gap in the one-dimensional case.

[12]D. T. Lawson, W. J. Gully, S. Goldstein, R. C. Richardson, and D. M. Lee, Phys. Rev. Lett. **30**, 541 (1973). Analyses that favor the anisotropic gap have been given by P. Wölfle, Phys. Rev. Lett., to be published; B. Patton, to be published.

[13]These were derived by Ambegaokar and Mermin (Ref. 3) from the weak-coupling model, but to leading order in A the deficiencies of that model that we are concerned with do not arise. Within the calculation of Ref. 3, the existence of the term linear in H depends on a violation of "particle-hole symmetry" and a second quadratic term $H^2 \, \mathrm{Tr}(AA^\dagger)$ is found to be negligibly small.

[14]For some values of the coefficients the second second-order phase boundary is suppressed completely.

[15]R. C. Richardson, private communication. Measurements of the ratio of the slopes of the split phase boundary and of the specific-heat discontinuities would be of great value in reducing the range of possible coefficients in the p-wave free energy.

[16]This difficulty was first pointed out by A. J. Leggett, and motivated the Anderson-Brinkman hypothesis that spin fluctuations play an important role.

Al₁₀V: An Einstein Solid

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Low-temperature specific-heat and electrical-resistivity measurements show that the intermetallic compound Al₁₀V has a local soft mode of characteristic temperature 22°K. The behavior is well described by an Einstein model. The number of such modes, taken together with x-ray evidence, indicates that the mode is associated with a loose Al atom occupying a large hole in the Al₁₀V structure. This and other peculiarities of the structure provide evidence of important bonding effects.

Truly localized vibrational modes are unusual in solids because of strong interatomic coupling; in this Letter we present experimental evidence for the existence of sharply defined local modes in the intermetallic compound Al₁₀V that are well-described by an Einstein[1] model with a characteristic temperature of 22°K. To the best of our knowledge this is the lowest such characteristic temperature to have been found in a metal.

Samples of Al₁₀V were prepared by arc melting 99.9 + %-purity vanadium and 99.999 + %-purity aluminum under an argon atmosphere; flat-bottomed buttons of weight 1 g were made for specific-heat measurements, and cast rods of 3 mm diameter and 30 mm length for electrical-resistivity measurements. After homogenization at 665°C for 80 h all samples were better than 95% single phase. Specific-heat measurements were performed on two samples, numbers 1 and 2; the vibrational specific heat of sample 2 had the same functional temperature dependence as 1 but was 15% smaller in magnitude. Samples number 3 and 4 were used for the electrical-resistivity measurements.

The measured low-temperature specific heat and electrical resistivity of our samples are shown in Figs. 1 and 2; in order to provide a yardstick we have included data for the compound Al₉Co₂, whose behavior is typical of all the other aluminum-rich aluminum–transition-metal intermetallics that we have investigated.[2] The extraordinary behavior of Al₁₀V is immediately apparent, with the temperature dependences being 2 to 3 orders of magnitude greater than those for Al₉Co₂. Such a rapid increase with temperature indicates the presence of a low-lying vibrational mode, and our specific-heat data are well-fitted by the Einstein formula

$$C = C_E + \gamma T,$$
$$C_E = 3N_i k_B \left(\frac{\Theta_E}{T}\right)^2 \frac{\exp(\Theta_E/T)}{[\exp(\Theta_E/T) - 1]^2}, \qquad (1)$$

