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Lattice Distortion Due to Isotopes in Solid Helium

P. G. KLEMENS AND A. A. MARADUDIN
Westinghouse Research Laboratories, Pittsburgh, Pennsylvania

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Observations of the thermal resistivity of solid helium containing He^3 isotopes have indicated that the phonon scattering cross section of the isotope is three times larger than the theoretical value obtained by considering only the mass-difference. Using as a model a helium atom in the potential well formed by its neighbors, and taking account of the zero-point energy of that atom and of the strain energy in the surrounding solid when the atomic cell is expanded, it is shown that around a He^3 isotope the lattice suffers an outward distortion of about 1–2%. This distortion can account for the discrepancy in the phonon scattering cross section.

I. INTRODUCTION

In order to test the theory of the scattering of lattice waves by substitutional atoms differing only in mass, Walker and Fairbank[1] measured the thermal conductivity of solid helium containing known amounts of the isotope He^3. Their results were violently inconsistent with a simple theory,[2] according to which the anharmonic N processes affected the phonon mean free path only at lowest frequencies and always in a manner independently of the relative strength of the N processes. Walker and Fairbank suggested that these results could be interpreted on that simple theory if one abandoned the supposition that the He^3 isotopes are randomly dispersed.

It had become increasingly obvious that the thermal resistance due to point defects depends not only on the scattering of phonons by point defects, but also on the strength of the N processes. In particular, measurements by Berman and co-workers[3] on the thermal resistivity of lithium fluoride due to various lithium isotope concentrations showed a marked nonlinearity of thermal resistance with isotope content even at lowest concentrations. Two different refinements of the theory can describe quantitatively the combined effect of point defects and N processes: a variational method due to Ziman and co-workers,[3] and an approximate treatment of the effect of momentum conservation on the effective relaxation time of N processes by Callaway.[4] The exact relationship between the two theories is at present still obscure, because of their widely different approaches, but they appear to give results which are at least superficially similar, and in the limit of infinitely strong N processes they both tend to the same limiting value, originally obtained by Ziman[5] from momentum balance considerations.

In view of these considerations, Sheard and Ziman[6] suggested that the thermal resistivities of isotopic mixtures of solid helium obtained by Walker and Fairbank could be described by a proper treatment of combined N processes and isotope scattering. Actually it is not difficult to see that this cannot be correct, because the observed resistivity exceeds Ziman's limiting value for infinitely strong N processes, and thus the theoretical value for any finite strength of N processes. Nevertheless, one could expect at least a considerable reduction of the discrepancy by such a treatment.

Callaway[7] has recently applied his theory to the case of solid helium. He empirically fitted the strength of N processes and point defect scattering to the observed resistivities, and obtained quite a good fit for the various isotope concentrations over the full temperature range. The strength of the N processes was in reasonable accord with the crude estimates of anharmonic interaction rates at present available. The theory of mass-defect scattering, however, is not subject to any substantial uncertainties, and it is thus extremely significant that Callaway had to assume a point defect scattering probability which was three times the theoretical value in order to fit the experimental data. That this cannot be blamed on a possible deficiency of Callaway's theory is, of course, borne out by the fact that the observed resistivity exceeds the Ziman limit for infinitely strong N processes.

One is thus forced to conclude either that the He^3 isotopes in solid helium are not randomly dispersed, so as to enhance the scattering by reinforcement, or that the scattering of phonons by these isotopes is not only due to their mass difference, but also due to some change in the effective interatomic forces around the isotopes, arising from a distortion of the surrounding lattice.

While the interatomic forces around an isotopic impurity are normally unchanged, so that isotopes scatter phonons only in virtue of their mass difference, in the case of solid helium, where the zero-point motion of the atoms plays a large role in the stability of the lattice, one can expect a mass difference to affect this motion and thus produce a distortion of the lattice around the isotope. Such a distortion, in turn, would contribute to the phonon scattering. To investigate whether this can indeed occur and could contribute appreciably to the

