PHYSICAL REVIEW B VOLUME 46, NUMBER 6 1 AUGUST 1992-II

Lattice dynamics of uranium chalcogenides and pnictides

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(Received 22 October 1991; revised manuscript received 20 April 1992)

Phonon dispersion relations in uranium chalcogenides and pnictides have been investigated with use of a three-body-force rigid-ion model that includes long-range three-body interactions due to charge-transfer effects. The dispersion curves for optical branches in almost all symmetry directions and the acoustic branches along the Λ directions are reproduced fairly well. The force constants derived from our theory follow a similar trend, as is revealed from an experimental fit with the rigid-ion model. The contribution of three-body interactions at the L point is significant.

Recently, considerable efforts have been made to investigate the phonon properties of uranium compounds. Besides their importance as reactor materials, the uranium compounds (UX, X=C, N, S, Se, Te, As, Sb) exhibit a wide variety of physical phenomena that are of great interest to solid-state scientists.

The UX compounds, referred to above, crystallize in the rocksalt structure. Lattice vibrations in these compounds have been extensively studied in the last decade.[1-3] A systematic study of the phonons in these compounds was reported recently by Jackman *et al.*[1] The phonon dispersion curves (PDC's) of uranium compounds show several unusual features, which result from charge fluctuation of the electrons in uranium atoms. In particular, some of these anomalies are (i) the optical modes are, in general, independent of wave vectors in all symmetry directions; (ii) the splitting between LO and TO at $\mathbf{q}=0$ is zero and $\nu_{\mathrm{LO}} \geq \nu_{\mathrm{TO}}$ along $(q,0,0)$ and $(q,q,0)$ while the reverse is the case along (q,q,q) directions; (iii) the LA and TA frequencies along (q,q,q) are almost identical in the uranium chalcogenides and pnictides; (iv) the magnitude of C_{12} is significantly small in uranium pnictides and chalcogenides except UTe, for which it is negative.

All these features are well known, while limited theoretical attempts have been made so far to interpret these anomalous characteristics. Rigid-ion and shell models fitted to neutron scattering results have been used to predict the interatomic forces in these compounds.[1] However, these interpretations are not entirely satisfactory to understand the peculiar nature of the dispersion of phonons in uranium compounds. The special features outlined above arise from the influence of charge fluctuations of the electron shells of U atom on the interatomic forces. This fact suggests that one must include long-range many-body forces in the crystal potential to take proper account of the anomalous features in the PDC. Jackman *et al.*[1] have also emphasized the necessity of developing approaches that include electronic effects in the lattice vibrations.

In the present paper we report a three-body force rigid-ion-model (TRIM) calculation of the PDC of uranium compounds, namely, UAs, USb, US, USe, and UTe. All of these compounds exhibit the phonon and elastic anomalies which necessarily arise from long-range ion-ion interactions through their ionic charges. The three-body force included in the present calculations arises from classical electronic charge transfer between the uranium ions and their nearest neighbors. Details of this type of interaction in ionic solids and semiconductors have been discussed by Singh[4] and briefly outlined below. As will be seen in what follows, these many-body forces are quite relevant in the case of uranium compounds. The nearly degenerate $5f$ and $6d$ bands of uranium ions give rise to f-d hybridization, and thereby result in charge fluctuations at the U-ion site. These fluctuating charges interact with all other charges in the lattice, resulting in long-range many-body interactions. Such a lattice dynamical model has already been used previously by Verma and Gupta[5] and Singh[6] to interpret the phonon dispersion in UC and other rare-earth compounds.

It is seen from literature that lattice vibrations in uranium compounds have been analyzed using rigid-ion or shell models[1] (RIM and SM, respectively), which are essentially two-body in nature and fail to explain the large Cauchy violation ($C_{12} \neq C_{44}$) in the elastic constants. For the U compounds studied in the present paper, $(C_{12}-C_{44})$ is negative and significantly large in magnitude. This fact suggests that long-range many-body forces are responsible for such elastic anomalies.

