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PHYSICAL REVIEW B VOLUME 3, NUMBER 1 1 JANUARY 1971

Mössbauer Recoilless Fraction of Solid Krypton. II

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The Mössbauer recoilless fraction of solid krypton is calculated in the temperature range 0–85 °K, using a simple treatment of the effects of lattice anharmonicity and thermal expansion upon the phonon frequency spectrum. The model calculation is compared to recent experimental and theoretical studies.

I. INTRODUCTION

In a recent paper[1] the present author presented a calculation of the Mössbauer recoilless fraction of solid krypton using a simple treatment of the effects of lattice anharmonicity[2] upon the phonon spectrum. The harmonic phonon spectrum used in I was based upon a sampling of the first Brillouin zone using a simple first-neighbor Born–von Karman force-constant model for the interaction of the atoms in the Kr lattice.[3]

In the present paper we also include the influence of thermal expansion upon the phonon frequencies, an effect which shifts the frequencies in the opposite direction from the anharmonicity correction included in the earlier paper.

In Sec. II we present a brief discussion of the relevant theory for the frequency shifts. In Sec. III the results of the calculations are presented, and a comparison is given with the recent experimental curve for the Kr 9.3-keV line obtained by Gilbert and Violet.[4] In addition, the present result is compared with recent calculations due to Mahesh[5] who used the Debye approximation for the phonon spectrum and included only the shift due to thermal expansion.

II. THEORY

The Mössbauer recoilless fraction f is given by

$$f = e^{-2W}, \qquad (1)$$

where the exponential factor is given by

$$2W = 2R\left(\frac{1}{3N}\sum_s \frac{1}{\omega_s}(\langle n_s\rangle + \tfrac{1}{2})\right)$$

$$= 2R\int \frac{d\omega\, g(\omega)}{\omega}\left(\frac{1}{e^{\beta\hbar\omega}-1}+\frac{1}{2}\right). \qquad (2)$$

In the above expression $R = \hbar^2 k^2/2M$ is the recoil energy and $s = (q, j)$ represents a phonon frequency of wave number q and polarization index $j = 1, 2, 3$ in the first Brillouin zone. $\langle n_s\rangle$ is the Bose factor

$$\langle n_s\rangle = (e^{\beta\hbar\omega_s} - 1)^{-1}, \qquad (3)$$

which gives the average occupancy of the sth phonon mode, and $\beta = 1/kT$.

We assume, as in I, that the effect of anharmonicity is to shift each phonon frequency by the amount

$$\Delta\omega/\omega = (A/3Nk)\langle e\rangle, \qquad (4)$$

where

$$\langle e\rangle = \textstyle\sum_s \hbar\,\omega_s(\langle n_s\rangle + \tfrac{1}{2}) = \displaystyle\int d\omega\, g(\omega)\hbar\,\omega\left(\frac{1}{e^{\beta\hbar\omega}-1}+\frac{1}{2}\right) \qquad (5)$$

is the average energy of a lattice oscillator.

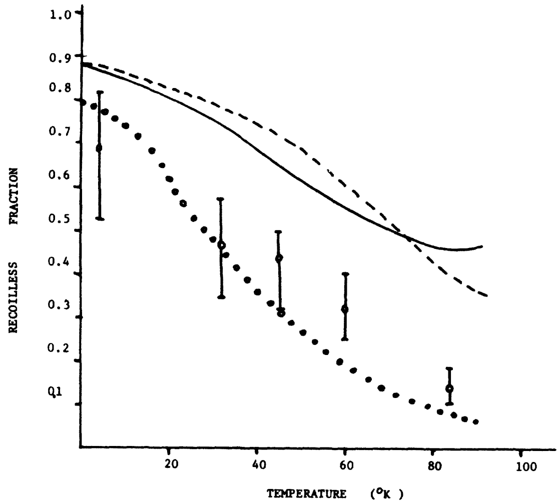

FIG. 1. Present calculation including anharmonic and thermal expansion frequency shifts compared with experiment and the harmonic calculation of GV. Present calculation is the solid curve. GV harmonic calculation is the dashed curve. Experimental data are indicated by the error bars. Small circles indicate the Debye-model results of Mahesh.

