

Memorandum M-1926

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SUBJECT: GROUP 63 SEMINAR ON MAGNETISM, XLII
 To: Group 63 Engineers
 From: Arthur L. Loeb, Philip K. Baltzer, John B. Goodenough, Norman Menyuk
 Date: March 23, 1953

At this meeting some articles referred to in Zener's series of papers were discussed. The first paper discussed was by Friedberg, Esterman, and Goldman.*

The specific heat, C_V , of several materials is measured at low temperature ($1^\circ - 4^\circ$ K.). The results were then used to evaluate the density of energy states at the top of the Fermi distribution. In general

$$C_V = \gamma T + \beta T^3$$

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wherein the term βT^3 is called the Debye** term and represents the contribution to specific heat due to lattice vibrations, and γT represents the electronic contribution. At high temperatures the major contribution is due to the Debye term, but at low temperature the effects can be separated.

The coefficient γ gives a direct measure of the density of electronic states at the Fermi surface, and can be determined experimentally by plotting $\frac{C_V}{T}$ versus T^2 and extrapolating this curve to $T = 0$ (figure 75)

* Friedberg, S. A.; Esterman, I.; Goldman, J.E.
 "The Electronic Specific Heat in Chromium and Magnesium,"
 Physical Review, 85, 375, (1952)

** See Lecture XVI

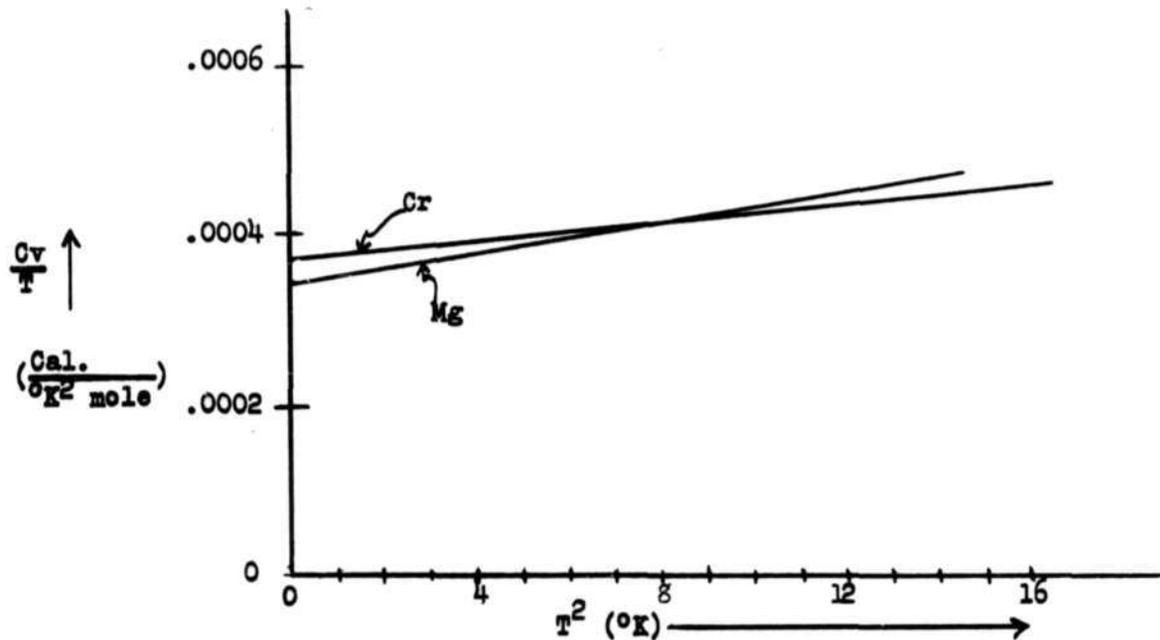


FIGURE 75

The results obtained for various elements are given in Table I, wherein $n(e)$ represents the density of states at the Fermi surface.