In the present model we consider the many-body interactions arising from overlap of electronic charges between the nearest-neighbor ions.[4] Accordingly, the dynamical matrix in the rigid-ion approximation is given by

$$\underline{D}_{\alpha\beta}(\mathbf{q},k,k') = \underline{R}_{\alpha\beta}(\mathbf{q},k,k') + \underline{Z}_m[\underline{C}_{\alpha\beta}(\mathbf{q},k,k') + \underline{T}_{\alpha\beta}(\mathbf{q},k,k')]\underline{Z}_m \;, \tag{1}$$

where $\underline{R}$ and $\underline{C}$ are repulsive and Coulomb matrices, $\underline{T}$ is the three-body force interaction (TBI) matrix,[4] and Z_m is the modified charge defined as

$$Z_m e = \pm Ze[1+2nf(r)/Z] \;, \tag{2}$$

where $f(r)$ is a TBI parameter, signifying the amount of overlap. The present model has seven parameters (six

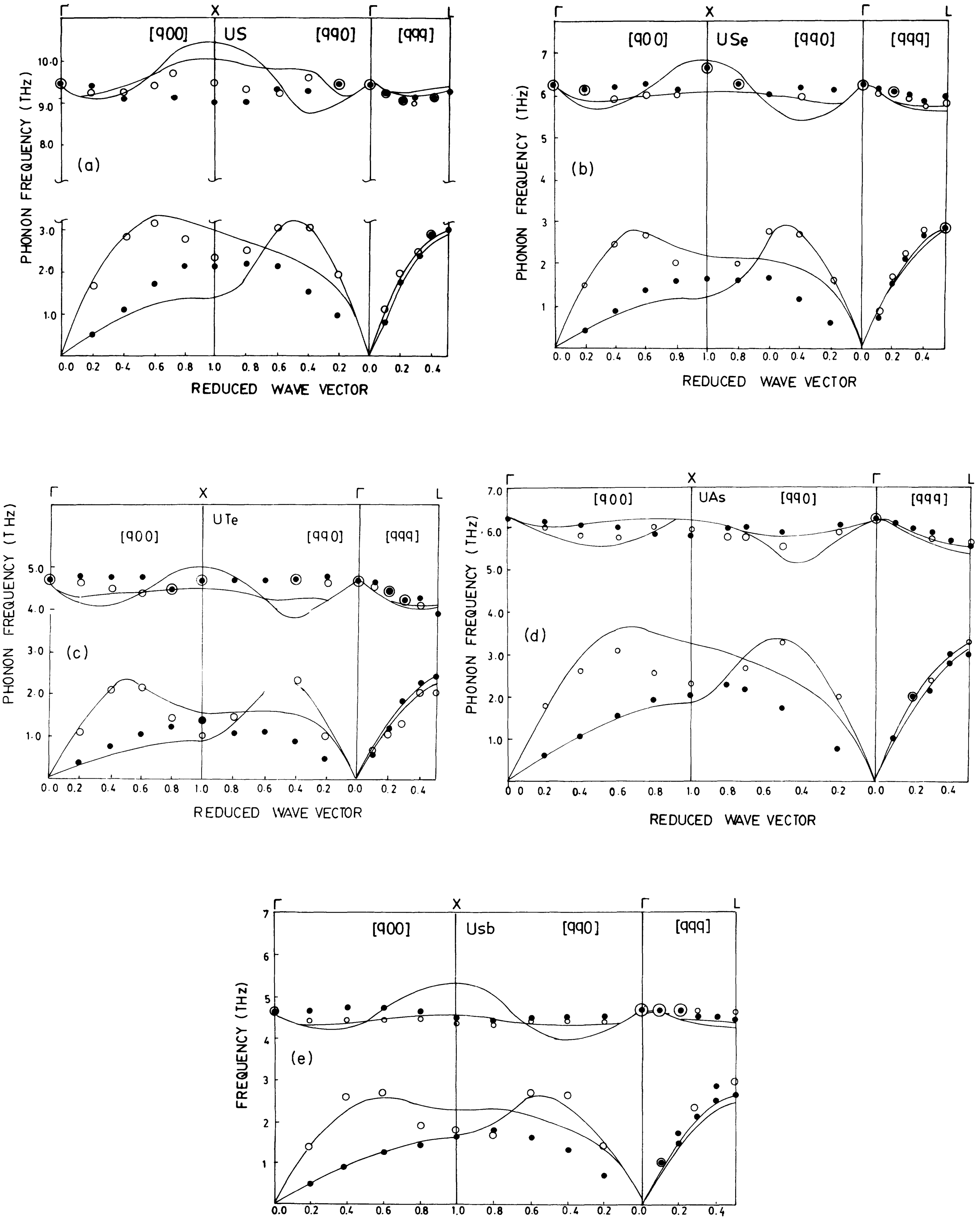

FIG. 1. Phonon dispersion curves for US, USe, UTe, UAs, and USb. Experimental points are taken from Ref. 1.

short-range and one TBI) which are obtained self-consistently from macroscopic quantities (e.g., elastic constants, lattice parameter, zone-center optic and zone boundary acoustic frequencies). The equations relating the macroscopic properties with the model parameters are already available in the literature.[4,6] However, since the zone-center LO and TO frequencies are the same for this family of solids, the modified charge is directly related to the elastic constants through the relation

$$Z_m = [-0.8583V(C_{12}-C_{44})/e^2]^{1/2} . \qquad (3)$$

The parameters calculated from these macroscopic properties are reported elsewhere.[7]

We have calculated the phonon dispersion curves for five uranium compounds (US, USe, UTe, UAs, and USb) using the model discussed above. The present model takes into account, phenomenologically, the effect of transfer of charge between the ions which results in long-range three-body interactions. The calculated phonon dispersion curves for uranium chalcogenides and pnictides are presented in Fig. 1 and compared with the measured data.