

Localized Impurity States in Metals: Dilute Alloys of Ni in Be[†]

A. P. KLEIN AND A. J. HEEGER*

*Department of Physics and Laboratory for Research on the Structure of Matter,
University of Pennsylvania, Philadelphia, Pennsylvania*

(Received 29 November 1965)

The results of an experimental study of the residual resistivity, specific heat, and magnetic susceptibility of dilute solid solutions of nickel in beryllium are presented. The addition of small amounts of Ni to the Be host metal gives rise to large changes in all three quantities. The residual resistivity due to the impurities is found to be $10 \mu\Omega \text{ cm}$ per at. % Ni, and each Ni atom contributes 1.15 states per eV to the total density of states at the Fermi level as measured by the linear term in the low-temperature specific heat. Susceptibility measurements indicate that there is no localized moment on the Ni, but the addition of Ni gives rise to a large change in the temperature-independent susceptibility. Comparison of the susceptibility and specific-heat results indicates that the added susceptibility is enhanced relative to the added state density arising from the Ni impurities. The Anderson theory of localized transition-atom impurity states is developed for the case of five-fold orbitally degenerate d states, and the equivalence of the Anderson approach and the scattering approach is demonstrated from the theory of resonance scattering. It is shown in this manner that the Anderson theory can be made consistent with the Friedel sum rule. Using the Anderson model the residual resistivity, specific heat, and d -state contribution to the susceptibility are calculated for dilute alloys where the host-metal density of states is a function of energy. The experimental results are found to be consistent with theoretical expectations and are used to determine magnitudes for the parameters of the theory. It is found that there are between 8 and 9 d electrons on each nickel atom, in agreement with the Friedel sum rule. The virtual level width is determined to be 0.4 eV, and the Coulomb-exchange quantity ($U+4J$) is evaluated as 7 eV. Analysis of similar data on Cu:Ni alloys yields values for these quantities which are fully consistent with the results obtained from the Be:Ni data.

I. INTRODUCTION

LOCALIZED impurity states in metals have been a subject of considerable interest in recent years. Stimulated by the discovery of the systematic occurrence of localized electron magnetic moments on Fe atoms dissolved in second row transition metals,¹ Anderson,² Wolff,³ and Clogston⁴ developed theories of localized magnetic states in metals. The Anderson theory is based on the effect of s - d mixing on the localized magnetic states of iron group atom impurities. The essential feature of the theory is the formation via this s - d mixing of virtual bound states within the host metal conduction band. Such virtual bound states were first introduced into the theory of dilute alloys by Friedel⁵ who approached the problem using the techniques of scattering theory. Although the points of view are somewhat different the results of the Anderson and Friedel-type theories are essentially equivalent. Having described the localized electronic states of the impurity by virtual bound states, the question of the existence of a magnetic moment resolves to determining the conditions under which the virtual states for electrons of spin σ are nondegenerate with those of spin $-\sigma$. Under these conditions $\langle n_{d\sigma} \rangle \neq \langle n_{d-\sigma} \rangle$, and a net magnetic

moment exists localized on the impurity site. The essential parameters needed to characterize such a virtual level are its width Δ , and its energy relative to the Fermi energy, $E_d^\sigma - E_F$. The parameter which determines whether the final state is magnetic is, in the case of a fivefold degenerate d state, the quantity ($U+4J$) where U and J are the Coulomb and exchange integrals between two electrons localized on the impurity atom in the metallic environment.

In this paper we present the results of an experimental study of the residual resistivity, specific heat, and susceptibility of the dilute alloy system Be:Ni. The experimental results are found to be consistent with the predictions of the Anderson theory, and their interpretation in terms of this theory allows the determination of the three parameters Δ , $E_d^\sigma - E_F$, and ($U+4J$).