TABLE I

Metal	$\gamma \times 10^4$	$n(e)$ in levels/atom/ev.
Copper	1.80	0.16
Magnesium	3.25	0.29
Titanium	8.3	0.74
Vanadium	14	—
Zirconium	6.92	0.62
Chromium	3.72	0.33

High values of δ for transition elements are to be expected in view of the high electron density associated with the incomplete 3d shell. However, the value of δ is much smaller for chromium than for vanadium, although they have the same crystal structure and nearly the same spacing between neighbors.

This can be explained in terms of the energy levels in the 3d and 4s bands, which were calculated by Slater* for copper, and are shown in figure 76.

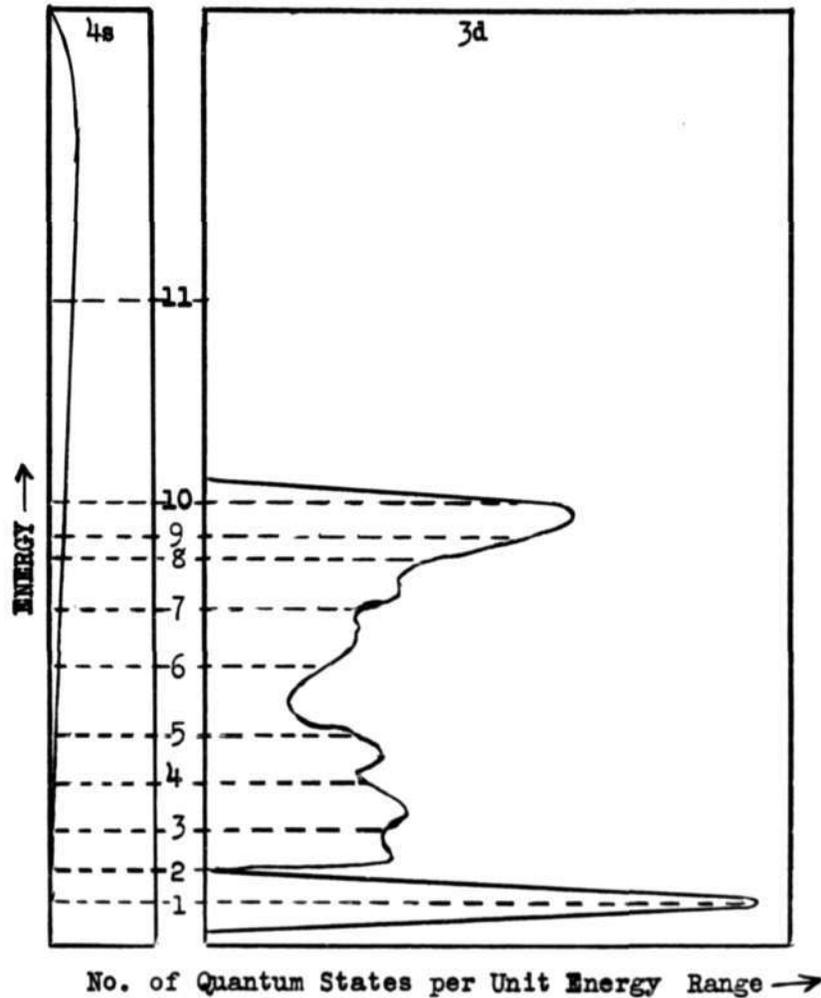


FIGURE 76

We see in figure 76 that the energy density is a minimum when the 3d shell is about half full, and chromium falls approximately in this minimal region.

This variation of δ for chromium and vanadium can also be explained in terms of the Zener model. According to this model, the chromium 3d shells are half full, and a transfer of a 3d electron from one atom to the 3d shell of a neighboring atom (figure 77) would require an energy greater than the exchange energy lost due to the loss of four exchange pairs.

* Slater, J. C., Physical Review, 49, 537 (1936)

Isenberg⁺ assumed short range interactions between tungsten atoms, and used the elastic constants to study the interactions between nearest and next-nearest neighbors. He found an attractive interaction with nearest neighbors and a repulsive interaction with next-nearest neighbors. This substantiates Zener's theory.

