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Thermal Expansion of Aluminum at Low Temperatures

P. G. Klemens
Westinghouse Research Laboratories, Pittsburgh, Pennsylvania

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The pressure of the electron gas gives rise to a contribution to the thermal expansion of metals proportional to the dilatational strain derivative of the electronic specific heat. It appears from the strain dependence of the superconducting phase boundary that the electronic specific heat of aluminum is extremely sensitive to dilatation. This would explain why the thermal expansion of aluminum between 20° and 30°K is much larger than expected from the Grüneisen theory. The extreme sensitivity of the electronic specific heat to strain is not inconsistent with the zone structure of aluminum.

I. ELECTRONIC THERMAL EXPANSION

It was pointed out by Mikura[1] that the volume dependence of the energy of the electron gas can lead to a contribution of the thermal expansion of metals of the form

$$(d\Delta/dT)_e=(1/kV)gC_e, \qquad (1)$$

where Δ is the dilatation, V the volume, k the bulk modulus, C_e the electronic specific heat, and g is a numerical constant. This contribution is additional to that arising from the lattice anharmonicity[2] and proportional to the lattice specific heat C_g, namely

$$(d\Delta/dT)_g=(1/kV)\gamma C_g, \qquad (2)$$

where γ is the Grüneisen constant. Since generally C_e is much smaller than C_g, the electronic thermal expansion is relatively small; only at low temperatures, where C_e and C_g are comparable, can we expect this term to be appreciable. One should then observe that the thermal expansion at very low temperatures does not vary with T as rapidly as indicated by (2), but decreases more slowly, tending to a variation linear with T. In general (1) should be comparable to (2) only at liquid helium temperatures, where the thermal expansion is already very small and its measurement exceedingly difficult. The possibility of observing this electronic contribution should be somewhat more favorable in transition metals which have a large value of C_e.

Essentially the same conclusions were drawn by Visvanathan[3] and later by Varley,[4] each of these authors being apparently unaware of the preceding work.

The treatment of Mikura and of Visvanathan is not sufficiently general, since they did not consider the possibility of a variation of the density of states with dilatation.[5] Hence these expressions for the coefficient g in (1) are not reliable, though in the case of free electrons they obtain correctly $g=\frac{2}{3}$.

Varley derived a relation between $(d\Delta/dT)_e$ and the strain dependence of the electronic specific heat essentially as follows:

The free energy of a solid of volume V may be written as

$$F=\tfrac{1}{2}Vk\Delta^2+F_g(\Delta,T)+F_e(\Delta,T), \qquad (3)$$

where F_e, F_g are the contributions of the electrons and of the lattice to the free energy, except that the components of F_e and F_g which depend on Δ without depending on T are already incorporated into the first term. Differentiating with respect to Δ and equating to zero, we obtain equilibrium values of Δ, additively composed of Δ_e and Δ_g. The latter leads to the Grüneisen thermal expansion (2), the former becomes

$$k\Delta_e=-(1/V)(\partial F_e/\partial\Delta)_T=p_e, \qquad (4)$$

where $p_e=-(\partial F_e/\partial V)_T$ is the pressure of the electron gas. The electronic dilatation Δ_e thus arises from this pressure of the electron gas, which tends to expand the metal against the restoring elastic forces. Now in general

$$k(d\Delta/dT)_p=(\partial p/\partial T)_V, \qquad (5)$$

and since F_e is a perfect differential

$$(\partial p_e/\partial T)_V=(\partial S_e/\partial V)_T, \qquad (6)$$

where S_e is the entropy of the electrons. Furthermore, in the case of a degenerate electron gas $S_e\propto T$, so that $C_e=S_e$. Hence the electronic contribution to the thermal expansion becomes

$$(d\Delta/dT)_e=(1/kV)(\partial C_e/\partial\Delta)_T, \qquad (7)$$

so that the coefficient g in (1) is the logarithmic derivative of C_e with respect to volume, i.e.,

$$g=(1/C_e)(\partial C_e/\partial\Delta). \qquad (8)$$

II. STRAIN DEPENDENCE OF THE ELECTRONIC SPECIFIC HEAT OF SUPERCONDUCTORS

While it is possible in principle to determine the logarithmic derivative (8) directly from measurements of the specific heat as a function of pressure, such measurements are difficult and have not yet been done. In the case of superconductors, however, one can deduce the normal-state electronic specific heat from the temperature dependence of the magnetic threshold curve

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[1] Z. Mikura, Proc. Phys. Math. Soc. Japan **23**, 309 (1941).

[2] E. Grüneisen, Ann. Physik **39**, 257 (1912).

[3] S. Visvanathan, Phys. Rev. **81**, 626 (1951).

[4] J. H. O. Varley, Proc. Roy. Soc. (London) **A237**, 413 (1956).