In the next section we give a description of the experimental results of measurements of residual resistivity, specific heat, and magnetic susceptibility for dilute solid solutions of nickel in beryllium. Following this we summarize the Anderson theory for orbitally degenerate d states. The equivalence of the Anderson approach and the scattering approach will be demonstrated in an explicit fashion, and it will be shown that the Anderson theory can be interpreted in a manner consistent with the well-known Friedel sum rule. The residual resistivity, specific heat, and magnetic susceptibility are considered in Secs. IV and V. Using the Anderson model, the specific heat and d -state contribution to the susceptibility are calculated for dilute alloys where the host metal density of states is a function of energy. The results are compared with experiment and used to determine magnitudes for the parameters of the theory.

[†] Work supported by the National Science Foundation and the Alfred P. Sloan Foundation.

* Alfred P. Sloan Foundation Fellow.

¹ A. M. Clogston, B. T. Matthias, M. Peter, H. J. Williams, E. Corenzwit, and R. C. Sherwood, Phys. Rev. Letters **5**, 542 (1960); Phys. Rev. **125**, 541 (1962).

² P. W. Anderson, Phys. Rev. **124**, 41 (1961).

³ P. A. Wolff, Phys. Rev. **124**, 1030 (1961).

⁴ A. M. Clogston, Phys. Rev. **136**, A1417 (1964).

⁵ J. Friedel, Can. J. Phys. **34**, 1190 (1956); Suppl. Nuovo Cimento **7**, 287 (1958); *Metallic Solid Solutions* (W. A. Benjamin Company, New York, 1963), Chap. XIX.

II. EXPERIMENTAL RESULTS

A preliminary account of the experimental results has been previously published.^{6,7} Beryllium was chosen as the host metal since it should conform to the fundamental theoretical assumption of the Anderson model that the host metal electron wave functions are not *d*-like. In addition, the small density of electronic states and the high Debye temperature⁸ of pure Be make it possible to detect small changes in density of states with relatively high accuracy.

Small concentrations of Ni are readily soluble in solid Be. This portion of the Be-Ni phase diagram has been studied in some detail⁹ with the conclusion that up to concentrations of about 4 at.% Ni the solid solution is the equilibrium phase at temperatures at least down to about 600°C. The solubility is roughly independent of temperature for temperatures above 600°C, and shows no evidence of decreasing significantly at lower temperatures. In any case, because of the very high Debye temperature for Be, if the solution is quenched to room temperature the Ni would be expected to stay in solution. We have restricted ourselves to samples well within the expected solubility range with the highest concentration being 2.2 at.% Ni in Be. The same samples were used in the susceptibility and specific-heat measurements. These samples were prepared by the standard arc melting technique after which the alloys were given a homogenizing anneal for 24 h at 1050°C followed by a fast quench to room temperature. Metallographic studies were made on each of the samples. A large number of grains and grain boundaries were evident, and the grain boundaries in all cases were clean. No evidence of precipitation could be seen. An x-ray pattern of the most concentrated sample showed no evidence of any of the known intermetallic compounds of Ni and Be. On the other hand, chemical analysis of the alloys yielded the expected amounts of nickel. We conclude that the samples are solid solutions of known impurity concentration.

The specific heats were measured by the usual continuous heating technique using a conventional cryostat designed for specific heat measurements in the pumped helium range of temperatures.¹⁰ The sample was suspended by fine silk threads in an evacuated can. Contact to the helium bath for cooling was achieved by pressing the sample against the bottom of the can. A small $\frac{1}{4}$ -W carbon resistor (room temperature resistance of about 70 Ω) was stripped down to the bare carbon and attached to the sample with a very small amount of

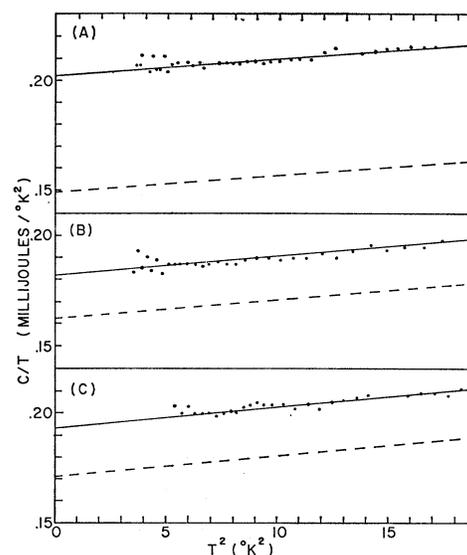


Fig. 1. Specific heat as a function of temperature for the Be:Ni alloys. (A) 2.2 at.% Ni, 6.69 g. (B) 1.45 at.% Ni, 6.97 g. (C) 1.1 at.% Ni, 7.23 g. The dashed line in each case represents the specific heat of the same number of atoms of pure Be.