According to the band theory of transition metals the outer d and s electrons are strongly perturbed by the proximity of other atoms, so all the outer electrons can move fairly freely to all parts of the crystal. Bloch wave functions are then used, and these represent a piling up of an electron cloud halfway between the cores, thereby causing binding.

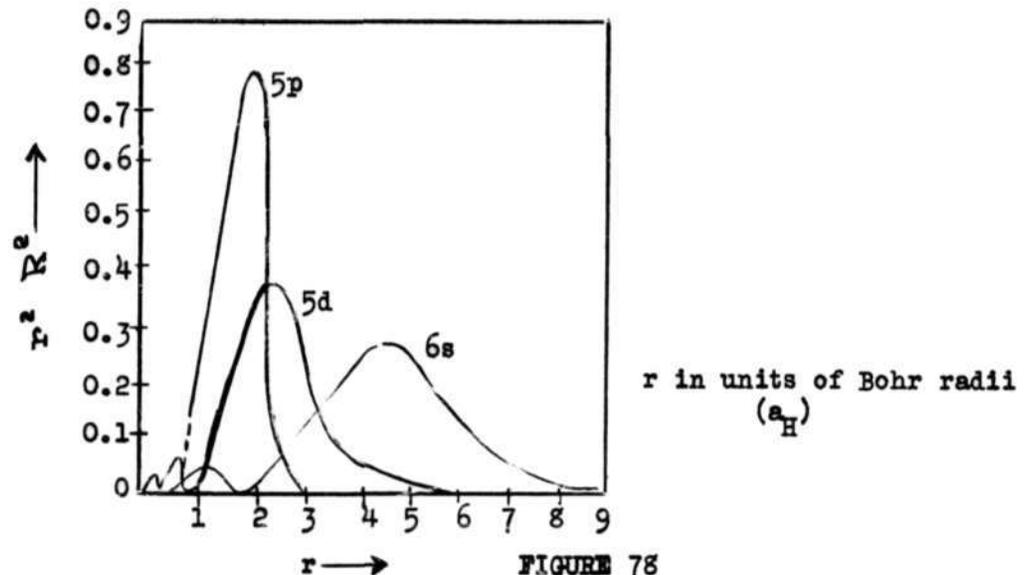
In the Pauling resonating valence bond theory of the transition metals one must use a combination of the (n-1) d, ns, and np orbitals. On the average, 2.44 d orbitals for each atom show weak interaction. The remaining 2.16 d orbitals combine with the s and p orbitals to give hybrid bond orbitals, and this hybridization gives rise to bonding.

While an actual transition metal does not conform exactly to any of these, Hsu is interested in determining whether a calculation based on the Zener model for a bcc lattice can give the major part of the binding energy. In this model the attraction between nearest neighbors is primarily due to the electrostatic interaction between rigid charge distributions.

In order to make this calculation it is necessary to make a Wigner-Seitz calculation about each atom. This involves the construction of a median plane between nearest neighbors, thereby subdividing the lattice into cells with an ion at the center. This was discussed at meeting 16, and the resultant polyhedral surface for a bcc is shown in figure 28b. This surface can be approximated by a sphere, and is referred to as a Wigner-Seitz sphere.

This calculation was done for the tungsten atom of configuration $5d^4 6s^2$. The possibility of demotion of a 6s electron into the 5d shell was not considered because a self-consistent field calculation had previously been worked out for the configuration being used. The radial charge density, which is proportional to the square of the radial wave function R is plotted in figure 78 for the 5p, 5d, and 6s electrons.

+ Isenberg, Physical Review, 83, 637 (1951)



The distances between nearest and next nearest neighbors are $5.17 a_H$ and $5.97 a_H$ respectively. The radius of the Wigner-Seitz sphere is therefore equal to $5.17/2$ or $2.56 a_H$. Comparing this with the results shown in figure 78, we see that the 5d and 6s electrons overlap the Wigner-Seitz sphere considerably. The overlap of the 6s electron is so great that it is not feasible to consider the 6s electrons as localized, and are treated as being in the conduction bands. The 5d electrons remain localized in this model. However, in view of the strong 5d overlap, a correction to the Wigner-Seitz calculation must be made to take into account the d-d interaction and the p-d interaction resulting from the overlap of the d electron of ion a with the p electrons of the neighboring ions. Since the radial wave function of the p electrons is small at the radial distance of the Wigner-Seitz sphere, p-p coupling can be neglected.

