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Debye temperatures of uranium chalcogenides from their lattice dynamics

S DURAI* and P BABU
Postgraduate and Research Department of Physics, A.M. Jain College, Chennai 600 114, India

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Abstract. Phonon dispersion relations in uranium chalcogenides have been investigated using a modified three-body force shell model. From the phonon frequencies, their Debye temperatures are evaluated. Further, on the basis of the spin fluctuation in the heavy fermion uranium compounds, UPt_3 and UBe_{13}, the possible superconducting transition temperatures of chalcogenides are theoretically predicted. The T_c values are in the same range as of those in UPt_3 and UBe_{13}.

Keywords. Uranium chalcogenides; *p*-wave electronic superconductor; phonon frequency; Debye temperature; spin fluctuation.

1. Introduction

Uranium compounds, besides their important use in reactor technology, possess more interesting and also controversial properties. Hence, over nearly last two decades they have attracted the attention of both experimental and theoretical solid state physicists. Chalcogenides (UX, X = S, Se, Te) show ferromagnetic ordering while the pnictides (UY, Y = N, P, As, Sb, Bi) order antiferromagnetically. Their lattice vibrational properties have been extensively studied. At the same time, UPt_3 and UBe_{13} have gained significance in another way. They belong to the heavy fermion system. They are characterized by large magnetic fluctuations and high values of g which is the coefficient of linear term in specific heat. UBe_{13} is the first *p*-wave electronic superconductor ($T_c = 0{\cdot}905$ K) and the next is UPt_3 ($T_c = 0{\cdot}54$ K) (Ott *et al* 1984; Aeppli *et al* 1985). The two compounds are characterized by very low coupling coefficient, l, the components of which are l_{ep} (electron–phonon) and l_{ee} (electron–electron) and very small value of coulomb pseudo potential, $\mu^* \sim 0{\cdot}25$, indicating a weak coupling.

This paper is presented with the main aim to study the lattice vibrations of uranium chalcogenides using the refined three-body force shell model and to obtain the Debye temperature from the phonon frequencies. Using modified McMillan equation and making use of conventional superconductivity theory to predict the possibility of these uranium compounds becoming superconductors on parallel lines with the behaviour of UPt_3 and UBe_{13}.

2. Theoretical background

2.1 *Evolution of various models in the study of lattice dynamics*

The lattice dynamics of NaCl was extensively investigated by Kellermann (1940) and the treatment is applicable to the ionic crystals of similar structure. The supporting theories of shell model (Dick and Overhauser 1958), subsequent modifications (Woods *et al* 1960) and inclusion of three-body forces between ions by Verma and Singh (1969) were the various stages of progress. The discrepancy in three-body force shell model was removed by Verma and Agarwal (1973). The various interactions between ions were taken to be equal in earlier treatment and it was Mohan *et al* (1986) who applied the three-body force shell model to the lattice dynamics of calcium oxide without making them numerically equal. The results were satisfactory and on that basis lattice dynamics of strontium oxide and cesium fluoride were studied (Durai *et al* 1987; Mohan and Durai 1988).

In the present work, we have chosen chalcogenides which crystallize in the rock-salt structure and exhibit unusual magnetic and elastic properties.

The earlier works related to such calculations are (i) rigid-ion and shell model by Jackman *et al* (1986) and (ii) inclusion of long range many-body forces and breathing shell model by Jha and Sanyal (1992). We have applied the modified three-body force shell model to obtain the phonon frequencies of UX (X = S, Se, Te) for the following specific reason. Though the uranium compounds have rock-salt structure, they are more metallic in nature rather than ionic and the curiosity is to know how the theory works in this case. Further, from the frequencies obtained, the Debye temperature, q_D, is calculated.

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*Author for correspondence (bagee29@rediffmail.com)

2.2 *Chalcogenides and heavy fermion superconductors*

The uranium compounds, UPt_3 and UBe_{13}, are heavy fermion superconductors. Oguchi and Freeman (1985) attempted to account for their superconductivity on the basis of conventional theory. We, inspired by this clue, are of the opinion that the other UX compounds could also attain superconductivity in the range close to that of UPt_3 and UBe_{13}. Making use of l and μ^* values similar to those of heavy fermion system, the T_c values have been calculated with the help of modified McMillan (1968) equation for which q_D values obtained from the preceding section are useful.