[1] It is revealed from these figures that the present model explains some of the phonon modes satisfactorily while it fails to do so for some others. This is partly because we have not made any attempt to fit the model completely to the PDC. On the contrary, we have tried to achieve reasonable agreement between theoretical and experimental results through a set of physically realistic force constants. Also, because of this reason, we have not compared the theoretical RIM and SM results of Jackman *et al.*[1] with our PDC's, as they necessarily fit the complete dispersion relations to the models.

In the case of U chalcogenides, dispersion of both optical and acoustic phonons are explained more or less satisfactorily in the Δ direction. Much of the discrepancies are observed at the X point. While experiments predict that LO and TO frequencies at the X point are the same for USe and UTe, this feature is absent in our calculation. We, however, observe LO frequencies over the TO branch from our calculation. This feature is also seen in the rigid-ion and shell model fits, reported by Jackman *et al.*[1]

In order to assess the validity of the present model, we have compared the frequencies at the X point for U chalcogenides and pnictides with the experimental data in Fig. 2. As pointed out earlier, the model predicts LO over TO for US. The difference between $\nu_{\rm LO}$ and $\nu_{\rm TO}$ in this case is, however, comparable to experimental results, though the magnitude is about 10% higher than the measured data. In two other chalcogenides the model predicts a difference between LO and TO modes of the order of 0.8 (USe) and 0.4 (UTe) THz, respectively. This fact, is however not a serious drawback of the present model which hardly aims to reproduce the spectrum.

From our calculations, we obtain a large discrepancy in the LA and TA splitting at the X point for uranium sulfide and selenide, while in the case of UTe, this difference is reasonable. This feature is also observed in the model calculation reported by Jackman *et al.*[1] A possible reason for such discrepancies can be polarizability of chalcogen ions, as well as small magnitudes of C_{12} and C_{44}. The latter property prevents one from achieving a reasonable magnitude for LA and TA at the X point from theoretical models.

