virtual phonon processes can be neglected which involve phonons of higher frequency.

CONCLUSION

The electronic specific heat coefficient of copper increases when the copper is alloyed with Zn or Sn at the same rate per unit valence-electron concentration, namely about 28%. The Debye temperature decreases faster when copper is alloyed with Sn than when alloyed with Zn, indicating that the electron-phonon enhancement factor does not explain the increase in γ.

Low-Temperature Specific Heats of Silver-Zinc Alloys. The Effect of Lattice Dilatation*

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The specific heats of silver and six silver-zinc alloys covering the alpha phase were measured between 2 and 4°K with a relative precision of 0.2% or better. The purpose is to compare the effect of Zn as a solute with Cd and Sn, which have been shown to increase the electronic specific-heat coefficient γ for silver as a function of electron concentration e/a at the rate $d(\ln\gamma)/d(e/a)=0.2$ to 0.3 in spite of their considerable difference in valence. The comparison should reveal the effect of atomic volume, since Zn contracts silver upon alloying, while Cd and Sn expand it at a constant rate per unit e/a. The result for Zn in Ag is $d(\ln\gamma)/d(e/a)=0.65\pm0.17$ (95% limit). The volume effect, although opposite in sign from that expected on the free-electron model, is shown to be consistent with the rigid-band model including—indeed, requiring—contact between the Fermi surface and the first zone boundary, as is well established on other evidence. We conclude that the sign of the above derivatives and the observed volume effect are most simply explained if the density of states in silver is an increasing function of energy at the Fermi level in spite of this contact. These results imply that the electronic-thermal-expansion coefficient of pure silver is negative. Experimental test of this prediction will constitute a sensitive test of the rigid-band model. The Debye temperatures of the AgZn alloys do not differ from that of pure silver by more than 2°K, a slight negative trend being suggested. A significant T^5 component in the specific heat appears with Zn addition, growing from less than 0.0001 mJ mole^{-1} °K^{-6} in pure Ag to 0.0005 units at 32 at.% Zn.

INTRODUCTION

THE fact that the electronic specific-heat coefficient γ of pure silver is increased when the silver is alloyed with cadmium,[1] for example, has been considered paradoxical, for it is well known that the Fermi surface of silver is in contact with the first Brillouin zone boundary; thus expansion of the Fermi surface should reduce its free area, leading, it is argued, to a decrease in the density of states at the Fermi level. The argument rests fairly heavily upon the assumption that the band structure of silver is unchanged with alloying to a sufficient approximation (the rigid-band model). The effect of alloying with B-subgroup elements is considered merely to add electrons to the conduction band in proportion to the excess in valence of the solute over the solvent.[2]

Attempts to relax the assumption of rigid bands,[3] or to conceive of other contributions to the linear temperature term in the specific heat,[4] or to invoke the effects of electron scattering by the solute[5] have not provided predictive power for subsequent experiments. For example, alloying silver with Sn[6(a),6(b)] has about the same effect as alloying with Cd when scaled according to relative valence. This is most simply explained with the rigid-band model. The effect is not peculiar to silver; in fact, it was first seen in copper alloys.[7]

As part of an effort to unravel this mystery, we were led to consider the possibility of varying another important parameter of silver, its molar volume.

If a metal cube is compressed, (1) the momentum states of its conduction electrons are displaced in a uniform expansion, reducing the density of states in k space, (2) all Brillouin-zone boundaries are displaced outward, and (3) the Fermi surface, although it may be distorted somewhat from its initial shape, must expand so as to contain a volume inversely proportional to the

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* Supported in part by the U. S. Atomic Energy Commission.

[1] H. Montgomery and G. P. Pells, Proceedings of a Conference on The Electronic Structure of Alloys, University of Sheffield, 1963 (unpublished).

[2] For general background on the electronic structure of alloys and the history of attempts at understanding it, see W. Hume-Rothery and G. V. Raynor, *The Structure of Metals and Alloys* (The Institute of Metals, London, 1962), 4th ed., especially pp. 41–45. See also J. Friedel, Advan. Phys. **3**, 446 (1954).

