atoms as substituted into the K^+ sublattice or the I^- sublattice respectively. In figures 1 and 2 where the impurity pairs are substituted into the light and heavy sublattice respectively, the pairs are always chosen so as to correspond to a pair of light mass impurities (Na^+Na^+, Cl^-Cl^-) a pair of heavy mass impurities (Cs^+Cs^+, X^-X^-) and a pair consisting of one light and the other heavy mass impurities (Cs^+Na^+, Cl^-X^-). Similarly in figure 3 the fixed mass dissimilar

*Here we point out that there is an error in sign of the second term of eq. (1) of Behera and Patnaik (1975) which effects the result in the inband region. In fact the sign should be negative. Hence a pair of similar impurities (either both of light mass or both of heavy mass) will give rise to resonant modes whereas dissimilar impurities will not. A numerical calculation shows that there exists a resonant mode for KI: Cl^- Cl^- system in agreement with the experimental data.

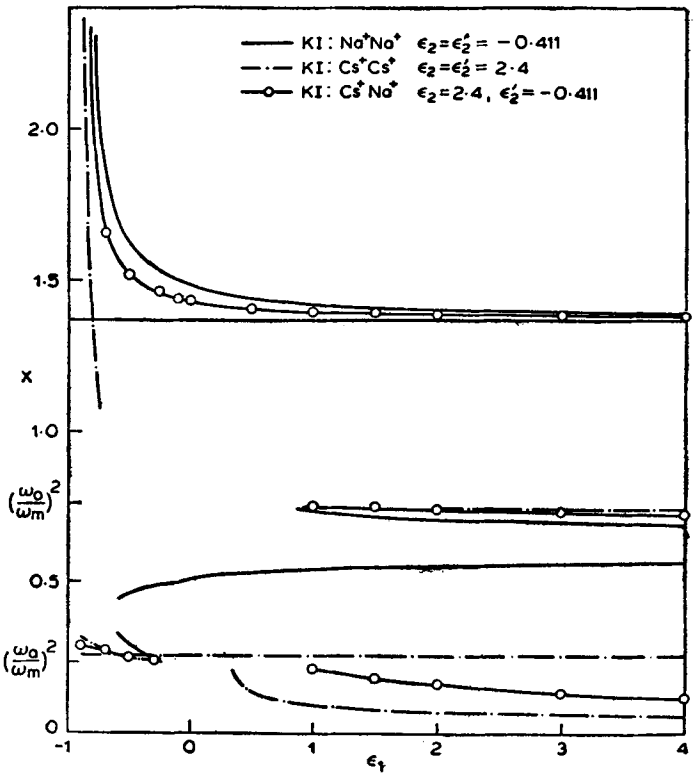

Figure 1. The variation of local, gap and inband mode frequencies for a three impurity cluster, with a similar impurity pair in the light mass sublattice is shown. The mass defect parameter ϵ_1 for the third impurity is varied from -1 to 4.

impurity pairs are so chosen as to correspond to the cases of two light mass (Na^+ Cl^-) impurities, two heavy mass impurities (Cs^+X^-) as well as a light mass impurity in the heavy sub-lattice and a heavy mass impurity in the light sublattice (Cs^+Cl^-).

It can be easily checked that in figures 1 and 2 if we allow the mass of the third impurity to be equal to the host mass (i.e. $\epsilon_1=0$) then the impurity modes corresponding to that of pairs occupying next-nearest-neighbour positions (Behera and Patnaik 1975) in the light mass sub-lattice and the heavy mass sublattice respectively are reproduced. Similarly $\epsilon'_2=0$ in figure 3 reproduces the results of the nearest neighbour pair case (Behera and Patnaik 1976). At this stage it is worthwhile examining whether the three impurity cluster spectrum can be interpreted as due to a pair plus a single impurity acting independent of each other. Examining the case of Cs^+Cs^+ in KI in figure 1, we note that for this heavy impurity pair there exists only a gap mode. Introduction of a third light impurity in the I^- sublattice produces one local and another gap mode as expected from the Mazur *et al* (1956) (MMP) theory. However, these single impurity modes as can be seen vanish as ϵ_1 tend to zero from -1 and the frequency of the pair gap mode gets modified. On the other hand, introduction of a third heavy impurity in the heavy mass sublattice should give rise to no new modes according to the MMP theory, but figure 1, reveals the existence of a high frequency gap mode and a low frequency acoustic resonant mode whose frequency decreases with increasing mass of the impurity. Hence these modes are typical

