For nearly *collinear* processes, we can go a step further by noting that

$$(v_{2x}^2+v_{2y}^2)^{1/2}/|v_{2z}| = \tan\rho_2 \approx \rho_2, \qquad \gamma = 2^{1/2}\rho_2/\delta_0, \tag{D17}$$

where ρ_2 is the double-refraction angle for the **j** photon. The criterion (D16) is then equivalent to the two criteria

$$\pi b_0 \gg l, \qquad \pi b_0 \gg 2l\rho_2/\delta_0. \tag{D18}$$

For noncollinear processes, γ is nonvanishing even if $\rho_2=0$. As $|v_{2z}| \to 0$, γ becomes large but (D10) breaks down in this limit. The criteria (D18) are readily satisfied in practice. Note that the second criterion is essentially equivalent to

$$l \ll l_a,$$

where $l_a=\pi^{1/2}\rho_2/w_0$ is the aperture length [see Eq. (3.41) of Ref. 21] of the pump (with the pump considered to have double-refraction angle ρ_2). Note that in this case (pump an ordinary wave) the relevant value of ρ is that of the unobserved photon **j**.

When the pump is an *extraordinary wave* in a uniaxial crystal, the relevant double-refraction angle is $|\rho_2-\rho_3|$. Let the optic axis be in the xz plane. Then x in (D6) becomes $x-\rho_3(z-f)$, and K_z in (D8) becomes $K_z+\rho_3 K_x$. The final result has the form (D10), with

$$\gamma = 2^{1/2}[(v_{2x}-\rho_3|v_{2z}|)^2+v_{2y}^2]^{1/2}/|v_{2z}|\delta_0. \tag{D19}$$

For nearly *collinear* processes, $v_{2y}\approx 0$ and $v_{2x}\approx\rho_2|v_{2z}|$, so that (D19) reduces to

$$\gamma = 2^{1/2}|(\rho_2-\rho_3)|/\delta_0 \tag{D20}$$

and (D18) is replaced by

$$\pi b_0 \gg l, \qquad \pi b_0 \gg 2l|\rho_2-\rho_3|/\delta_0, \tag{D21}$$

which includes (D18) as a special case. Thus we see that the *relative* double-refraction angle between the pump and **j** photon is significant in the plane-wave approximation.

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Debye-Waller Factors in Rare-Gas Solids*

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Mean-square amplitudes for inert-gas solids neon, argon, krypton, and xenon have been calculated as a function of temperature. The results are presented for the cases of zero pressure and constant volume. A nearest-neighbor (m-6) Mie-Lennard-Jones potential was used, and lowest-order anharmonic contributions were taken into account by the frequency-shift method.

I. INTRODUCTION

RECENT experiments on the Mössbauer effect in solid krypton[1,2] in addition to measurements of the elastic neutron scattering in solid neon[3] have yielded measurements of the Debye-Waller factor as a function of temperature. In this paper the mean-square nuclear displacement is calculated as a function of temperature for the rare-gas crystals neon, argon, krypton, and xenon. Anharmonic effects are included by using the approximate frequency-shift method.[4,5] The calculations are based on an (m-6) Mie-Lennard-Jones central force potential, with interactions between nearest neighbors only. This model has been successful in accounting for other properties of rare-gas crystals.[6]

II. THEORY

The substances we are considering assume an fcc Bravais lattice and for these the Debye-Waller factor, which in the Mössbauer effect describes the temperature dependence of the fraction of recoilless transitions, can be expressed as[7]

$$M = e^{-k^2\langle u^2\rangle/3},$$

where k is the wave number of the emitted γ ray and

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[1] K. Gilbert (private communication).

[2] M. Pasternak, A. Simopoulos, S. Bukshpan, and T. Sonnino, Phys. Letters **22**, 52 (1966).

[3] D. G. Henshaw, Phys. Rev. **111**, 1470 (1958).

[4] T. H. K. Barron, in *Lattice Dynamics* (Pergamon Press, Inc., New York, 1965), p. 247.

[5] J. L. Fledman, G. K. Horton, and J. B. Lurie, J. Phys. Chem. Solids **26**, 1507 (1965).

[6] G. K. Horton, Am. J. Phys. **36**, 93 (1968).

[7] A. Abragam, *L'effet Mössbauer* (Gordon and Breach Science Publishers Inc., New York, 1964). We have neglected "anomalous" terms due to anharmonicity which lead to anisotropy in the Debye-Waller factor. These have been shown to be quite small in general (see Ref. 8).