[3] M. H. Cohen and V. Heine, Advan. Phys. **7**, 395 (1958).

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

[5] H. Jones, Phys. Rev. **134**, A958 (1964).

[6] (a) B. A. Green, Jr., and H. V. Culbert, Phys. Rev. **137**, A1168 (1965); (b) T. B. Massalski and L. L. Isaacs, *ibid.* **138**, A139 (1965).

[7] J. A. Rayne and W. R. G. Kemp, Australian J. Phys. **9**, 569 (1956); J. A. Rayne, Phys. Rev. **108**, 22 (1957); **110**, 606 (1958); B. W. Veal and J. A. Rayne, *ibid.* **130**, 2156 (1963); L. C. Clune and B. A. Green, Jr., preceding paper, Phys. Rev. **144**, 525 (1966). The results of L. L. Isaacs and T. B. Massalski, *ibid.* **138**, A134 (1965), show a decrease.

volume of the metal. These effects will in general change the density of states with respect to energy at the Fermi surface, which in turn is proportional to the electronic specific-heat coefficient.[8]

It is not easy to measure the specific heat of a body which is simultaneously subjected to great hydrostatic pressure. The requirement that the sample be thermally isolated conflicts with the requirement that pressure be transmitted to it through some medium. An alternative suggests itself, however. Just as the electron concentration is varied by alloying, so may the atomic volume be varied.

Alloying silver with Cd, In, Sn, and Sb not only affects γ in proportion to the change in the number of conduction electrons per atom (e/a), but also expands the silver lattice in proportion to the change of e/a. The rate for all of these solutes is[9]

$$d(\ln V)/d(e/a)=0.14\pm0.03.$$

(The very precise data available show a consistent trend within this range, but the range is nonetheless small.) Thus upon alloying silver with these fifth-row solutes, both e/a and V are changed in constant proportion. The effects of the two variables N (number of conduction electrons per mole of atoms) and V (volume per mole of atoms) are thus confused.[10]

When one alloys silver with the fourth-row element zinc, however, the molar volume of the lattice contracts at the rate[9]

$$d(\ln V)/d(e/a)=-0.14.$$

Thus if the valence effect of Zn in Ag is the same as that of Cd in Ag, both solutes being from column II, then one can hope to exhibit explicitly the volume effect. The equality of valence effects between rows is not established, but it is suggested by the agreement in the concentration limits[11] of the alpha phases of *Ag*Cd and *Ag*Zn, and in the agreement in changes in Knight shift of silver with alloying.[12] In any case, the possibility of exploring the volume effect was considered sufficiently interesting to warrant the measurement of the low-temperature specific heats of *Ag*Zn alloys in the alpha phase.

The chief result is that $d(\ln\gamma)/d(e/a)$ for *Ag*Zn exceeds that for solutes of the fifth row by a clear margin: 0.65 ± 0.17, compared to 0.25 ± 0.08. Thus the volume contraction has increased γ, whereas the model of free electrons including zone contact predicts a decrease in γ with volume contraction.[13] We suggest in the discussion below that the contrary sign of the volume effect not only agrees with but is required by the contrary sign of the number effect. Furthermore, we find that the hypothesis of contact is necessary to the argument, if we wish to find an untortured explanation. Thus, for the first time, the calorimetrist can agree with the rest of the physical world about a Fermi-surface phenomenon in the noble metals.

EXPERIMENTAL PROCEDURE

The calorimeter and the measurement method were the same as that described by Green ahd Culbert[6] with some improvements in technique described by Green and Valladares.[14] Briefly stated, the sample is maintained near a temperature of measurement T_2 by balancing the heat loss through the mounting by electrical heat. Then the sample is precooled through a metal contact, and an additional electrical heat is supplied, causing the temperature to rise rapidly. One then measures the time which the sample requires to heat between two temperatures T_1 and T_3 symmetrically disposed about T_2. The interval T_3–T_1 is made to be about 5% of T_2. This heating cycle may be indefinitely repeated at the same temperatures. By this technique, the random error due to stray heat leaks is kept below 0.1%. For further details, the reader is referred to the abovementioned papers.