The Wigner-Seitz calculation for two s electrons requires a self-consistent field calculation of the motion of one s electron in the field of another. Raimes* has outlined the procedure for such a calculation. In this calculation it is assumed that s electrons of opposite spins are in any one Wigner-Seitz sphere in order to minimize the exchange energy.

Taking the coupling and extra conduction electron corrections into account, the binding energy per atom is found to be

$$E_b = -E_I - 2\epsilon - 2E_k - 2E_{ex} + E_B' \quad \text{XLII-1}$$

where E_I = energy required to ionize two 6s electrons

ϵ = eigenvalue obtained in the Wigner-Seitz method.

E_k = average Fermi kinetic energy per conduction electron

E_B' = represents the interaction energy

* S. Raimes, Philosophical Magazine, 41. 568 (1950)

The unit of energy is taken as 2 rydbergs, where a rydberg is the energy required to remove the electron from the normal hydrogen atom (13.53 electron volts).

The correction term E_B^i is expressed by

$$E_B^i = -\frac{1}{2N} \sum_{a \neq b}^N \left(V_{ab} - \frac{4}{r_{ab}} - 2V_{ab}^i \right) \quad \text{XLII-2}$$

where V_{ab} represents the interaction between two cores, one situated at lattice point \underline{a} , the other at point \underline{b} .

V_{ab}^i represents the electrostatic correction due to p-d and d-d overlap.

$-\frac{4}{r_{ab}}$ represents the electrostatic interaction between the two cores, each with charge $+2e$.

The summation is carried over all the N lattice points; the unit of distance is taken as the Bohr radius (a_H) which is the radius of the first circular Bohr orbit in the hydrogen atom (0.528 angstrom units).

The determination of E_B^i therefore requires the calculation of V_{ab} and V_{ab}^i . Assuming a uniform distribution of conduction electrons it can be shown that

$$V_{ab}^i = \frac{2}{\sqrt{\epsilon_0}} \int_{r_0} \frac{Z_p (|\vec{r} - \vec{r}_a|)}{|\vec{r} - \vec{r}_a|} d^3 r \quad \text{XLII-3}$$

In XLII-3 lattice point \underline{b} is taken as the origin, and \vec{r}_a represents the position vector of point \underline{a} with respect to \underline{b} . The integration is carried on over the volume of the Wigner-Seitz sphere bounding \underline{b} , of volume \dots . $Z_p(r)/r$ is the potential due to a nuclear charge $Z_0 - Z$ as well as the core electrons surrounding it, where Z_0 is the total nuclear charge of the atom. Z_p is usually tabulated in the self-consistent field calculation for a free atom, and V_{ab}^i is evaluated by numerical integration. The resultant values for V_{ab}^i are given in table II.

The interaction term V_{ab} may be expressed in terms of the coulomb electrostatic contribution, the kinetic energy increase due to the superposition of two Thomas-Fermi distributions, and the exchange interaction.

Then

$$V_{ab} = \frac{4}{r_{ab}} + C_{ab} + K_{ab} + X_{ab} \quad \text{XLII-4}$$

where $\frac{4}{r_{ab}}$ = electrostatic interaction due to the net charge of the core

C_{ab} = remainder of the electrostatic interaction

K_{ab} = increase in the Fermi kinetic energy

X_{ab} = exchange interaction

In order to better understand the physical aspects of these terms consider two neighboring atoms a and b each surrounded, for simplicity, by a sphere in which there is an appreciable charge distribution. As explained previously, this sphere will be larger than the Wigner-Seitz sphere, and there will be a region of overlap, indicated by the shaded region of figure 79.