The characteristic features of the PDC along the zone boundary are explained more or less satisfactorily for the chalcogenides. The primary reason for a better agreement between the experiment and present theory is that TBI contribute significantly along the Λ direction. This can be visualized from the fact that in NaCl structure, there are six nearest-neighbor uranium ions, for a chalcogen or pnictide ion. This symmetry of vibration along the Λ direction reveals that the ionic size of the U atom suffers considerable deformation.

In the case of uranium pnictides, the features of the PCD's are very similar to those observed in the case of chalcogenides. The optical and acoustic branches along the Δ direction are more or less satisfactorily reproduced. This is, however, not the case for the LA branch along the X direction. Also, the model fails to explain the optical branches in (q,q,q) direction for USb. In principle, such limitations can be overcome by considering the po-

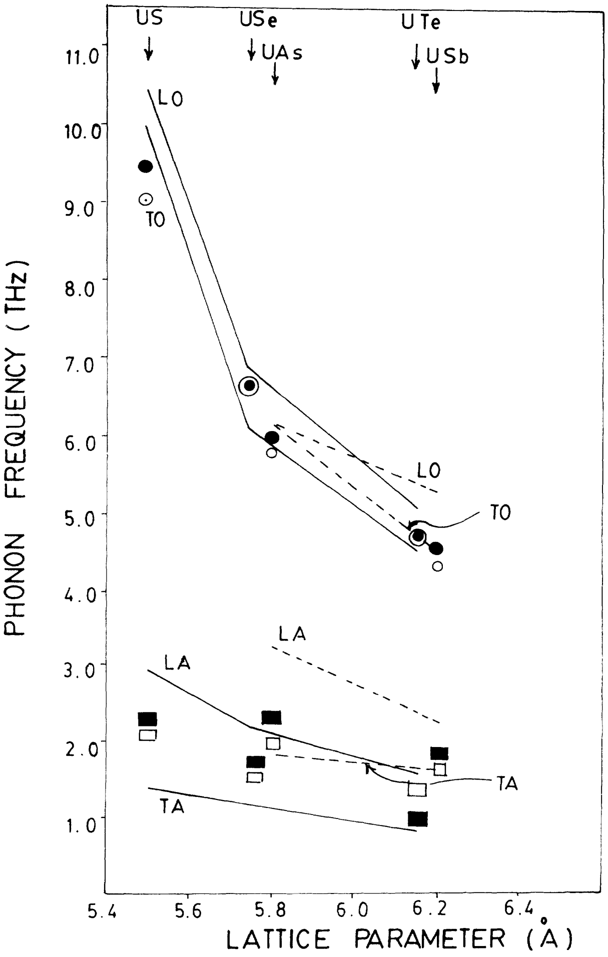

FIG. 2. X-point frequencies as a function of lattice parameter. Solid lines and dashed lines are for chalcogenides and pnictides, respectively. Open circles, closed circles, open squares, and closed squares represent experimental TO, LO, TA and LA, respectively (Ref. 1).

larizability of the ions. A systematic and consistent type of behavior can be observed in the case of chalcogenides where the ratio of the X-point LA frequency to the maximum LA frequency falls from 0.89 (US), to 0.75 (USe) to 0.55 (UTe). These magnitudes, are, however, a little higher than the RIM fit to the dispersion curves (0.71, 0.61, and 0.4 for US, USe, and UTe, respectively) as reported by Jackman *et al.*[1]

The effective radial force constants calculated from the present TRIM are plotted in Fig. 3 as functions of the lattice parameter. In this figure we have compared our results with those reported by Jackman *et al.*[1] fitted from RIM. It is worthwhile mentioning here that in the present analysis we have made efforts not to fit the dispersion curve but to reproduce the gross features of the PDC of U compounds. The salient feature of the dominance of the U-X force constant in all U compounds has been perfectly reproduced. The U-X force constant is fairly constant across the series. The difference in magnitude between our force constants and those of Jackman *et al.*[1] lies in the difference of models. The small (or negative) magnitude of the U-U force constant for U chalcogenides could be reproduced fairly well. However, we observe a large difference for these force constants in the case of UAs and USb. This fact can be explained from the fact that these materials are trivalent and the bulk modulus is significantly small in magnitude. These facts influence the U-U as well as X-X force constants. In the case of chalcogenides, we find a similar trend of the X-X force constants which vary systematically in magnitude.