The samples were prepared by melting the weighed constituents in sealed silica envelopes under argon. The melts were quenched in water and annealed in air near the solidus temperatures for about 48 h. The starting materials were all of 99.9999% purity as stated by the supplier.[15] Spectroscopic analysis[16] of the alloys showed no impurities at the 1-ppm level from the class (Fe, Mn, Co, Ni, Cr, Si, Cu, Al). It was necessary to etch the chips of alloy to be analyzed in dilute NHO_3 after they were machined off with a diamond tool. Unetched samples showed as much as 3 ppm of Fe and one alarming example of 24 ppm Co.

The working thermometer, a 0.1-W, 47-Ω Ohmite resistor, was stable over 11 runs in this laboratory in August and September, 1965 to within about 2 mdeg between 2 and 4°K. Consequently, the thermometer was recalibrated during the present work only after every three runs. Since the scatter in specific-heat values was somewhat reduced when the data were analyzed using the mean calibration instead of the calibration nearest in time to the run, we conclude that any apparent variation in thermometer calibration was probably less than the random error in a single calibration.

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[8] See, for example, J. M. Ziman, *Electrons and Phonons* (Oxford University Press, London, 1960), p. 105.

[9] T. B. Massalski and H. W. King, Progr. Mater. Sci. **10**, 33 (1961), Table 4.

[10] Although one might expect from their definitions that $N=e/a$, we will use N when we wish to emphasize changes at constant volume, and e/a when we intend to change both N and V due to alloying. Thus $e/a=\Delta Z\times$(solute concentration).

[11] Reference 9, Table 2, p. 25, gives 32% Zn and 37% Cd as the alpha-phase limits.

[12] T. J. Rowland, Phys. Rev. **125**, 459 (1962), gives rates of shift equal within 3%.

[13] A volume effect proportional to $V^{2/3}$ for free electrons was found by Z. Mikura, Proc. Phys.-Math. Soc. Japan **23**, 309 (1941).

[14] B. A. Green, Jr., and A. A. Valladares, Phys. Rev. **142**, 379 (1966).

[15] Cominco Products, Inc., Spokane, Washington.

[16] Done by National Spectroscopic Laboratories, Inc., Cleveland, Ohio.

The calibrations were made relative to the 1958 He^4 vapor pressure scale.

RESULTS

The specific heat of all samples was fitted by the equation

$$C=\gamma T+AT^3+BT^5.$$

Table I gives the fitted values of the coefficients, together with the Debye temperatures at 0°K deduced from the value of A. The γ values are also presented in Fig. 1. Because of the recent interest in the possibility of a detectable T^5 term in pure silver,[17] the values of C/T and corresponding values of T^2 are listed for both pure silver runs in Table II. Sample 18 consists of 0.999999% silver from Cominco, melted under argon and annealed in air, while sample 19 consists of 0.999999% silver from United Mineral and Chemical Corporation prepared by L. L. Isaacs in his laboratory and kindly lent to us by him for intercomparison.

It is clear that γ rises strongly with Zn concentration. Fitting all data below 25 at.% with a straight line yields

$$d(\ln\gamma)/d(e/a)=0.65\pm0.17,$$

with 95% confidence limits. Below 3%, of course, the slope cannot be accurately estimated. The theorist's demand for the *initial* slope of these curves can never be satisfied as long as there remains any finite error in the determination of γ for the individual alloys.

The value 0.65 may be compared with that expected for free electrons without contact, $\frac{1}{3}$, for free electrons with contact, -1, and with that found for silver alloyed with Cd (0.26) or Sn (0.22). The *Ag*Zn result clearly exceeds all of these by a considerable margin.