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[2] P. G. Klemens, Proc. Roy. Soc. (London) **A208**, 108 (1951).
[3] R. Berman, P. T. Mottley, F. W. Sheard, A. N. Spencer, R. W. H. Stevenson, and J. M. Ziman, Proc. Roy. Soc. (London) **A253**, 403 (1959).
[4] J. Callaway, Phys. Rev. **113**, 1046 (1959).
[5] J. M. Ziman, Can. J. Phys. **34**, 1256 (1956).
[6] F. W. Sheard and J. M. Ziman, Phys. Rev. Letters **5**, 138 (1960).
[7] J. Callaway, Phys. Rev. **122**, 787 (1961).

phonon scattering, we have investigated the crudest model of solid helium: a helium atom confined in the potential well formed by its neighbors. It is indeed found that since a He^3 isotope has a larger zero-point energy, there is a tendency for the potential well to expand. This is counteracted by the resistance of the surrounding lattice to shear. The resulting outward distortion of the lattice is about 1–2% of the atomic radius, and this will significantly enhance the phonon scattering.

II. STABILITY OF HELIUM ATOM IN A DEFORMABLE POTENTIAL WELL

Consider a helium atom (of mass M) in a spherical potential well of radius R and, for the sake of simplicity, of infinite depth. Its zero-point energy is

$$E_0 = h^2/8MR^2. \tag{1}$$

Let the walls of the potential well be subjected to an inward pressure p. We identify the volume of the potential well with the volume per atom of the solid (V_a), and the pressure p with the external pressure acting on the solid.

In the first instance we fix on a normal atom, and consider the stability of the system against an expansion of all the potential wells. The change in free energy per atom is then given to first order by

$$\delta F = (\partial E_0/\partial R)\delta R + p\delta V_a + \cdots, \tag{2}$$

where $\delta R = \epsilon R$ is the change of radius, and $\delta V_a = 3\epsilon V_a$ is the change of volume. In a stable configuration $\partial F/\partial\epsilon = 0$, so that, using (1) and dividing by ϵ,

$$2E_0 = 3pV_a. \tag{3}$$

Consider now the case when one atom is replaced by an atom of mass $M+\delta M$. There is a change in energy due to the change in E_0 given by (1), together with a change in E_0 due to a distortion ϵ, work done by the distortion against the external pressure, and strain energy due to the inhomogeneous distortion of the surrounding solid.

The strain energy due to the outward expansion of a spherical inclusion of radius R is given by[8]

$$E_{\mathrm{el}} = 8\pi\mu R^3\epsilon^2, \tag{4}$$

where ϵ is the fractional radial expansion and μ the shear modulus. Thus the increase in free energy due to a change of mass and an outward expansion of a single atomic cell is given by

$$\begin{aligned}\delta F &= \frac{\partial E_0}{\partial R}\delta R + \frac{\partial E_0}{\partial M}\delta M + p\delta V_a \\ &\quad + \frac{1}{2}\frac{\partial^2 E_0}{\partial R^2}(\delta R)^2 + \frac{\partial^2 E_0}{\partial R\partial M}\delta R\delta M + \cdots + E_{\mathrm{el}} \\ &= -2E_0\epsilon + 3pV_a\epsilon - E_0(\delta M/M) \\ &\quad + 3E_0\epsilon^2 + 2E_0\epsilon(\delta M/M) + \cdots + 8\mu\pi R^3\epsilon^2. \end{aligned} \tag{5}$$

The first two terms cancel because of (3), the third term denotes a change in the free energy due to the change in mass, and the last three terms determine the new condition of stability. This stability criterion is now

$$(\partial F/\partial\epsilon)_{\delta M} = 0, \tag{6}$$

which becomes, in view of the last three terms of (5),

$$6E_0\epsilon + 2E_0(\delta M/M) + 16\pi\mu R^3\epsilon = 0$$

or

$$\epsilon = -\frac{1}{3}\frac{\delta M}{M}\left(\frac{3E_0}{3E_0 + 8\pi\mu R^3}\right). \tag{7}$$

Thus a reduction in mass is accompanied by an outward expansion of the deformable potential well.