Glyptal. The samples and resistors were weighed separately and then again after attachment so that the known specific heats of the carbon, copper leads, and Glyptal could be subtracted from the total. These corrections amounted to 7% of the measured T^3 term and 0.1% of the linear term of the alloys. The carbon resistor was used both for supplying the input power and monitoring the sample temperature. Data were taken over a wide range of power levels (always below approximately 10^{-7} W) and no power-dependent effects were observed indicating that the sample resistor system remained in equilibrium. Power was applied for 5-min intervals and the system was then allowed to drift for 5 min in continuing cycles. The typical temperature change during the 5-min on cycle was between 0.03 and 0.1°K. The off-cycle temperature drift was used to determine the vibrational heat leak into the system. The low-temperature limit on the data was set by a finite uncompensated vibrational heat leak into the system of about 0.5 erg/sec. For temperatures greater than 2°K this heat leak could be effectively counterbalanced by holding the bath temperature somewhat below that of the sample so that the off-cycle ΔT was always less than 10% of the on-cycle ΔT . Below 1.9°K this was no longer possible and the off-cycle temperature change became comparable with the on-cycle value with the result that the accuracy rapidly decreased. The low-temperature limit is determined by the specific heat of the sample. Even with the relatively small vibrational heat input of the system the very small specific heat of Be set the low-temperature limit at about 1.9°K in the present experiment. For larger specific heats (e.g., Cu or other metals with typical

⁶ A. P. Klein and A. J. Heeger, Proceedings of the Eleventh Conference on Magnetism and Magnetic Materials (to be published).

⁷ A. P. Klein and A. J. Heeger, Phys. Rev. Letters **15**, 786 (1965).

⁸ R. W. Hill and P. L. Smith, Phil. Mag. **44**, 636 (1953).

⁹ R. G. Bellamy and N. A. Hill, *Extraction and Metallurgy of Uranium, Thorium and Beryllium* (MacMillan Company, New York, 1963), p. 182.

¹⁰ S. Pollack and K. Atkins, Phys. Rev. **125**, 1248 (1962).

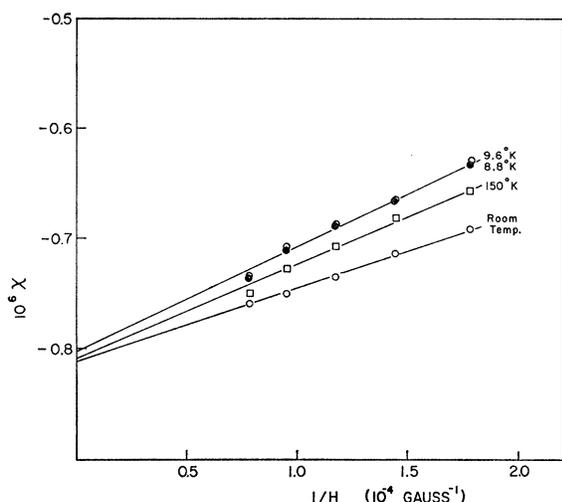


FIG. 2. Honda-plot of the measured susceptibility as a function of magnetic field for the 2.2 at.% Be:Ni alloy. The susceptibility extrapolated to infinite field is $-0.81 \times 10^{-6}/g$. The small slope results from trace amounts of precipitated ferromagnetic impurity.

state densities and Debye temperatures) the 0.5 erg/sec heat leak would not be a limitation. The data for the three samples measured are shown in Fig. 1. As seen from the small scatter of the points in the figure, the coefficient of the linear term is obtained with an accuracy of somewhat better than 2%.