The Debye temperature is apparently unaffected by addition of Zn. If the 17% sample is rejected as an outlier, then one sees in Fig. 2 a slight trend in the data, giving a 1.5°K drop in Θ_D over the entire alpha phase.

TABLE I. Values of the parameters γ, A, Θ_D, and B found by fitting the observed specific heat C for silver-zinc alloys to the expression $C/T=\gamma+AT^2+BT^4$, where $\Theta_D=(12\pi^4R/5A)^{1/3}$. Units are mJ, mole, °K appropriately combined.

Sample No.	Zinc concentration (at.%)	γ	A	Θ_D	$B\times10^4$
18[a]	0.0	0.654	0.1702	225.2	−0.3
19[b]	0.0	0.644	0.1706	225.0	−0.8
45	3.0	0.652	0.1700	225.3	−0.3
46	6.0	0.672	0.1699	225.4	+0.6
41	9.0	0.683	0.1709	224.9	1.3
42	17.3	0.730	0.1666	226.8	5.0
44	20.5	0.724	0.1709	224.9	3.6
43	31.9	0.741	0.1732	223.9	4.9
Mean standard deviation		0.005	0.0010	0.5	0.5

[a] Same sample previously reported, Refs. 6(a) and 14.
[b] Sample furnished by L. L. Isaacs, reported in Ref. 6(b).

By the Kopp-Neumann rule (linear mixing of the lattice specific heats of the constituents), one would expect a rise of about 25°K in this range, since the Debye temperature of zinc[18] is about 300°K.

The more concentrated alloys show a T^5 component in their specific heats which rises smoothly with concentration. The slightly negative T^5 coefficients obtained for pure silver are probably not significant. We have also found in other experiments on copper a slight negative (and unbelievable) component. This may be traceable to the temperature scale used (1958 He^4 vapor pressure scale) or, at least, our procedure of calibration. The positive T^5 terms found in the alloys beyond 9% are highly significant (statistically). Figure 2 shows the behavior of both Θ_D and the coefficient of T^5.

DISCUSSION

We shall show that if the cause of the rise in γ on alloying silver with Cd, etc., is an *increase* in surface area of the Fermi surface, then a decrease in volume should likewise cause a decrease in γ, contrary to the present experimental finding. (This would be the case for free electrons.) On the other hand, if the rise in γ on alloying is due to a strong increase in the mean reciprocal velocity of surface electrons which outweighs a *decrease* in surface area (implying contact with the zone boundary without overlap), then the present finding is easily explained on the rigid-band model.

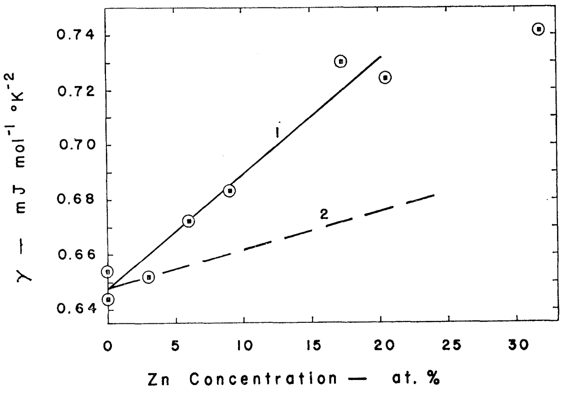

FIG. 1. The electronic-specific-heat coefficient γ versus zinc concentration in silver-zinc alloys. Line (1) is fitted to the data up to 21%. Line (2) shows the results for silver-tin alloys of Ref. 6(a), plotted at corresponding electron concentration.

The various ways that volume changes can affect the density of states at the Fermi surface are best seen by expressing the molar density of states as[19]

$$n(E_F)=(V/4\pi^3)S_F\langle 1/v\rangle_{FS}, \qquad (1)$$

where V is the molar volume, S_F is the area of the Fermi

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[17] Compare Refs. 6(a) and 6(b).