3. Formulae and calculation

3.1 *Evaluation of phonon frequencies and Debye temperature*

The three-body force shell model equations in the matrix form are given by

$$-Mw^2 u = (R + ZC' Z)u + (T + ZC' Y)w,$$
$$0 = (YC' Z + T)u + (YC' Y + S)w,$$

Table 1. Input parameters.

Compound	C_{11}	C_{12}	C_{44}	w_{LO}	a_0	a_1	a_2
US	3·056	0·205	0·1702	9·50	5·489	0·40	9·875
USe	2·08	0·07	0·17	6·25	5·744	0·3	11·31
UTe	1·47	– 0·16	0·119	4·75	6·155	0·20	13·923

(C_{11}, C_{12}, C_{44} in 10^{12} dynes/cm^2, w_{LO} in THz, a_0 in Å and a_1, a_2 in Å^3 (Jha and Sanyal 1992).

Table 2. Model parameters.

Compound	$Z\,[Z + 12f(a)]$	$Z\,[a(df/da)]$	A	B	Y_1	Y_2
US	26·824	– 0·537	623·769	31·250	0·556	0·002
USe	32·130	– 3·376	588·832	37·432	0·497	0·128
UTe	21·462	7·481	406·298	– 29·128	0·608	0·205

Table 3. Calculated phonon frequencies (10^{12} Hz) for US.

	Acoustical branch		Optical branch	
Symmetry direction	Longitudinal	Transverse	Longitudinal	Transverse
q 0 0				
0·2 0 0	1·8506	0·5432	9·3256	9·5281
0·4 0 0	2·8436	1·0896 (1·0062)	9·0805	9·5094
0·6 0 0	3·1468	1·5508	9·3568	9·4815
0·8 0 0	2·8561	1·6526	9·6215	9·4058
1·0 0 0	2·8054	1·7218 (1·8250)	9·6817	9·4008
q q 0				
0·2 0·2 0	0·7892	1·7832 (T_1) 1·6531 (T_2)	9·4180	9·4805
0·4 0·4 0	1·4687	2·9654 (T_1) 2·7543 (T_2)	9·4202 (9·2352)	9·4973
0·6 0·6 0	2·0891	3·0852 (T_1) 3·1049 (T_2)	9·4308	9·5238
0·8 0·8 0	2·2572	2·2508 (T_1) 2·3048 (T_2)	9·3804	9·5876
1·0 1·0 0	2·3156	1·7053 (T_1) 1·7852 (T_2)	9·4008 (9·5080)	9·6805
q q q				
0·1 0·1 0·1	0·8072	0·8548	9·4800	9·4189
0·2 0·2 0·2	1·5132	1·4540 (1·6805)	9·3642	9·3018
0·3 0·3 0·3	2·0158	2·0458	9·2612	9·2176
0·4 0·4 0·4	2·9192	3·0185	9·1943	9·1089
0·5 0·5 0·5	3·1081	3·1805 (3·0840)	9·1108	9·0085

The values in parantheses are from Jackman *et al* (1986).

with $ZC'Z = Z[Z + 12f(a)] + V$, where R, S, T are matrices specifying core–core, shell–shell and core–shell interactions, respectively and $f(a)$ is related to overlap integrals of electron wave functions. V is the force constant derived from the purely three-body part of the lattice potential. The basic equations pertaining to TSM are the same as given by Agarwal (1977). In the present approach, R, S, T elements are treated as different i.e. $R \neq S \neq T$. The R and C elements are calculated from the dimensionless coefficients of Kellermann. Short range force constants A_1, B_1, A_{11} and B_{11}, are used to find out the T matrix elements. Further, the variation in the T-matrix elements with respect to symmetry directions are identical to the corresponding variations in the R-elements. A simple manipulation leads to the result that $S = 2T–R$. The V-matrix elements are calculated using the coefficients (revised values) given by Verma and Singh (1969).

The input data necessary for the calculations of the model parameters are the elastic constants, C_{11}, C_{12}, and C_{44}, long wave optical frequencies, w_{LO}, and w_{TO}, the lattice constant, a_0, and the electrical polarizabilities, a_1 and a_2. The repulsive forces between ions are connected with polarization of ions and hence the polarizabilities of positive and negative ions, a_1 and a_2, are essential for solving the equations. The model parameters are the constants A, B, overlap integral constant, $f(a)$, (a df/da) and the shell charges, Y_1 and Y_2. With these data the secular equation is solved to obtain the phonon frequencies. Using the maximum values of phonon frequency, the Debye temperature, q_{D}, is calculated.