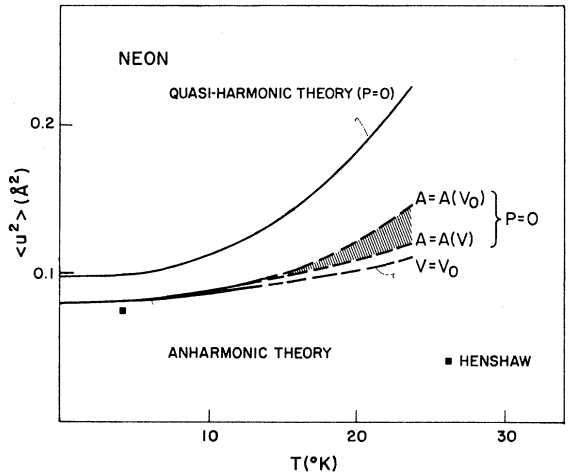

FIG. 1. $\langle u^2\rangle$ for neon as a function of temperature for $m=12$. The shaded region represents our estimate of the actual value of $\langle u^2\rangle$ at zero pressure. Anharmonic effects were included by assuming a frequency shift of the form $\Delta\omega/\omega=A(V)E/3Nk$. V_0 is the volume of the crystal at $T=0$°K and zero pressure.

$\langle u^2\rangle$ is the mean-square nuclear displacement from equilibrium positions.

In the quasiharmonic approximation (in which second-order force constants are dependent upon strains and volume changes) $\langle u^2\rangle$ can be expressed as

$$\langle u^2\rangle=\frac{1}{MN}\sum_{qj}\frac{\epsilon(q,j)}{\omega^2{}_{qj}}, \tag{1}$$

where M is the nuclear mass, N is the number of atoms,

TABLE I. Values of the lattice parameters a_0 and A, and of the potential parameters, obtained for four rare-gas solids with an m-6 potential.

	M (10^{-24} g)	a_0 (Å)	ϵ (10^{-16} erg)	σ (Å)	A (10^{-3} °K^{-1})
Ne $m=12$	33.51	4.46368	72.09	3.032	10.9
$m=13$			73.10	3.029	12.2
Ar $m=12$	66.28	5.31109	236.2	3.707	1.74
$m=13$			237.1	3.707	1.85
Kr $m=12$	139.05	5.64587	324.8	3.966	1.11
$m=13$			325.4	3.965	1.18
Xe $m=12$	217.90	6.132	457.6	4.318	0.74
$m=13$			458.2	4.317	0.79

ω_{qj} are the quasiharmonic phonon frequencies corresponding to the wave vector q and polarization j, and

$$\epsilon_{qj}=[\tfrac{1}{2}+(e^{\hbar\omega_{qj}/kT}-1)^{-1}]\hbar\omega_{qj}$$

represents the average energy of each mode. Although anharmonic effects on the Debye-Waller factor have been given using a perturbation expansion,[8] no reliable numerical estimates of these effects have been presented for rare-gas crystals. It has been shown[4–6] that anharmonic effects can be estimated in a reliable fashion for our model by assuming

$$\Delta\omega/\omega=A(V)E/3Nk, \tag{2}$$

where $\Delta\omega$ refers to the anharmonic frequency shift and $E=\sum_{qj}\epsilon_{qj}$. A is volume-dependent and for our model increases monotonically with increasing volume.[9] Based on the work of Klein, Feldman, and Horton,[10] it is