with an Einstein temperature Θ_E of $22 \pm 2°$K, and a density of local (three-dimensional) oscillators N_i equivalent to 0.11 ± 0.03 per Al₁₀V formula unit. The Einstein formula is an extremely sensitive function of Θ, so that although we are uncertain
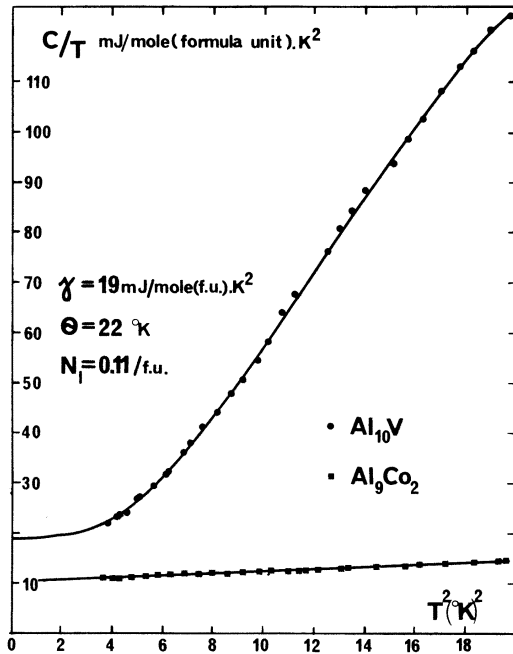
FIG. 1. The measured specific heats C of $Al_{10}V$ (sample 1) and Al_9Co_2 plotted in the usual form of C/T versus T^2. The straight line is the calculated Einstein function [Eq. (1)] with the parameters given in the figure. C for Al_9Co_2 is given by $C = \gamma T + \beta T^3$, with $\gamma = 10.3$ mJ/mole (formula unit) °K^2 and $\beta = 0.195$ mJ/mole (formula unit) °K^4.

FIG. 2. The temperature-dependent part of the resistivity $\rho(T) - \rho(0)$, of $Al_{10}V$ (sample 3) and Al_9Co_2 plotted on logarithmic scales. The solid curve is a fit to the Einstein resistivity that is discussed in the text. The straight line represents a T^4 dependence. Note the factor of 10 difference in resistivity scales for the two compounds.

as to what T^3 contribution there may be to the specific heat of $Al_{10}V$, the value of Θ is little affected. However, in order to maintain a good fit with a slightly different value of Θ the number of oscillators must alter considerably.

We attribute the remarkable low-temperature behavior of $Al_{10}V$ to particular features of its crystal structure: X-ray investigations[3,4] have shown it to be based on an Al_3V network with unusually short Al-to-V interatomic distances. In addition there is one large hole to every two $Al_{10}V$ formula units in the unit cell (which contains 16 formula units). The microhardnesses of $Al_{10}V$ and Al_9Co_2 are similar, so that $Al_{10}V$ cannot be a conventional soft solid. The hole is sometimes filled by an additional Al atom and sometimes not, so that the composition range for the phase extends from $Al_{10}V$ to $Al_{10.5}V$. The samples studied by Brown[3] had about 10% of the holes occupied, and those by Ray and Smith[4] about 50%. The loose Al atom placed in a hole is well spaced from the Al atoms that surround the hole, about 3.2 Å (center to center) compared with the 2.8 Å of pure aluminum. We suggest
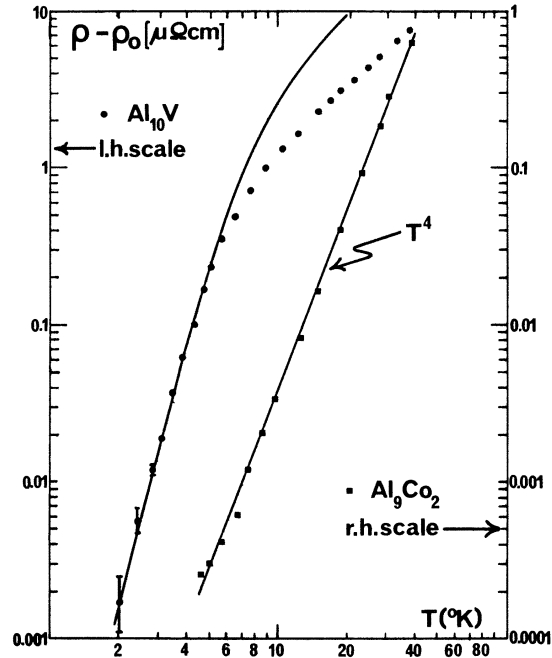
that the low-frequency oscillator is to be identified with the loose Al atom and N_l represents the number of such atoms; in that case the specific heat indicates that about 20% of the holes are occupied for Sample 1. The intermetallic compound Al_7V has a similar Al_3V framework, but the structure is without holes; we have found no anomalously large vibrational specific heat in that compound. The low Einstein temperature indicates a potential for the loose atom that is exceedingly shallow near the center, but it must rise steeply for displacements of order 0.4 Å as the normal Al-Al interatomic spacing is approached. The amplitude of oscillation is easily estimated for a parabolic potential, and in our case is 0.4 Å at about 13 °K; we can anticipate, therefore, deviation from simple Einstein behavior at temperatures of this order and somewhat below. A square well should be a good approximation to the potential we have described (i.e., zero interaction near the center of the hole), and sets a lower bound to the energies involved. The zero-point energy for an Al atom in such a square well is about 5 °K.