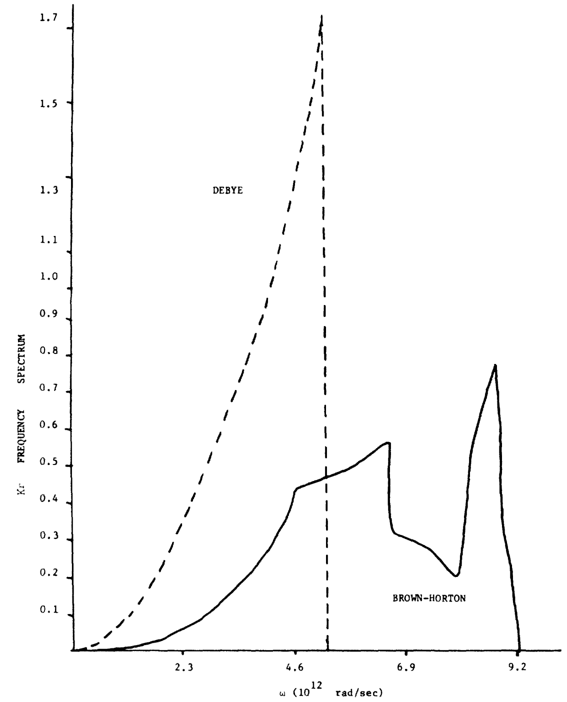

FIG. 2. Harmonic phonon spectrum of Brown and Horton (solid curve) compared to the Debye spectrum used in Mahesh's calculations.

In addition we include the shift in frequency due to thermal expansion of the lattice, given by

$$\Delta\omega/\omega = -\gamma\,\Delta\Omega/\Omega, \qquad (6)$$

where γ is the Grüneisen constant, and $\Delta\Omega/\Omega$ is the relative change in lattice volume due to thermal expansion.

A phonon frequency ω is shifted to $\omega' = \omega(1+\xi)$ owing to the combined effects of anharmonicity and thermal expansion, where $\xi = \xi_{\text{anh}} - \xi_{\text{th exp}}$ and

$$\xi_{\text{anh}} = (A/3Nk)\langle e\rangle; \quad \xi_{\text{th exp}} = \gamma(\Delta\Omega/\Omega). \qquad (7)$$

As in our first paper, the exponential factor given in Eq. (2) becomes

$$2W = 2R(1+\xi)^{-1}\int \frac{d\omega\, g(\omega)}{\omega}\left(\frac{1}{2}+\frac{1}{e^{\beta\hbar\omega(1+\xi)}-1}\right), \qquad (8)$$

where $g(\omega)$ is the harmonic phonon spectrum.[6] The effect of both of the above mechanisms can be described by the formula

$$2W_{\mathrm{anh}}(T)=\frac{2W_{\mathrm{har}}(T')}{1+\xi}\ , \tag{9}$$

where $T'=T/(1+\xi)$. In other words, anharmonicity and thermal expansion effects reduce the factor $2W$ by $1+\xi$, and shift the temperature at which $2W$ is to be calculated using the harmonic spectrum.

III. CALCULATIONS AND DISCUSSIONS

In Fig. 1 we have plotted the Mössbauer fraction e^{-2W} including both thermal expansion and anharmonicity corrections. The harmonic phonon spectrum of Brown and Horton[3] was used. The constant A appearing in the anharmonic shift was taken to be 1.0×10^{-3} as suggested by calculations of Feldman and Horton[7] on corrections to the lattice heat capacities in the solidified inert gases.

To calculate the shift due to thermal expansion, we have used the experimentally determined Kr Grüneisen constant plotted in Fig. 25 of Klein, Horton, and Feldman[8] (KHF). In addition, the volume shifts $\Delta\Omega/\Omega$ are taken from the experimental plots in Fig. 17 of KHF.

For comparison we have plotted the Mössbauer fraction calculated by Mahesh,[5] who based his calculations on the Debye model. The value of the Mössbauer characteristic temperature θ_M used by Mahesh was obtained from the data of Pasternak *et al.*,[9] who estimated the Mössbauer temperature to be 37 °K. This value was obtained at 50 °K, however, and when extrapolated to 0 °K according to the relation $\theta_{MT}=\theta_M(1-\beta\gamma T)$, Mahesh found $\theta_M=42$ °K.

Because of the differences between the phonon spectrum used here and that obtained from the Debye model at low frequencies, the Mössbauer fraction at 0 °K obtained by Mahesh is in better agreement with the GV data. In Fig. 2 we present a plot of the Brown-Horton[3] spectrum with the Mahesh-Debye spectrum superimposed upon it. It is noted that the anharmonic shift in the present model is nonzero at 0 °K, while the shift due to thermal expansion vanishes there. Nevertheless the effect is not large enough to shift the curve by a significant amount from the harmonic value.

For higher T, the Mahesh curve falls well below the GV data. Mahesh's shift includes only thermal expansion effects and consequently overestimates the anharmonic correction, which is smaller if we use the experimental data to calculate $\xi_{\mathrm{th\,exp}}$. On the other hand, our present curve falls significantly above the GV data. In our earlier paper, the temperature shift was incorrectly included in the exponential factor, and if included correctly it would have shifted our curve farther away from the GV curve. However, over the entire temperature range the shift due to thermal expansion is larger in magnitude than the anharmonic shift, so the net effect is to shift the anharmonic curve closer to the experimental one.