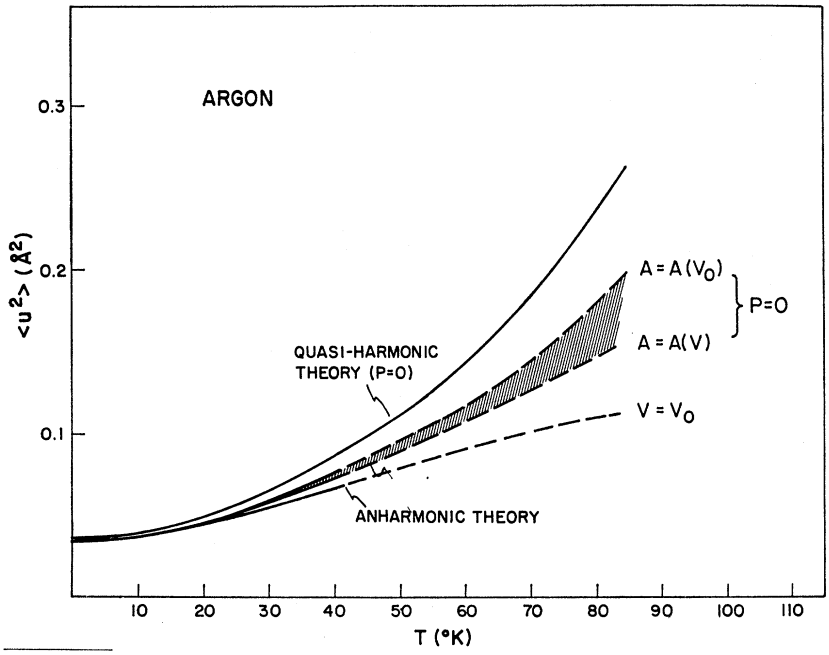

FIG. 2. $\langle u^2\rangle$ for argon as a function of temperature for $m=12$. The shaded region represents our estimate of the actual value of $\langle u^2\rangle$ at zero pressure. Anharmonic effects were included by assuming a frequency shift of the form $\Delta\omega/\omega=A(V)E/3Nk$. V_0 is the volume of the crystal at $T=0$°K and zero pressure.

[8] See, e.g., A. A. Maradudin and P. A. Flinn, Phys. Rev. **129**, 2529 (1963).
[9] J. L. Feldman and G. K. Horton, Proc. Phys. Soc. (London) **92**, 227 (1967).
[10] M. L. Klein, J. L. Feldman, and G. K. Horton (private communication).

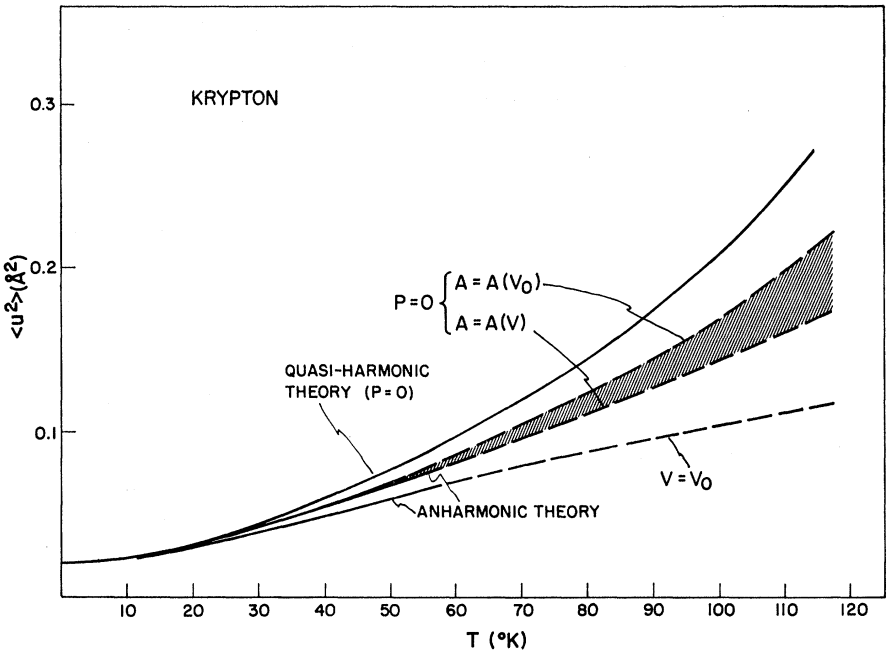

FIG. 3. $\langle u^2\rangle$ for krypton as a function of temperature for $m=12$. The shaded region represents our estimate of the actual value of $\langle u^2\rangle$ at zero pressure. Anharmonic effects were included by assuming a frequency shift of the form $\Delta\omega/\omega=A(V)E/3Nk$. V_0 is the volume of the crystal at $T=0$°K and zero pressure.

reasonable to assume that the results presented in this paper will be reliable at least up to about half the melting temperature. Beyond this temperature our results become increasingly uncertain because perturbation theory breaks down. A crude estimate of the uncertainty in our results at higher temperatures is made in Sec. III.