[18] P. L. Smith, Phil. Mag. **46**, 744 (1955).

[19] Reference 8, pp. 106–107. Ziman calculates the density of states per unit crystal volume. We wish the density per mole; hence the factor V above.

surface (FS), v is the magnitude of $\mathrm{grad}_k E(\mathbf{k})$ (aside from a factor of $\hbar$, the group velocity of electrons in state $\mathbf{k}$), and the brackets denote an average over FS. We wish to examine the probable effect of variation of each of the independent variables N and V (electron number and volume per mole) upon each of the three factors. Let us write

$$d\ln n(E_{\mathrm{F}})=\left(\frac{\partial \ln n(E_{\mathrm{F}})}{\partial \ln N}\right)_V d(\ln N)+\left(\frac{\partial \ln n(E_{\mathrm{F}})}{\partial \ln V}\right)_N d(\ln V). \quad (2)$$

If we consider $n(E_{\mathrm{F}})$ as a product of three factors, then each of the above partial derivatives will consist of a sum of three corresponding terms, which we shall estimate for pure silver. The results are collected in Table III.

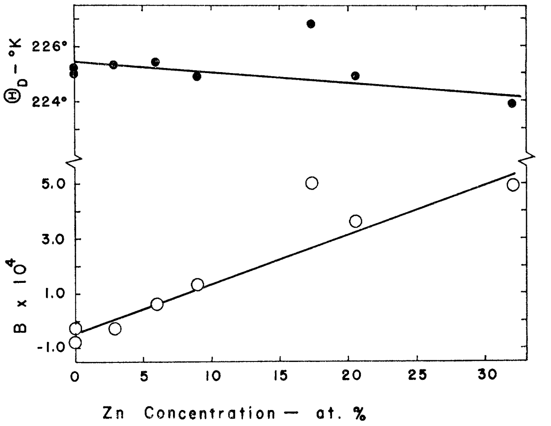

FIG. 2. The Debye temperature Θ_{D} and the coefficient B of the T^5 term in the specific heat versus zinc concentration in silver-zinc alloys. The units for B are mJ mol^{-1} °K^{-6}. The negative value of B for pure Ag can be accounted for by a very small systematic error in thermometer calibration.

TABLE II. A comparison of two silver samples, No. 18 and No. 19. The specific heats fitted to $C/T=\gamma+AT^2$ (weighted by $1/\sigma^2$) give $(0.652+0.16977T^2)$ and $(0.651+0.16907T^2)$, respectively. The table lists the differences δ_{18} and δ_{19} in C/T from the mean line, $C/T=0.653+0.1694T^2$. A 0.2% change in C/T is listed for comparison. Units are mJ, mole, °K, appropriately combined.

T^2	$\delta_{18}\times 10^3$	$\delta_{19}\times 10^3$	(0.2% of C/T)$\times 10^3$
3.9	4.6	−2.4	2.6
5.9	5.7	−6.0	3.2
7.9	4.9	−4.2	4.0
9.9	9.2	−3.5	4.6
11.8	7.9	−4.9	5.2
13.7	6.8	−6.1	6.0
15.7	8.7	−9.6	6.6

Number effect. The volume factor $V/4\pi^3$ is independent of N. The surface factor S_{F} is the one which crucially depends on the existence of contact between FS and the zone boundary. Without contact, S_{F} goes as $N^{2/3}$ for free electrons. For nearly free electrons, the exponent should not differ much from $\frac{2}{3}$, since the surface-to-volume ratio of a figure is insensitive to slight changes of shape. With contact, however, the expansion of FS reduces its free area. A sufficient estimate of the rate can be had by approximating FS by a sphere in slight contact with eight planes (the (111) zone faces). An easy calculation shows that the surface area decreases just after contact in proportion to $N^{-2/3}$. The velocity factor $\langle 1/v\rangle_{\mathrm{FS}}$ is the most sensitive to the details of the band structure. (Regions of FS where v becomes small will dominate the average.) We shall name the corresponding exponent of N by the letter a. For free electrons, the velocity is proportional to k_{F}; thus $a=-\frac{1}{3}$ with or without contact.