3.2 *Estimation of superconducting transition temperatures*

On the basis of strong coupling theory, McMillan (1968) suggested the following equation for the theoretical estimation of superconducting transition temperature, T_c,

$$T_c = (q_{\mathrm{D}}/1\cdot 45)\exp[-\,1\cdot 04(1 + l)/(l - \mu^*\,(1 + 0\cdot 62\,l))],$$

where l is the electron–phonon coupling constant (l_{ep}) and μ^* the coulomb coupling constant. However, another factor relevant to the present work is the spin fluctuations. If its influence is to be incorporated in the above equation, then l is to be modified as $l = l_{\mathrm{ep}}/(1 + l_{\mathrm{sf}})$, where l_{sf} is the component due to spin fluctuation. l_{sf} is estimated from a knowledge of mass enhance factor. Since the coupling is not a strong one, there is no chance of large values of l or μ^* being associated with the compounds. In comparison with heavy fermion superconductors, two values have been considered for μ^* and l_{ep} and l_{sf} values are chosen keeping in mind the trend of q_{D} values. The chosen value for l is around 0·33 and for μ^* the values considered are 0·1 and 0·12. The reason for such selec-

Table 4. Calculated phonon frequencies (10^{12} Hz) for USe.

Symmetry direction	Acoustical branch Longitudinal	Acoustical branch Transverse	Optical branch Longitudinal	Optical branch Transverse
q 0 0				
0·2 0 0	1·7539	0·5178	6·0028	6·2829
0·4 0 0	2·6538	0·8039 (0·9030)	5·7096	6·2986
0·6 0 0	2·7089	1·2041	5·7008	6·3089
0·8 0 0	2·2123	1·4536	6·0890	6·3525
1·0 0 0	1·8090	1·4098 (1·5078)	6·2428	6·3896
q q 0				
0·2 0·2 0	0·7435	1·7081 (T_1) 1·8132 (T_2)	6·0972	6·1972
0·4 0·4 0	1·1817	3·0817 (T_1) 3·2006 (T_2)	5·5036 (5·6840)	6·2085
0·6 0·6 0	1·4813	2·7090 (T_1) 2·8132 (T_2)	5·4732	6·2196
0·8 0·8 0	1·6581	2·0581 (T_1) 2·1054 (T_2)	5·8142	6·2253
1·0 1·0 0	1·8156	1·4108 (T_1) 1·8132 (T_2)	6·2013 (6·2240)	6·2483
q q q				
0·1 0·1 0·1	0·7431	0·7381	6·0315	6·108
0·2 0·2 0·2	1·2492 (1·4320)	1·2508	5·9518	5·9450
0·3 0·3 0·3	1·7645	1·7895	5·8160	5·7480
0·4 0·4 0·4	2·2108	2·3945	5·8009	5·7021
0·5 0·5 0·5	2·7563 (2·9084)	2·9813	5·7843	5·6805

The values in parantheses are from Jackman *et al* (1986).

Table 5. Calculated phonon frequencies (10^{12} Hz) for UTe.

Symmetry direction	Acoustical branch Longitudinal	Acoustical branch Transverse	Optical branch Longitudinal	Optical branch Transverse
q 0 0				
0·2 0 0	1·2054	0·2508	4·7582	4·7620
0·4 0 0	2·1087	0·6574 (0·7056)	4·2358	4·7519
0·6 0 0	2·2576	0·8508	4·0078	4·7328
0·8 0 0	1·5786	0·9048	4·3152	4·7192
1·0 0 0	1·2583	0·9048 (0·8560)	4·6829	4·7052
q *q* *q*				
0·2 0·2 0	1·2538	0·3095 (T_1) 0·3783 (T_1)	4·6804	4·7126
0·4 0·4 0	1·8170	0·8172 (T_1) 1·0056 (T_2)	4·2154 (4·1582)	4·7234
0·6 0·6 0	1·8090	1·2105 (T_1) 1·3248 (T_{12})	4·0058	4·7325
0·8 0·8 0	1·3421	1·2359 (T_1) 1·2864 ($T_{12)}$)	4·2814	4·7681
1·0 1·0 0	0·9050	1·0897 (T_1) 1·1720 (T_{12})	4·7238 (4·9560)	4·8091
q *q* *q*				
0·1 0·1 0·1	0·5198	0·5208	4·7512	4·7678
0·2 0·2 0·2	1·2108 (1·2268)	1·3024	4·6278	4·6013
0·3 0·3 0·3	1·5321	1·7532	4·5832	4·5032
0·4 0·4 0·4	1·7835	2·0871	4·4972	4·2081
0·5 0·5 0·5	2·0028 (2·1008)	2·4092	4·4278	4·0075

The values in parantheses are from Jackman *et al* (1986).