The specific heat results show the expected electronic contribution (linear in T) and lattice contribution (T^3) as shown by the linear dependence of C/T versus T^2 in Fig. 1. Examination of the figure indicates that no significant change can be detected in the very small coefficient of the T^3 term as compared with pure Be.⁸ The linear term shows a relatively large and easily detectable increase with the addition of Ni impurities. This increase is not unexpected and clearly gives information on the added state density at the Fermi level resulting from the addition of the transition atom impurities.

The absence of an observable change in the T^3 term is at first thought somewhat surprising since the mass of the Ni atom is much greater than that of the Be atom. This interesting result may be understood from the following argument. As a result of the large mass difference one would expect localized phonon modes to appear at an energy

$$E \sim \left(\frac{m}{M}\right)^{1/2} k\Theta_D \sim 450^\circ\text{K},$$

where m is the Be mass, M the Ni mass, k the Boltzmann constant and Θ_D the Be Debye temperature. Because the mass difference is so great one would expect these modes to be quite narrow. Consequently their contribution to the specific heat at low temperatures would be of the Einstein form and exponentially

small in the liquid-helium range ($\sim e^{-100}$). At high temperatures such modes would contribute to the specific heat although separating this contribution from the normal Debye background might prove difficult.

The susceptibility was measured by the Faraday technique using a calibrated inhomogeneous field and a sensitive electronic balance. Measurements were taken as a function of magnetic field, and the results plotted on a Honda-type graph of χ versus $1/H$. The extrapolated value to infinite H gives the true susceptibility, and the slope of the line measures the residual ferromagnetic moment due to contamination, precipitation, etc. Typical data for the most concentrated alloy, 2.2 at.% Ni, are shown in Fig. 2. The total susceptibility is diamagnetic as a result of the large diamagnetic susceptibility of the host metal.¹¹ Assuming that the small slope arises from precipitated Ni, one concludes that only about 10^{-3} of the total 2.2 at.% Ni present is in the form of Ni metal. This negligible amount of precipitated Ni gives some indication of the homogeneity of the alloys. The susceptibility shown in Fig. 2 is temperature-independent. Similar data were obtained for the more dilute alloys. The susceptibility for pure Be was obtained from an appropriate average of the parallel and perpendicular susceptibilities¹¹ assuming a random array of crystallites in the arc melted alloy. The small temperature dependence of the average susceptibility of pure Be disappears with the addition of increasing amounts of Ni. The dominant feature of the data is therefore a large and, to within the experimental accuracy, linear change in susceptibility with increasing concentration of Ni impurities as if each Ni atom contributes a large paramagnetic susceptibility to the alloy. The room temperature susceptibility as a function of Ni concentration is shown in Fig. 3.

The specific heat and magnetic susceptibility results are summarized in Fig. 4. Both χ/μ^2 and the true density of states as determined directly from the specific heat data are given as a function of impurity concentration for dilute solutions of Ni in Be. A diamagnetic correc-

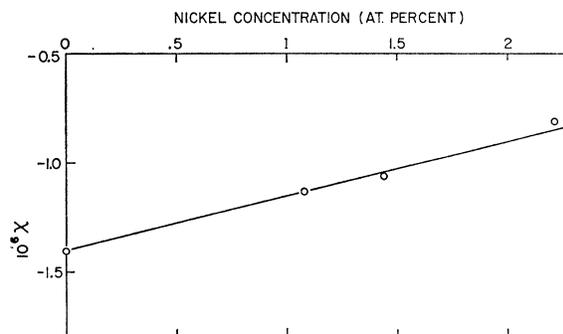


FIG. 3. Gram susceptibility of Be:Ni alloys as a function of Ni concentration.

¹¹ B. L. Varkin, L. M. Dmitrenko, and L. V. Svehkarev, *Zh. Eksperim. i Teor. Fiz.* **40**, 670 (1961) [English transl.: *Soviet Phys.—JETP* **13**, 468 (1961)].

tion has been made to the susceptibility such as to give the true density of states for pure Be.⁸ The results therefore indicate an enhancement of the added susceptibility due to the nickel impurities with an enhancement factor approximately equal to 6. In presenting the results in this manner, it is assumed that the host metal susceptibility is not changed with the addition of the nickel impurities. This point will be discussed at some length in following sections.