Volume effect.[20] The volume factor obviously contributes a volume exponent +1. The surface factor, curiously, is here independent of contact. Without contact, the closed FS merely shrinks, containing a volume inversely proportional to V. Again for any reasonable surface, we expect a surface-to-volume ratio about like that of a sphere. Thus S_{F} must go roughly as $V^{-2/3}$. With contact, the volume enclosed by FS must still contract; at the same time, the zone boundaries contract in the same proportion. The neck diameter stays in roughly constant proportion to the belly diameter. Thus we still find the volume exponent $-\frac{2}{3}$. The velocity factor is again the most sensitive. Its volume exponent we call b; free electrons imply $b=\frac{1}{3}$, by a simple calculation.

Note that for free electrons

$$a+b=0. \quad (3)$$

Since we shall base an argument later upon the sign of $a+b$, let us elaborate slightly upon its meaning. We may change variables from N and V to D and V, where $D=N/V$ is the electronic spatial density. By definition

TABLE III. The sensitivity of each of three factors in the density of states $n(E_{\mathrm{F}})$ to electron-number change at constant volume V and volume change at constant number N expressed in terms of logarithmic change as indicated. The row sums appear in the last column. "Contact" refers to contact between the Fermi surface and the first zone boundary.

	$\ln V$	$\ln S_{\mathrm{F}}$	$\ln\langle 1/v\rangle_{\mathrm{FS}}$	$\ln n(E_{\mathrm{F}})$
$\left[\dfrac{\partial}{\partial \ln N}\right]_V$	0	if contact, $-\frac{2}{3}$ if no contact, $+\frac{2}{3}$	free electrons $-\frac{1}{3}$ in general a	free electrons contact, -1 no contact, $+\frac{1}{3}$ in general contact, $a-\frac{2}{3}$ no contact, $a+\frac{2}{3}$
$\left[\dfrac{\partial}{\partial \ln V}\right]_N$	1	$-\frac{2}{3}$	free electrons $+\frac{1}{3}$ in general b	free electrons $\frac{2}{3}$ in general $b+\frac{1}{3}$

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[20] J. H. O. Varley, Proc. Roy. Soc. (London) **A237**, 413 (1956), has treated the volume effect in a general formulation.

of a and b,

$$d(\ln\langle 1/v\rangle_{\mathrm{FS}})=ad(\ln N)+bd(\ln V),$$

or

$$\begin{aligned} d(\ln\langle 1/v\rangle_{\mathrm{FS}}) &= ad(\ln D+\ln V)+bd(\ln V) \\ &= ad(\ln D)+(a+b)d(\ln V). \end{aligned} \tag{4}$$

Thus

$$\left(\frac{\partial \ln\langle 1/v\rangle_{\mathrm{FS}}}{\partial \ln D}\right)_V=a,$$

and

$$\left(\frac{\partial \ln\langle 1/v\rangle_{\mathrm{FS}}}{\partial \ln V}\right)_D=a+b.$$

The process of varying V at constant D can be visualized as keeping the volume enclosed by the Fermi surface fixed while moving the zone boundaries in and out. Thus if $a+b=0$, the mean reciprocal velocity is not sensitive to the presence of the zone boundaries.

If we squeeze a FS of constant interior volume by collapsing the zone boundaries, the surface is forced out into the corners of the zone. Thus, even for free electrons with contact, it will not be true that $a+b=0$ after considerable contact has occurred. But a little analysis shows that the initial value of $a+b$ just after contact is still zero, although it grows negative for free electrons.