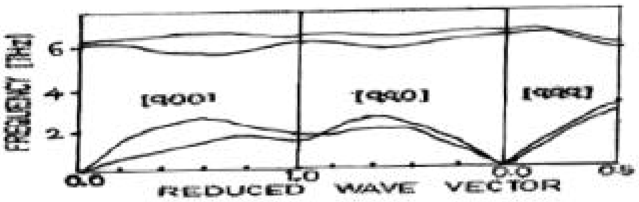

Figure 1. Phonon dispersion curve for USe.

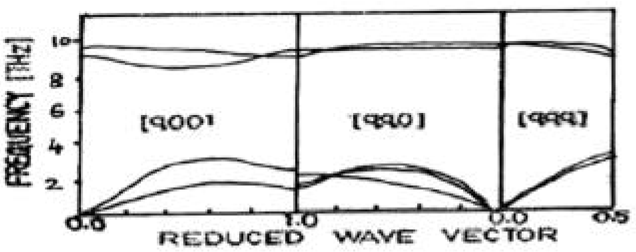

Figure 2. Phonon dispersion curve for US.

tion is the fact that the fermions are coupled to a low-energy set of spin fluctuation. This may be compared with a value of $\mu^* = 0{\cdot}13$ in the case of metallic glass superconductors where the T_c value lies in the approximate range from 3–0·6 K (Altounian and Strom-Olsen 1983).

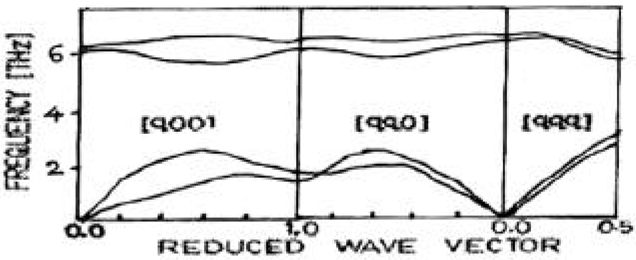

Figure 3. Phonon dispersion curve for UTe.

4. Results and discussion

Tables 1 and 2 are the input data and the model parameters for three-body force shell model. Tables 3–5 give the estimated values of phonon frequencies in the symmetry directions for US, USe and UTe. Figures 1–3 give the phonon dispersive curves for USe, US and UTe.

Some of the salient features are:

(i) The *L*0 and *T*0 frequencies in *q*00 directions have a separation of 0·3561 and 0·1273, 0·24 and 0·1067 and 0·0753 and 0·0568 THz for US, USe and UTe, respectively. The *LA* and *TA* frequencies are separated by 0·0452 and 1·1786, 0·0551 and 0·8920 and 0·0529 and 0·6540 THz, with a maximum separation.

Table 6. l_{ee}, l_{sf} l_D and T_c values.

				T_c	
Compound	l_{ee}	l_{sf}	l_D	$\mu^* = 0{\cdot}1$	$\mu^* = 0{\cdot}12$
US	– 0·06	0·33	138·71	0·212	0·103
USe	– 0·06	0·34	138·71	0·258	0·132
UTe	– 0·07	0·35	114·79	0·279	0·153

(ii) For *qq*0 direction the variation is small in optical mode for all compounds whereas the acoustical mode shows a wide variation.

(iii) For *qqq* symmetry direction there appears to be an overlapping tendency between transverse and longitudinal frequencies in both optical and acoustical modes. The frequencies are almost identical for each direction. The trend is due to the fact that the compounds are more metallic than ionic.

(iv) Some of the earlier values are given for comparison in order to appreciate the theoretical approach.

In table 6, l_{ep}, l_{sf}, q_D and T_c values are presented. From the phonon frequencies obtained, the Debye temperatures have been estimated. Comparing these values with 210 K for UPt_{13} and 122 K for UBe_{13}, the values estimated by us are reasonable. The T_c values obtained for $\mu^* = 0{\cdot}1$ and 0·12 are given. The values down to 0 K region may be one day supported by experimental values.

5. Conclusions

The behaviour of UPt_3 and UBe_{13} has been taken as the ground for this investigation and the lattice dynamical studies are used in predicting the phonon frequencies and also the superconducting temperature. The results provide scope for a new line of investigation.

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