III. CALCULATIONS AND RESULTS

The Mie-Lennard-Jones (m-6) potential can be expressed as

$$\phi(r)=\epsilon\left(\frac{6m}{m-6}\right)\left[\frac{1}{m}\left(\frac{\sigma}{r}\right)^m-\frac{1}{6}\left(\frac{\sigma}{r}\right)^6\right],$$

where ϵ is the well depth and σ is the position of the minimum. Quasiharmonic parameters were used for krypton and xenon, while for neon and argon anharmonic potential parameters were used.[11]

The experimental lattice parameters for neon, argon, and krypton used in this work were obtained from the results of measurements due to Simmons and co-

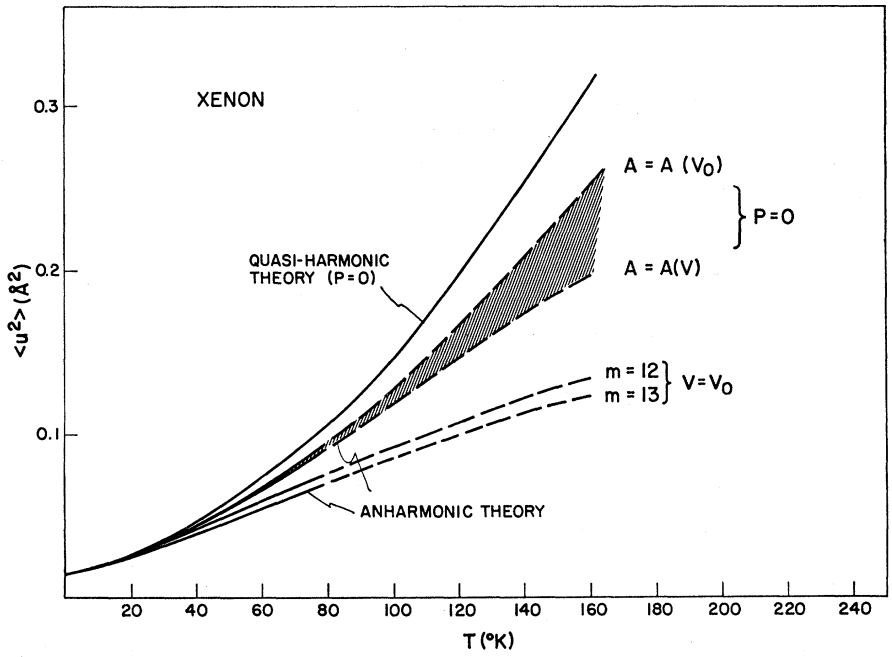

FIG. 4. $\langle u^2\rangle$ for xenon as a function of temperature for $m=12$. The shaded region represents our estimate of the actual value of $\langle u^2\rangle$ at zero pressure. Anharmonic effects were included by assuming a frequency shift of the form $\Delta\omega/\omega=A(V)E/3Nk$. V_0 is the volume of the crystal at $T=0$°K and zero pressure. The $m=13$ anharmonic case at 0°K volume is also shown.

[11] See references mentioned in Ref. 6.

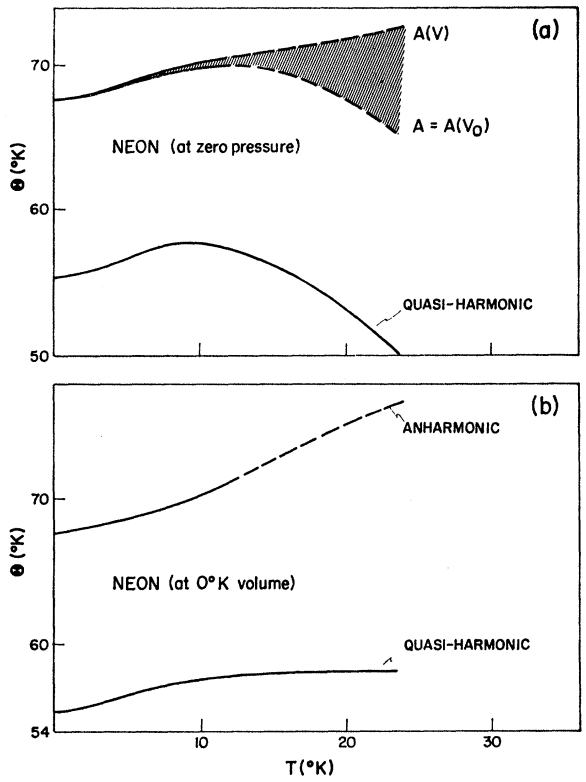

FIG. 5. Effective Debye Θ for neon as a function of temperature for $m=12$. The shaded region represents our estimate of the actual value of Θ at zero pressure. Anharmonic effects were included by assuming a frequency shift of the form $\Delta\omega/\omega=A(V)E/3Nk$.

workers.[12] For xenon the volumes listed by Trefny[13] were used. Following Cowley and Cowley,[14] who computed the Debye-Waller factor for alkali halides, the frequency shifts appropriate to neutron scattering were used to incorporate anharmonic effects. The values of A in Eq. (2) were computed by Feldman and Horton.[9] Table I shows the $T=0$°K values of the lattice parameters a_0 and A together with the potential parameters for the four substances.