The residual resistivity of a similar set of dilute alloys was measured by the standard four-terminal technique. The samples were in the form of wires, 2 mm in diameter and 3 cm in length to which leads were attached with indium solder. Data were taken above 4.2°K by boiling off helium and following the slow temperature rise with a copper-constantin thermocouple. The final results have an estimated error of 10% due principally to uncertainties in sample dimensions and surface irregularities. Figure 5 shows the temperature-independent residual resistivity observed at low temperatures plotted as a function of alloy composition. For a concentration of 1 at.% Ni, $\Delta\rho = 10 \mu\Omega \text{ cm}$.

These results, although somewhat larger in magnitude, are qualitatively similar to those obtained from solution of transition atom impurities in other metals as reviewed by Friedel.⁵ In the following sections we attempt to give a detailed interpretation of the experiments in terms of the more quantitative Anderson model.

III. THE ANDERSON THEORY AND RESONANT SCATTERING

We consider the case of a transition atom impurity with degenerate d orbitals dissolved into a simple metal. This degenerate case was studied briefly by Anderson² in the appendix to his paper and more thoroughly by Yosida *et al.*¹² We shall review the theory here since the results will be needed in later sections, and in order to explicitly make a connection with the

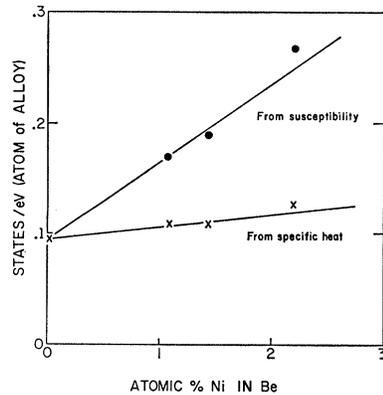


FIG. 4. True density of states as measured by specific heat and apparent density of states as measured by susceptibility for dilute alloys of Ni in Be.

¹² K. Yosida, A. Okijo, S. Chikazumi, *Progr. Theoret. Phys.* Kyoto 33, 559 (1965).

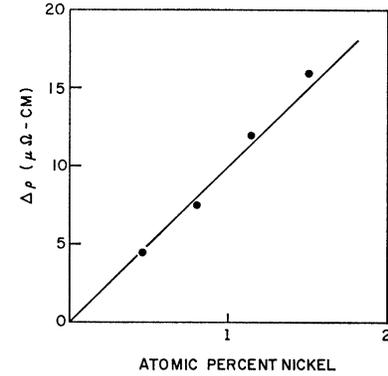


FIG. 5. Residual resistivity of $\frac{1}{2}$ Be:Ni alloys as a function of the concentration of nickel impurities.

scattering approach to the problem. The Anderson Hamiltonian for the localized transition atom d orbitals and the host-metal conduction electrons takes the form

$$H = H_s + H_d + H_{sd}, \quad (1)$$

where

$$H_s = \sum_{k\sigma} E_k C_{k\sigma}^\dagger C_{k\sigma}, \quad (2)$$

$$H_d = \sum_{m\sigma} E_m^0 C_{m\sigma}^\dagger C_{m\sigma} + (U - J) \sum_{m < n, \sigma} C_{m\sigma}^\dagger C_{m\sigma} C_{n\sigma}^\dagger C_{n\sigma} + U \sum_{m,n} C_{m\sigma}^\dagger C_{m\sigma} C_{n-\sigma}^\dagger C_{n-\sigma}, \quad (3)$$

$$H_{sd} = \sum_{km\sigma} (V_{km} C_{k\sigma}^\dagger C_{m\sigma} + V_{mk} C_{m\sigma}^\dagger C_{k\sigma}). \quad (4)$$

H_s and H_d are the Hamiltonians for the conduction electrons and the d electrons, respectively, and H_{sd} represents the s - d mixing interaction. The C^\dagger and C are the usual creation and destruction operators with subscripts k denoting the conduction electron wave vector, σ denoting the spin, and m or n labeling the various d orbitals. E_k are the host-metal conduction electron state energies and E_m^0 are the d -state energies in the metal. U and J are the Coulomb and exchange integrals as defined above, and V_{mk} is the admixture matrix element between d states and conduction-electron states.