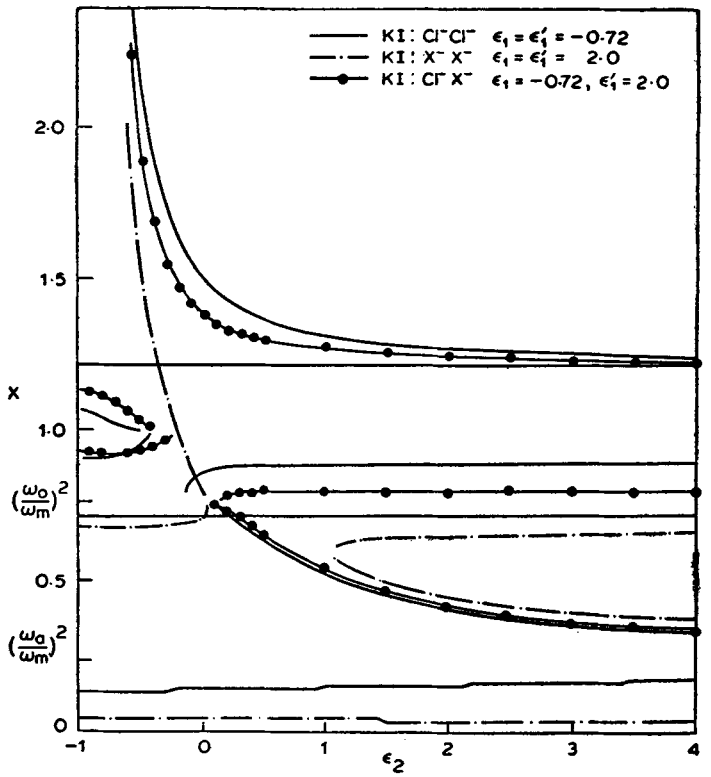

Figure 2. Variation of local gap and inband mode frequencies for a three impurity cluster, with a similar impurity pair in the heavy mass sublattice. The impurity mass in the light mass sublattice is varied.

characteristic three impurity cluster modes and cannot be explained in terms of a pair and a single impurity which are uncorrelated. Such modes exist for almost all cases considered in figures 1, 2 and 3. Similar new modes can also exist when a pair of similar impurities are introduced around an existing single impurity. The variation of the cluster mode frequencies with varying host properties can also be studied and shows similar behaviour as in the pair case (Behera and Patnaik 1975).

Yet another new feature which is observed for a three impurity cluster, and which is not present in the case of a pair is the independence of certain pair modes to the presence of the third impurity in the cluster. It can be seen from figures 1, 2 and 3 that most of the pair mode frequencies get altered and vary as the mass of the third impurity is varied. However, there appears some modes as for example one local mode for Na^+Na^+ pair and a gap mode for Cs^+Cs^+ pair in figure 1, whose frequencies remain constant as the third impurity mass is varied from $\epsilon_1 = -1$ to 4. Similar local and gap modes can be seen for the Cl^-Cl^- pair in figure 2, and a gap mode for Cs^+Cl^- pair in figure 3. We have examined (numerically) these local and gap modes to find an upper bound, if any, on the varying impurity mass beyond which the frequency of the mode might show variation. This showed that the KI: Na^+Na^+ local mode vanishes for $\epsilon_1 \geqslant 9{\cdot}85$ and the KI : Cl^-Cl^- local mode vanishes for $\epsilon_2 \gtrsim 10^3$; whereas the gap modes have no such upper bound. Furthermore, a numerical check on the coefficient of $\epsilon_{1(2)}$ in eqs (2) and (3) showed that it is small or large compared