We shall now estimate a and b from the specific-heat data. Table III shows that the observed initial slopes of γ versus e/a should obey the relation

$$\frac{d\ln\gamma}{d(e/a)}=(a\mp\tfrac{2}{3})+(b+\tfrac{1}{3})\frac{d(\ln V)}{d(e/a)}, \tag{5}$$

where the negative sign applies if contact exists, the positive sign if contact does not exist. [We have used the fact that γ is proportional to $n(E_{\mathrm{F}})$, and that $N=e/a=1$ in silver.] A plot of the experimental numbers should be a line (to some approximation) whose intercept and slope will furnish values of a and b under each hypothesis.

Table IV shows the specific-heat results from AgCd and AgSn experiments together with the present result.

TABLE IV. Results of calorimetric and lattice parameter measurements on silver alloys. The quantity listed is the estimated initial slope at infinite dilution of the solute.

System	$\frac{d\ln\gamma}{d(e/a)}$	$\frac{d\ln V}{d(e/a)}$
AgCd[a]	0.29±0.07[f]	0.17[g]
AgCd[b]	0.22±0.08	0.17
AgSn[c]	0.22±0.06	0.11
AgSn[d]	0.16	0.11
AgZn[e]	0.65±0.17	−0.14

[a] Reference 1, differential comparison of one alloy with silver.
[b] Reference 1, conventional measurements on nine alloys.
[c] Reference 6(a).
[d] Reference 6(b). Estimated from three points (up to 3 at.%, beyond which the curve rises rapidly).
[e] Present work.
[f] 95% confidence limits.
[g] Reference 9.

These data are plotted in Fig. 3. Line (1) is fitted to the data. It gives

$$\text{intercept}=0.45,$$
$$\text{slope}=-1.5.$$

Thus $b=-1.8$; and $a=1.1$ (with contact) or -0.22 (without contact).

We have promised to show that if the "paradoxical" increase in γ upon alloying were due to an increase in S_{F} (due, say, to overlap into the second zone or to lack of contact), then the predicted volume effect has the wrong sign. Translated into the present notation, this means that if we choose the positive sign in Eq. (5), thus finding $a=-0.2$, then there is an argument to prove that $(b+\frac{1}{3})$ should be positive. The argument turns upon the expected value of $a+b$: Given no contact, what happens to grad$_kE$ as the zone boundaries move in toward the center a little? For a nearly spherical surface, grad$_kE$ can either remain constant or can decrease as the zone face approaches part of the FS. Thus $1/v$ cannot decrease; therefore, $a+b$ must be positive; therefore, $b>0.2$; therefore, $(b+\frac{1}{3})>0$.

We also promised to show that the existence of contact alters the above argument. First of all, we must choose the negative sign in Eq. (5) thus finding $a=+1.1$. Even if we could argue that $a+b$ must again be positive, it is still permitted for $(b+\frac{1}{3})$ to be negative. Actually we cannot clearly argue even that $a+b$ cannot be negative. On the belly of the FS, $1/v$ cannot decrease, just as before. But on the neck surfaces, it could and probably does decrease. By symmetry, the point L in the center of the (111) zone face must have minimum energy with respect to displacement on the face itself. Thus if the zone face collapses a bit, the neck gets thicker, and grad$_kE$ increases. Thus the sign of $a+b$ depends upon a balance between belly and neck con-

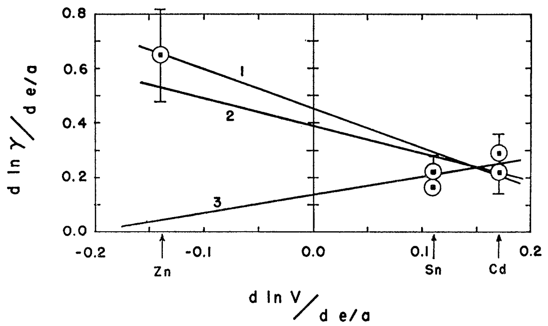

FIG. 3. A plot relating the observed rates of increase of γ upon alloying (reduced to unit solute valence excess by referring rates to changes in e/a) to the observed rates of lattice dilatation upon alloying (again referred to changes in e/a). The intercept, about 0.4, is claimed to be the rate of increase of γ at constant volume for alloys of silver with B-subgroup elements. Line (1) is fitted to the data. Line (2) is a hypothetical line satisfying the condition $a+b=0$ (see text). Line (3) has slope $\frac{2}{3}$, as required for free electrons, and is otherwise fitted to the AgSn and AgCd data. Error limits are 95% confidence limits.