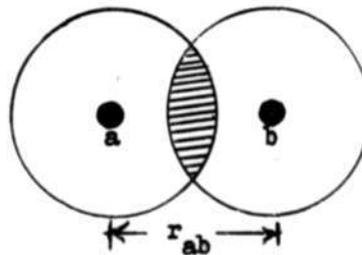


FIGURE 79

The nuclei are still shielded from each other by all the electrons, so the net electrostatic interaction of the nuclei is $\frac{4}{r_{ab}}$. This is a repulsive interaction, and is therefore positive.

In the shaded region there are electrons of atom b which are inside the outer shells of atom a. These electrons are therefore only partially shielded from nucleus a, and there is an attractive electrostatic interaction between these electrons and nucleus a. Similarly, there will be electrons of atom a in the overlap region attracted to nucleus b. This attractive interaction is greater than the repulsive energy due to increased electron-electron coulomb energy. The term C_{ab} is therefore negative.

If the electron distribution of each atom is assumed to be unchanged in the overlap region the electron density ρ in this region will be increased by a factor of two. Further, it was found at meeting 33 (eqn. XXXIII-6) that the Fermi energy E_0 is proportional to $N \left(\frac{N}{V}\right)^{2/3}$.

Therefore the energy per unit volume is proportional to $\left(\frac{N}{V}\right)^{5/3} = \rho^{5/3}$.

Thus in the overlap region, the electron density increase will give rise to an increase in the Fermi energy. This is accounted for by the positive interaction term K_{ab} .

Finally, the exchange effect leads to a greater separation of electrons of the same spin orientation. This was discussed at meeting 33. This greater spacing effectively lowers the electrostatic repulsion between electrons, so X_{ab} is negative.

Equation XLII-2 can be rewritten

$$E_B^i = \frac{1}{2N} \sum_{a \neq b}^N (C_{ab} + K_{ab} + X_{ab} - 2V_{ab}^i) \quad \text{XLII-5}$$

The calculated values of these terms are shown in table II for tungsten.

The interactions drop off rapidly with increasing interatomic distance, so the summation is carried out only over nearest and next-nearest neighbors, yielding

$$\begin{aligned} E_B^i &= -4 (C_{ab} + 2V_{ab}^i + K_{ab} + X_{ab}) \quad (8 \text{ nearest}) \\ &= -3 (C_{ab} + 2V_{ab}^i + K_{ab} + X_{ab}) \quad (6 \text{ next-nearest}) \end{aligned} \quad \text{XLII-6}$$

TABLE II

	NEAREST NEIGHBORS (PARALLEL SPIN)	NEXT-NEAREST NEIGHBORS (ANTI-PARALLEL SPIN)
r_{ab}	5.17 a_H	5.97 a_H
C_{ab}	-0.149 ry	-0.038
$2V_{ab}^i$	-0.120 ry	-0.039
K_{ab}	+0.223 ry	+0.137
X_{ab}	-0.061 ry	-0.057
TOTAL	-0.107 ry	+0.003

In equation XLII-1

$$E_B = \{-E_I - 2\epsilon - 2E_K - 2E_X\} + E_B'$$

The first part $\{-E_I - 2\epsilon - 2E_K - 2E_X\}$ can be considered the same in tungsten as in mercury. Since the $5d$ shells of mercury are full and therefore have no appreciable interaction, this first part of E_B can be taken as the total binding energy of mercury which has the configuration $5d^{10} 6s^2$. This is very small compared with the binding energy of tungsten as evidenced by mercury's low melting point. We can therefore neglect this term and take

$$E_B \approx E_B'$$

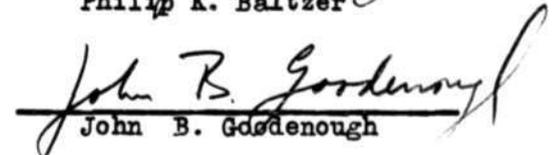
XLII-7

From XLII-6, XLII-7 and the results tabulated in table II, one gets $E_B = 0.42$ ry/atom. The observed heat of vaporization is 0.68 ry/atom. In view of the approximations made this agreement is quite good. It shows the coulomb interaction is the major factor in the binding energy calculation, which agrees with the postulations of Zener.

Signed


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Group 62 (20)