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The resistivity contributed by a set of Einstein oscillators to a free-electron gas is

$$\rho(T) - \rho(0) = G\frac{1}{\Theta_E}\frac{N_l}{\exp(\Theta_E/T) - 1},\qquad(2)$$

where $G = 2.06(m^2/ne^2\hbar Mk_B)$, with n being the conduction-electron density and M the oscillator mass; the other symbols have their usual meanings. Our resistivity data (Fig. 2) cover a wider range of temperature than the specific-heat measurements, and, as expected, clear deviations from simple Einstein behavior are evident at the higher temperatures. Such a limited fit could easily be fortuitous, for the coefficient G has been used as a fitting parameter, except that we can get some idea of what magnitude G ought to have in a free-electron approximation: If the formula for G is interpreted literally (with a free-electron estimate of the conduction-electron density in $Al_{10}V$), we find that it corresponds to $N_l = 0.12$ per formula unit for sample 3, and $N_l = 0.36$ for sample 4; these inferred occupancies, of 22% and 70%, respectively, are in good accord with other estimates.

It is easy to understand why the loose Al atoms are independent of each other, for the holes are about 7 Å apart, and the interaction between two such atoms is strongly screened by conduction electrons; we estimate the coupling to correspond to a temperature of order 10^{-1} °K. It is far less easy to understand why the central potential is so flat, and why the local mode is not strongly coupled to bulk phonon modes of the same frequency. These two questions both involve interaction with the Al atoms surrounding the hole, and must surely be related. In order to emphasize how low a frequency we have (and it is the square of the characteristic temperature or frequency that measures the interaction) it is worthwhile making a comparison with other soft modes in solids. Metallic Cs has the lowest Debye temperature, 38°K, of any pure metal; the atomic weight is 5 times greater than that of Al, the interatomic spacing is 5.2 Å, and the average conduction-electron density is a factor of 20 less than that in our compound. These factors make for an extremely low Debye temperature, but even so it is nearly twice as large as the characteristic temperature of our loose Al atom. The weakest kind of bonding is that involving in-

ert gases, and soft local modes are found in inert gas clathrates; for example an argon atom (radius 1.7 Å) can be trapped in a cage in quinol clathrate whose radius is 3.95 Å, and the low-temperature specific heat corresponds to an Einstein temperature of 48°K.[5] The weak dipole-induced-dipole interactions in the clathrate still manage to be stronger than the binding we have in the compound.

The extremely weak binding of the loose Al atom in $Al_{10}V$ leads on to the broader question of the stability of this relatively open structure. It appears that the spatial distribution of Al to V bonds, which leads to the Al_3V network, is of sufficient importance to outweigh the penalty of rather low bulk density; in other words, covalent bonding is of major importance in this (and other) aluminum-vanadium intermetallic compounds. In this connection we may note also that the electronic specific-heat coefficients in $Al_{10}V$ of 1.7 and in Al_7V of 1.5 mJ°K^{-2} per mole of average atom are markedly higher than in all other aluminum-rich aluminum intermetallics that we have measured,[2] where γ always lies in the range 0.96 to 1.3 mJ°K^{-2} per mole of average atom.

Perhaps the singular character of V compounds is to be explained by the nearly empty d shell of the ionic configuration, but it is clear that they deserve careful and detailed physical examination.

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