The sums over the normal modes were carried out in 1/48 of a Brillouin zone using a grid in which all zone faces and most symmetry points are avoided.[15] All the results in this paper are for 32 000 points in the full zone; for the given potential the values for $\langle u^2\rangle$ are good to 1% or better.

Figures 1–4 represent plots of anharmonic $\langle u^2\rangle$ for the four substances at zero pressure. These graphs also show anharmonic $\langle u^2\rangle$ in which the volume is kept at its $T=0$°K value and quasiharmonic $\langle u^2\rangle$ at zero pressure. The corresponding Debye-Θ curves, obtained using the tables of Benson and Gill,[16] are shown in Figs. 5–8. In presenting the zero-pressure anharmonic results, two curves are shown. In the first the volume dependence of A in Eq. (2) has been taken into account properly. As mentioned earlier, this represents the leading term in the standard perturbation expansion. For high temperatures, the true values may lie somewhere between this curve and the quasiharmonic curve because the perturbation expansion is alternating in sign. In terms of frequency shifts, this means that the effective value of A at high temperatures has been overestimated. Therefore, a second curve has been included in which A is held at its $T=0$°K value. For low temperatures the effect is small; above half the melting temperature the shaded region between the two curves may indicate the range of predictions of the model.

All our results are presented for the $m=12$ case unless otherwise indicated. $\langle u^2\rangle$ values for $m=13$ are uniformly lower than those for $m=12$ and the temperature dependence is roughly model-independent. For compari-

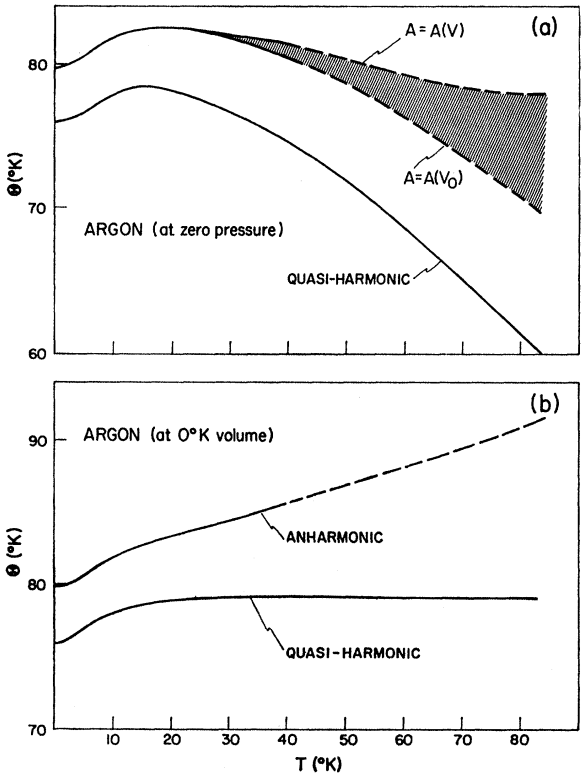

FIG. 6. Effective Debye Θ for argon as a function of temperature for $m=12$. The shaded region represents our estimate of the actual value of Θ at zero pressure. Anharmonic effects were included by assuming a frequency shift of the form $\Delta\omega/\omega=A(V)E/3Nk$.

[12] O. G. Peterson, D. N. Batchelder, and R. O. Simmons, Phys. Rev. **150**, 703 (1966); D. N. Batchelder, D. L. Losee, and R.O. Simmons, *ibid.* **162**, 767 (1967); R. O. Simmons (to be published).

[13] J. Trefny, Rutgers University, Ph.D. thesis, 1968 (unpublished). These are interpolated data from experimental results by J. R. Packard and C. A. Swenson, J. Phys. Chem. Solids **24**, 1405 (1963).

[14] E. R. Cowley and R. A. Cowley, Proc. Roy. Soc. (London) **A292**, 209 (1966).

[15] C. Feldman, Rutgers University, Ph.D. thesis, 1967 (unpublished).

[16] G. C. Benson and E. K. Gill, *Tables of Integral Functions Related to the Debye-Waller Factor* (National Research Council of Canada, Ottawa, 1966).