For the shear modulus of solid helium we take a value of $\mu = 2.1\times10^8$ ergs/cm^3, which is consistent with a velocity of transverse waves of 3.2×10^4 cm/sec and a density of 0.208 g/cm^3 quoted by Walker and Fairbank. To calculate E_0 we can use two methods. According to the first (method I), E_0 is obtained from (1), using for R the radius of a sphere of volume V_a, where V_a is the volume per atom. Thus

$$\epsilon = -\frac{1}{3}\frac{\delta M}{M}\left(\frac{1}{1+6.3}\right). \tag{8I}$$

But it may be argued that the numerical constant in (1), which depends on the shape of the potential well, is not well known, and that it may be better to use the stability condition (3) to give E_0 in terms of the external pressure. Thus in method II we use (3) and obtain from (7)

$$\epsilon = -\frac{1}{3}\frac{\delta M}{M}\left(\frac{3p}{3p+4\mu}\right). \tag{9}$$

The experiments of Walker and Fairbank were carried out under an external pressure of $p = 9.8\times10^7$ ergs/cm^3 (96 atm). Method II yields thus a somewhat higher value of ϵ, namely

$$\epsilon = -\frac{1}{3}\frac{\delta M}{M}\left(\frac{1}{1+2.85}\right). \tag{8II}$$

In the case of the isotope He^3, $\delta M/M = -0.25$, so that $\epsilon = 1.2\%$ according to method I, and 2.2% according to method II.

III. SCATTERING OF PHONONS BY THE STRAIN AROUND THE ISOTOPE

The phonon scattering cross section of a point defect can be written[9] in the form

$$\sigma = \frac{3(V_a)^2}{\pi v^4}\omega^4 S^2, \tag{10}$$

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[8] J. D. Eshelby, *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1956), Vol. 3, p. 79.

[9] P. G. Klemens, Proc. Phys. Soc. (London) **A68**, 113 (1955).

where v is the phonon velocity and S^2 is a parameter describing the strength of the point defect scattering. For mass-difference scattering alone, $S^2=(\delta M/M)^2/12$. If there is a radial distortion around the point defect, the anharmonic nature of the interatomic forces causes a change in the effective elastic constants in the region of this strain field. In that case

$$S^2=(\delta M/M)^2/12+S_3^2, \tag{11}$$

where S_3 is a measure of the phonon perturbation Hamiltonian due to the strain field, and depends on the cubic anharmonicities. Using the Grüneisen constant γ as a measure of these anharmonicities, and taking account of the change of the force constants of individual linkages in the distortion field around the point defect, the following expression was obtained for S_3:

$$S_3^2=\tfrac{2}{3}(4.2\gamma\epsilon)^2. \tag{12}$$

In (12) we may take $\gamma=2$, irrespective of the thermal expansion data, for reasons discussed elsewhere.[10] Thus, in order that the total scattering cross section should be three times the cross section calculated from the mass difference alone, we would require that $|\epsilon| =(\delta M/M)/17$. Since $\delta M/M=0.25$, we would require $|\epsilon|$ to be about 1.5%, which is certainly consistent with the estimate of the distortion given above.

IV. DISCUSSION

The present crude considerations have shown that it is quite likely that there is a distortion around a He^3 isotope in solid helium, the distortion corresponding to an expansion of the effective atomic radius by about 1–2%. Such a distortion field would enhance the phonon scattering cross section of the He^3 isotope sufficiently to account for the observed thermal resistance according to Callaway's theory without the need to assume any but a random distribution of the isotopes. It should be emphasized, however, that one cannot ascribe quantitative significance to the present results. In the first place, the present model of the isotope in a deformable potential well, with the surrounding solid treated as an elastic continuum, is undoubtedly a considerable oversimplification. In the second place, one must remember that (12) is based on extremely crude considerations. In that connection it must be mentioned that Carruthers,[11] using a continuum theory of the anharmonic scattering of phonons by static strain fields, obtained a value of S_3 higher than (12) by a factor of about 20. Nevertheless it is significant that where we have evidence of the phonon scattering cross section due to the distortion field of a point defect, such as in the case of zinc in copper,[12] Eq. (12) seems to be quantitatively correct, while Carruthers' expression definitely overestimates the scattering.

Thus it is still an open question whether the reasonable quantitative agreement obtained by the present considerations is more than just fortuitous.

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[10] P. G. Klemens, *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1958), Vol. 7, p. 1.

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[12] W. R. G. Kemp, P. G. Klemens, R. J. Tainsh, and G. K. White, Acta Met. **5**, 303 (1957).