The solutions to the above Hamiltonian are readily obtained using the Green's function technique as shown by Anderson. In the degenerate case considered here the coupled Green's function equations take the form, in the Hartree-Fock approximation

$$(\epsilon - E_{m\sigma}) G_{mn}^\sigma = \delta_{mn} + \sum_k V_{mk} G_{kn}^\sigma, \quad (5)$$

$$(\epsilon - E_k) G_{kn}^\sigma = \sum_m V_{km} G_{mn}^\sigma, \quad (6)$$

$$(\epsilon - E_{m\sigma}) G_{mk}^\sigma = \sum_{k'} V_{mk} G_{k'k}^\sigma, \quad (7)$$

$$(\epsilon - E_{k'}) G_{k'k}^\sigma = \delta_{k'k} + \sum_m V_{k'm} G_{mk}^\sigma. \quad (8)$$

The resulting Green's functions for the virtual d levels

and conduction-band states are

$$G_{mm}^\sigma = \left[\epsilon - E_{m\sigma} - \sum_k \frac{|V_{mk}|^2}{\epsilon - E_k} \right]^{-1} = [\epsilon - E_{m\sigma} - \Sigma(\epsilon)]^{-1}, \quad (9)$$

$$G_{kk}^\sigma = (\epsilon - E_k)^{-1} + \frac{\sum_m |V_{mk}|^2 G_{mm}^\sigma}{(\epsilon - E_k)^2}. \quad (10)$$

In decoupling Eqs. (5) through (8) we have used the identity

$$\sum_k \frac{V_{mk} V_{kn}}{\epsilon - E_k} = \delta_{mn} \sum_k \frac{|V_{mk}|^2}{\epsilon - E_k},$$

the proof of which follows by writing the quantity on the left in the form of a matrix element

$$[V[1/(\epsilon - H_s)]V]_{mn}.$$

V is the admixture interaction and H_s is the host electron energy operator. The operator in the brackets must have the lattice symmetry and thus is invariant under all the operations of the point-symmetry group. Since the d -function spherical harmonics form bases for representing these operations, nondiagonal matrix elements of the operators vanish.¹³ The d -state energies are given by

$$E_{m\sigma} = E_m^0 + (U - J) \sum_{n \neq m} N_{n\sigma} + U \sum_n N_{n-\sigma}. \quad (11)$$

$N_{m\sigma}$ is the occupation number for the level $m\sigma$, and $\Sigma(\epsilon)$ is the self-energy of the interacting system. The total number of electrons at $T = 0^\circ\text{K}$ is given by

$$\begin{aligned} N_{\text{tot}} &= \sum_{k\sigma} N_{k\sigma} + \sum_{m\sigma} N_{m\sigma} \\ &= -\frac{1}{\pi} \int_0^{E_f} \text{Im} \sum_{k\sigma} \frac{1}{\epsilon - E_k} d\epsilon \\ &\quad - \frac{1}{\pi} \int_0^{E_f} \text{Im} \sum_{m\sigma} \left[\frac{1 - (d/d\epsilon)\Sigma(\epsilon)}{\epsilon - E_{m\sigma} - \Sigma(\epsilon)} \right] d\epsilon. \end{aligned} \quad (12)$$