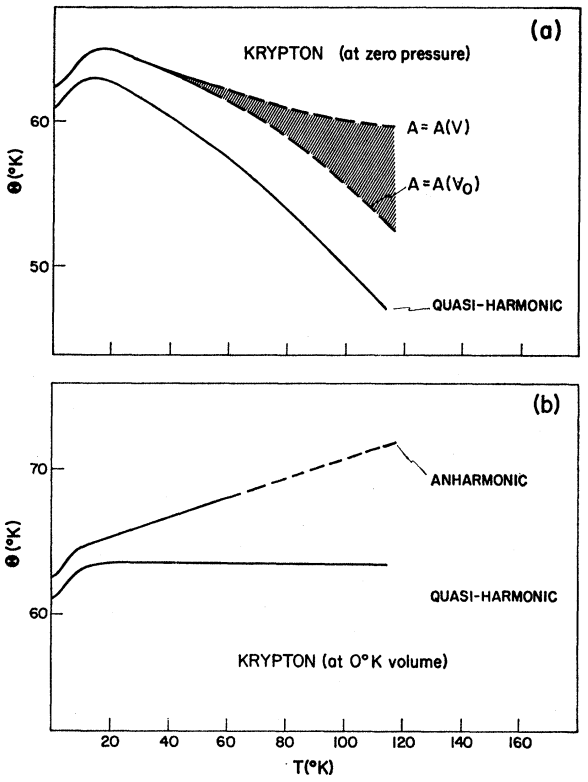

FIG. 7. Effective Debye Θ for krypton as a function of temperature for $m=12$. The shaded region represents our estimate of the actual value of Θ at zero pressure. Anharmonic effects were included by assuming a frequency shift of the form $\Delta\omega/\omega=A(V)E/3Nk$.

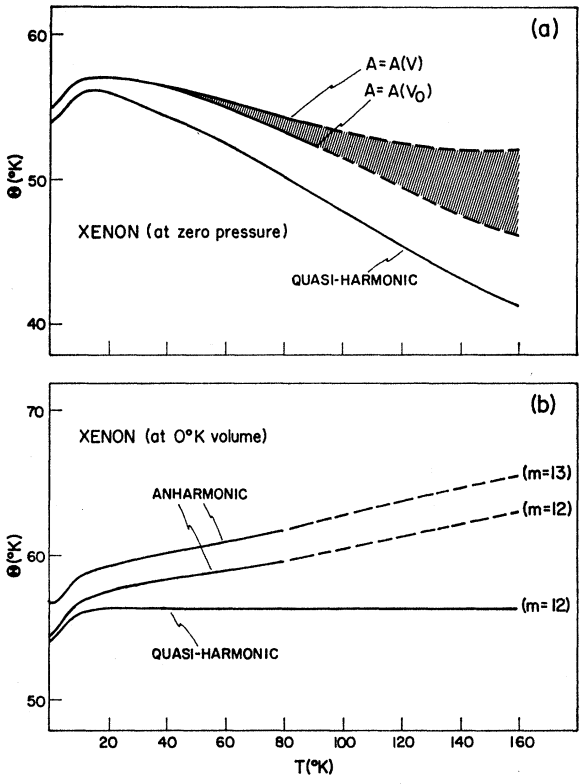

FIG. 8. Effective Debye Θ for xenon as a function of temperature for $m=12$. The shaded region represents our estimate of the actual value of Θ at zero pressure. Anharmonic effects were included by assuming a frequency shift of the form $\Delta\omega/\omega=A(V)E/3Nk$. The $m=13$ anharmonic case at 0°K volume is also shown.

son, typical results for $m=12$ and $m=13$ in xenon are shown in Figs. 4 and 8(b) for the anharmonic case at constant volume.

IV. CONCLUSIONS

In summary, anharmonic mean-square nuclear displacements at zero pressure and at constant volume have been calculated for rare-gas crystals. A nearest-neighbor Mie-Lennard-Jones central-force model was used for the calculations. Henshaw's[3] single measurement in solid neon yielded $\Theta_m=73$°K at 4.2°K which lies above the calculated values of 68°K for $m=12$ and 70°K for $m=13$. The corresponding mean-square displacement is shown in Fig. 1.

Pasternak *et al.*[2] have reported a Debye Θ of $\sim$37°K for solid krypton in the 30–60°K range using Mössbauer measurements. Our model calculations suggest that this experimental value is unreasonably small (the experimental value of Θ would imply a root-mean-square amplitude of vibration of $\sim$16% at melting). A new measurement would be most welcome.

ACKNOWLEDGMENTS

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