tributions. In the case of silver, we find $a+b=-0.7$. However, the data are not precise enough to rule out $a+b=0$; in Fig. 3, we show a line such that $a=-b=1.1$ (line 2), which the data cannot deny. By contrast, line 3, having the free-electron volume dependence $V^{2/3}$ and otherwise fitted to the previously known data, can be denied.

The correctness of this analysis can be tested by more alloy experiments which vary the dilatation. Particularly good candidates are silver plus Al, Ga, or Ge, whose dilatation rates are -0.046, -0.025, and $+0.009$, respectively. Another interesting possibility is to try ternary AgZnCd alloys of varying proportions to cover the dilatation range between -0.14 and $+0.17$.

On the other hand, there is available another test of this analysis in the thermal-expansion behavior of silver. Thermodynamics tells us that

$$\begin{aligned}(\partial V/\partial T)_P &= (\partial S/\partial P)_T \\ &= (\partial C/\partial V)_T(\partial V/\partial P)_T,\end{aligned}$$

since for electrons $S=C=\gamma T$. Thus

$$(\partial \ln\gamma/\partial \ln V)_T = 3\alpha_e VK/C,$$

where α_e is the electronic part of the linear thermal expansion coefficient of pure silver (which may be separated from the lattice part by its linear temperature dependence), and K is the bulk modulus. Our experiment gives the value -1.5 to the left side.Since all other quantities on the right are positive, we conclude that α_e must be negative, if this rigid-band analysis is correct.

This suggests two experiments to test the rigid-band model further: (1) measure the thermal expansion of silver with sufficient precision to resolve the electronic part; (2) measure the volume effect upon the specific heat of copper by alloying, since Carr, McCammon, and White[21] have already determined that the electronic thermal expansion of copper is positive. This is the first experimentally feasible test we know of in which properties of the pure metal are related to those of the alloys through the rigid-band model.

CONCLUSION

The chief experimental finding is that γ increases as silver is alloyed with zinc at a rate significantly greater than when silver is alloyed with B-subgroup elements of the fifth row. It is shown that, in spite of what one expects for free electrons, this finding can be understood as a dilatation effect on the rigid-band model for silver where the band is very un-free-electron-like. The explanation requires either of two independent assumptions (which, given the data and the rigid-band model, imply each other): (1) the assumption of contact between FS and the first zone boundary (well-known), and (2) that the mean reciprocal group velocity of surface electrons depends primarily upon the spatial density of electrons, and little upon the crystal volume (with constant density).

On this hypothesis, one may conclude that in silver this mean reciprocal velocity varies directly as the first power of the electron density at constant volume, instead of inversely as the cube root as one expects for free electrons. Thus the seemingly paradoxical specific-heat results in noble metals in recent years need not lead us to question that the electronic specific heat is proportional to the density of states; they may be explained directly in terms of a density of states at the Fermi level which increases as a function of energy in spite of the acknowledged contact at the zone boundary.

Note added in proof. Preliminary measurements made since submission of this manuscript indicate that contraction of copper also increases γ, which in view of the thermal-expansion data[21] contradicts the argument of this paper. We let the discussion stand as an analysis of volume effects on the rigid-band model, but we are now less confident that other alloying effects can be neglected, such as the possible change in electron-phonon enhancement of the density of states. The latter is being investigated through its dependence upon the mass ratio of solute and solvent.

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[21] R. H. Carr, R. D. McCammon, and G. K. White, Proc. Roy. Soc. (London) **A280**, 72 (1964).