We note that if, in addition, Mahesh's model included the anharmonic shift, the net effect would be to raise the curve and bring it up closer to the GV curve. In effect his inclusion of only thermal expansion has overemphasized the shift.

As mentioned earlier, Mahesh's calculation is based on a Debye approximation, using a characteristic temperature of 42 °K which is obtained from Pasternak's experimental curve. In fact GV fit their experimental data to a Debye model with characteristic temperature 25 °K. The Brown-Horton[3] spectrum leads to a value of 63 °K for the characteristic temperature. Neither this calculation nor Mahesh's is able to account for this discrepancy.

In summary, we have presented a calculation of the Mössbauer fraction of solid Kr, including the frequency shifts due to anharmonicity and thermal expansion. A comparison with the Debye-model calculations of Mahesh show that the curve so obtained does not agree well with experiment or with his curve. It is noted that the inclusion of anharmonicity in Mahesh's calculation would shift his curve into much better agreement with the experimental results.

In conclusion, we stress that the problem is by no means solved; any explanation which might be forthcoming must explain the discrepancies between the Debye temperature obtained by fitting a Debye spectrum to the 0 °K value of f, and the Debye temperature found from the phonon dispersion curves,[3] as the Brown-Horton spectrum was determined. As noted by the present calculation, the combined effects of the anharmonic shift and the shift due to thermal expansion is to shift our theoretical curve closer to the GV curve. On the other hand, the shift does not account for the above discrepancy in Debye temperatures and leaves the basic problem still unresolved.

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Approximate Self-Consistent-Field Study of the $(NiF_6)^{4-}$ Cluster

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An approximate Hartree-Fock self-consistent-field (SCF) calculation has been carried out for the $(NiF_6)^{4-}$ cluster. Exponential-type orbitals with four independent radial functions were employed for the nickel 3*d* electrons, two radial functions for the fluorine 1*s* and 2*s* electrons, and one for the fluorine 2*p* electrons. A core potential was used to represent the metal (1*s*-3*p*) electrons. All one-electron integrals and all one- and two-center two-electron integrals were evaluated. A closed-shell SCF program was used with orbital occupation numbers adjusted to approximate the open shell. The results of comparisons at different stages in the convergence of the SCF iteration show large differences in 10*Dq* and the degree of delocalization. This implies that some of the earlier simplifications of the SCF treatment are not valid; that is, significant ligand $(2s\text{-}2p_\sigma)$ mixing is found and the metal 3*d* functions make an important contribution to the bonding orbitals.

I. INTRODUCTION

Although crystal and ligand field theory have been highly successful in fitting experimental data for transition-metal complexes when used in a semiempirical framework,[1] attempts to study such system from a fundamental theoretical viewpoint have been less satisfactory. Each new calculation has revealed that parts of previously used theoretical models are inadequate. As a result, a generally accepted description is not yet available.

A number of recent efforts[2-8] have concentrated on a common subject, the $(NiF_6)^{4-}$ cluster of crystalline $KNiF_3$, because of the detailed experimental results that exist for this system.[9,10] The pioneering calculation of Sugano and Shulman[2] was soon followed by that of Watson and Freeman.[3] The disagreements between these two studies, both of which involved severe approximations, stimulated a series of papers that attempted to analyze some of the possible shortcomings.[4-7] All of the papers followed closely the work of Sugano and Shulman in that only an approximate self-consistent-field (SCF) calculation or its Heitler-London analog was attempted, that a minimum basis set was used, that the inner-shell Ni electrons were replaced by a core potential, and that only two-center two-electron integrals and some three-center one-electron integrals were included. More recently, Ellis, Freeman, and Ros[11] and Gladney and Veillard[11] have carried out limited basis set SCF calculations involving all the electrons and free of additional approximations. Since the former used a one-center (Ni or F) expansion, whereas the latter employed Gaussian functions, it is important to have an exponential orbital SCF calculation for comparison.

In this paper we report the first step in such a treatment of the $(NiF_6)^{4-}$ cluster of $KNiF_3$, with primary emphasis on the analysis of the approximations introduced in earlier studies. A basis set consisting of four *d* orbitals on Ni and the minimum set for the ligands is used; the $1s^2 2s^2 2p^6 3s^2 3p^6$ core electrons are replaced by an effective potential. Because of the magnitude of the work required to evaluate the integrals over these exponential orbitals, the calculation includes all one- and two-electron one- and two-center integrals, and one-electron three-center integrals, but neglects, all two-electron three- and four-center integrals. Although this approximation is a limitation on the relation between the present work and that of