[5] Visvanathan's treatment contains a further error.

at lowest temperatures. Olsen[6] has determined the electronic specific heat in this way as a function of pressure, and deduced the logarithmic derivative (8), for aluminum. He found the surprisingly large value of $g=130\pm60$.

Another method of determining g is through the change in volume δV of the metal when passing from the normal to the superconducting state, as discussed by Olsen and Rohrer.[7] Since in the superconducting state C_e/T vanishes in the limit of lowest T, $d(\delta V)/dT$ in this limit is a measure of the electronic thermal expansion in the normal state and hence, by (7), of g. Values of g of a number of superconductors have thus been deduced.[7,8] These are generally of order unity, but for mercury $g\sim+10$ while for tantalum $g\sim-40$. In the case of aluminum g could not be determined in this way to any accuracy, but there were indications that it is large and positive.[7]

III. LOW-TEMPERATURE THERMAL EXPANSION OF ALUMINUM

If the logarithmic derivative g is indeed as large as suggested by Olsen's measurements, then the electronic contribution of thermal expansion should be detectable with available techniques. Figgins, Jones, and Riley[9] have measured the lattice spacing of aluminum by x-ray diffraction at 20°K, 32°K, and at a number of higher temperatures up to room temperature. The average thermal expansion between 20 and 32°K was found to be

$$(d\Delta/dT)_{26}\simeq3\times10^{-6}\ \mathrm{deg}^{-1}, \tag{9}$$

and about twice as much in the interval from 32° to 44°K.

The Grüneisen expression (2) for the thermal expansion would yield a value of

$$(d\Delta/dT)_{26}\simeq1\times10^{-6}\ \mathrm{deg}^{-1}, \tag{10}$$

if we use a value of $\gamma=2.2$, which fits the thermal expansion data at high temperatures. We have used here a value of $k=7.7\times10^{11}$ dynes/cm^2 and $C_{26}=4.5\times10^5$ ergs/deg cm^3. This would indicate an electronic contribution to the thermal expansion of

$$(d\Delta/dT)_{e,26}\simeq2\times10^{-6}\ \mathrm{deg}^{-1}; \tag{11}$$

furthermore this separation into terms proportional to T and T^3, respectively, also fits the expansion in the interval from 32° to 44°K.

It is, of course, also possible to explain the large thermal expansion at low temperatures not in terms of an electronic contribution, but in terms of a rapid increase of γ as T is decreased. It is, however, unlikely that γ should increase so rapidly and reach a value of 6 at lowest temperatures, particularly as the theoretical treatment of Barron[10] predicts a much smaller variation of γ, and actually a decrease at low temperatures.

The value of $(d\Delta/dT)_e$ of (11) would require a value of $g\sim+40$. This is somewhat smaller than the value deduced by Olsen, but it must be remembered that there are considerable uncertainties associated with both estimates. Nevertheless, one can conclude with some confidence that for aluminum g is much larger than unity, and is positive.

The extreme sensitivity to volume change of the electronic specific heat of aluminum, although at first sight surprising, is not inconsistent with Harrison's model of the electronic band structure.[11] The sphere containing three electrons per atom, transformed into reduced $\mathbf{k}$ space, extends into three zones. The Fermi surface is close to the zone boundary almost everywhere; the small pockets of the electrons in the highest zone are probably eliminated by the crystalline field. Since the Fermi surface is close to the zone boundary one would expect the density of states to be sensitive to small perturbations. It is of interest that in the case of lead, where the Fermi surface is generally further removed from the zone boundaries, the logarithmic derivative g is much smaller.[7]

The absence of an abnormal pressure dependence of the room-temperature electrical conductivity is not easily reconciled to the high value of g. It is, however, possible that different groups of electrons contribute mainly to the electrical conductivity and to the strain-sensitive fraction of the specific heat.

It would be very interesting to know the variation of C_e and of g of aluminum alloys with electron concentration.

Finally one should remember that the separation of the specific heat into an electronic and a lattice term may not be justified in cases when the Fermi surface lies close to a zone boundary.[12] For purposes of the present argument, however, it is sufficient that there should be a component of specific heat linear in T, irrespective of its origin, and that this component should be volume sensitive. *Note added in proof.* Dr. G. K. White, National Standards Laboratory, Sydney, Australia has measured the thermal expansion of aluminum from 7° to 20°K, using a sensitive capacitance method. His results indicate an electronic thermal expansion smaller than that of (11) by a factor of about 8, and a corresponding reduction in g. I am grateful to Dr. White for his permission to quote these results.

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[7] J. L. Olsen and H. Rohrer, Helv. Phys. Acta **30**, 49 (1957).

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[9] B. F. Figgins, G. O. Jones, and D. P. Riley, Phil. Mag. **1**, 747 (1956).

[10] T. H. K. Barron, Phil. Mag. **46**, 720 (1955).

[11] W. A. Harrison, Phys. Rev. **116**, 555 (1959).

[12] H. Jones, Proc. Roy. Soc. (London) **A240**, 321 (1957).