From our present model calculations, we find that the effect of charge transfer takes partial account of phonon and elastic anomalies in U compounds. Also the force constants can be fairly reproduced even without any rigorous fitting. The effects of valency transition in U compounds on the force constants have been discussed by Jackman *et al.*[1] Similar arguments also hold in our case. The TBI parameter Z_m derived from elastic constants is small but takes into account the Coulomb attraction in the dynamical matrix. However, in the present analysis we did not consider the effect of screening due to localized f electrons at the U-atom site. Inclusion of screening effect might improve a part of the results presented here. A better understanding of the phonon anomalies in the compounds, however, can be revealed by extending the theory[8] which considers the metallic nature of the system.

Finally, in the present paper we have reported the calculated PDC's for five U compounds using a three-body interaction rigid-ion model with seven parameters. In general the model reproduces the gross features of the PDC though not entirely satisfactorily. The discrepancies along the X-Γ directions can be, however, minimized by introducing polarizability of the ions in the model. The model also predicts that many-body interactions play a dominant role in the phonon dispersion of U compounds.

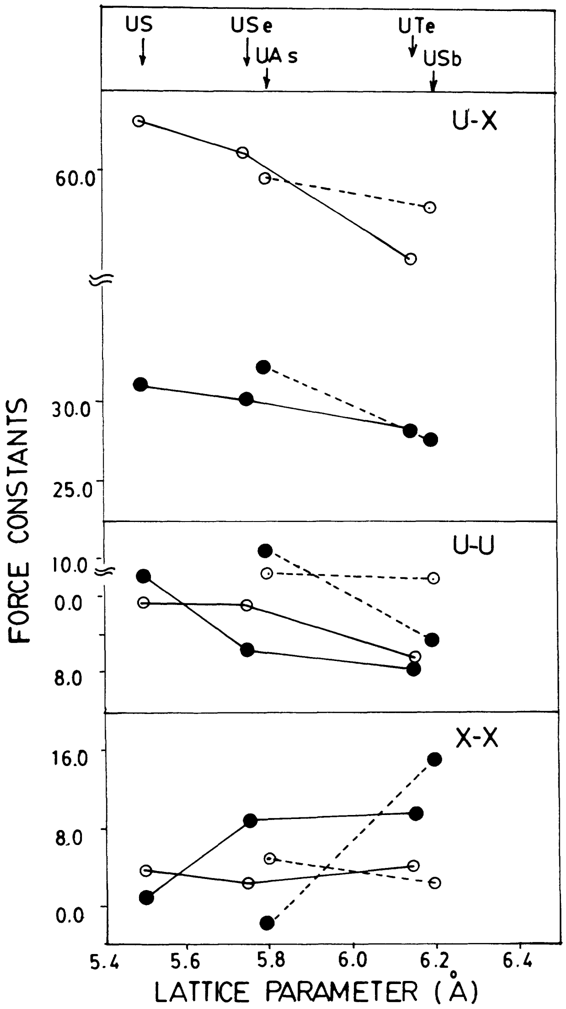

FIG. 3. The U-X, U-U, and X-X radial force constants as a function of lattice parameter. Solid circles represent calculated and open circles represent the values of experimental fit to RIM (Ref. 1). Solid and dashed curves are for chalcogenides and pnictides, respectively. (Experimental values are in N m^2.)

The authors are grateful to the Department of Atomic Energy, Government of India for financial support for this Research Project. P.K.J. would like to thank CSIR for partial support.

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