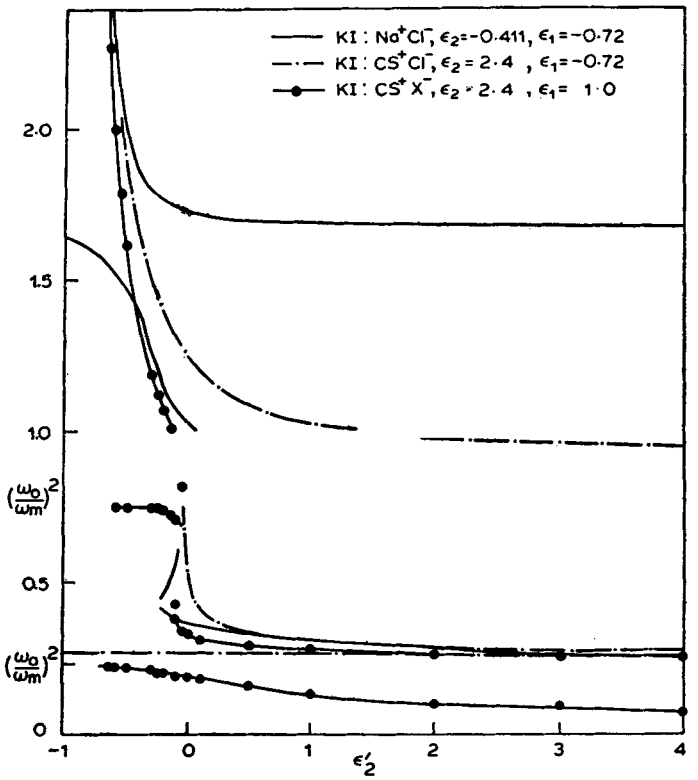

Figure 3. Variation of three impurity cluster modes for the case of a dissimilar pair, with the mass of the third impurity varying.

to the terms independent of the varying parameter $\epsilon_{1(2)}$ in case of local and gap modes respectively and in neither case it is negligible. This eliminates the possibility that these modes are independent of the third impurity mass because the coefficient of this impurity parameter goes to zero. Hence these modes can be interpreted as arising due to the antisymmetric vibration of the pair, while the third impurity remains stationary (either at the centre of mass as in the case of next-nearest-neighbour pairs or outside the pair as in the case of the nearest-neighbour pairs). It can be argued that such modes could also exist for three impurity clusters in a three dimensional crystal if the cluster configuration is linear and symmetrical. Moreover for a cluster of $(Z+1)$ impurity atoms, there will exist breathing modes which will be independent of the central impurity mass, hence whose frequency will be the same as that of a mode for the Z-impurity cluster, (Z being the number of nearest neighbours).

4. Conclusion

In concluding we would like to remark that the frequencies of the three impurity cluster modes can be calculated for various systems and compared with the experimental data available. For this purpose the applicability of the diatomic linear chain model to real three dimensional systems can be justified by using the criterion proposed

by Lucovsky *et al* (1970) and improved by Behera *et al* (1977) as was shown for the impurity pair case (See Behera and Patnaik 1975). However as remarked in the introduction, experimental data exist for only one system namely H^-—Na^+—H^- in KCl. For this system, the diatomic linear chain model fails to reproduce the local mode frequencies because of the extreme light mass of the H^- impurities. Similar difficulties have also appeared in the case of H^--pairs as discussed by Behera and Patnaik (1975).

At this stage it is worthwhile pointing out the fact that the presence of three impurity cluster modes which coincide with the pair mode, may have some significant consequeences on the experimental observation of these cluster modes. As is well known the pair modes are identified by looking for the quadratic (c^2) variation of the strength of absorption with the impurity concentration. However, if the frequencies of a pair mode and three impurity cluster mode coincide, then the strength of absorption of this mode will have both a, c^2 as well as a, c^3 dependence. Hence some modes, which are hitherto thought of, as not a mode due to a pair because of the deviation from c^2 behaviour might as well be a pair mode with a three impurity cluster mode superposed on it.

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