Assuming an energy-dependent host-metal density of states $\rho(\epsilon)$ and writing

$$\Sigma(\epsilon) = \Delta E_m - i\Delta(\epsilon), \quad (13)$$

where $\Delta(\epsilon) = \pi \langle V^2 \rangle_{\text{av}} \rho(\epsilon) / 2$ is the width of the virtual level, Eq. (12) becomes

$$\begin{aligned} N_{\text{tot}} &= \int_0^{E_f} \rho(\epsilon) d\epsilon - \frac{1}{\pi} \int_0^{E_f} \text{Im} \sum_{m,\sigma} \frac{d}{d\epsilon} \ln[\epsilon - E_{m\sigma} + i\Delta(\epsilon)] d\epsilon \\ &= N_0 + \frac{1}{\pi} \sum_{m\sigma} \cot^{-1} \frac{E_{m\sigma} - E_f}{\Delta(E_f)}, \end{aligned} \quad (14)$$

where the real part of the self-energy has been included

¹³ M. Tinkham, *Group Theory and Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1964), p. 80.

in $E_{m\sigma}$. Thus, the total number of occupied states introduced by the impurity is

$$N = N_{\text{tot}} - N_0 = \sum_{m\sigma} N_{m\sigma}' = \frac{1}{\pi} \sum_{m\sigma} \cot^{-1} \frac{E_{m\sigma} - E_f}{\Delta(E_f)}. \quad (15)$$

We assume throughout the paper a complete fivefold orbital degeneracy so that $E_{m\sigma} = E_d^\sigma$ for all m . This assumption requires that any crystal field splitting be less than a virtual level width and is in agreement with experiment as discussed by Yosida *et al.*¹³ In this case, Eq. (15) reduces to

$$N = 5 \sum_{\sigma} N_{\sigma}' = \frac{5}{\pi} \sum_{\sigma} \cot^{-1} \frac{E_d^\sigma - E_f}{\Delta(E_f)}. \quad (16)$$

The d -state density at the Fermi level is, in the nonmagnetic case,

$$\begin{aligned} \rho_d(E_f) &= -\frac{10}{\pi} \text{Im} G_{dd}(E_f) \\ &= \frac{10}{\pi} \frac{\Delta(E_f)}{(E_f - E_d)^2 + \Delta^2(E_f)} = 10 \frac{\sin^2(\pi N/10)}{\pi \Delta(E_f)}. \end{aligned} \quad (17)$$

The resulting system is characterized by a set of virtual levels in the continuum. In the nonmagnetic case the parameters needed to describe these virtual levels are the width, $\Delta(E_f)$, the number of occupied states introduced by the impurity, N [or equivalently $(E_d - E_f)$], and the integrals U and J defined above. Physically, one expects N to be simply the number of d electrons initially on the transition group atom when outside the metal in order that the system be locally neutral.

Let us re-examine the transition atom impurity problem from the point of view of scattering theory. When an impurity atom of higher nuclear charge is substituted for an atom of the host metal, a number of outer electrons corresponding to those shells whose atomic energies lie within the host-metal conduction band will be de-localized and go off into the conduction band. Consequently, there will result an excess charge Ze at the impurity site. The electrostatic field around the impurity will locally perturb the metal, and the conduction-electron wavefunctions must be recalculated as solutions of the Schrödinger equation for motion in the self-consistently screened impurity potential. Although the carrying out of such a first principles calculation would be extremely difficult, in the spirit of the Friedel-Anderson model we expect to find virtual bound states at energies E_d within the conduction band. When a conduction electron approaches the impurity site with an energy near E_d it will be caught and resonantly scattered before going off once again. In general if the host metal is treated in the nearly free-electron approximation, the solutions outside the region of the impurity

potential are simply phase-shifted outgoing spherical waves as would be expected on the basis of scattering theory. For incident energies far from the resonance energies the phase shifts are small, and are the result of simple potential scattering. However, for energies near the resonance energy, the particular phase shift corresponding to the angular momentum l of the resonant state will be large. Such resonance scattering is well known in nuclear physics, and in fact the corresponding phase shifts were first calculated by Breit and Wigner¹⁴ for the compound nucleus problem. The Breit-Wigner formalism gives the result

$$\eta_l^{\text{Resonant}} = \cot^{-1}[(E_0 - \epsilon)/\Delta(\epsilon)], \quad (18)$$

where E_0 is the resonance energy corresponding to a virtual bound state with angular momentum l and width Δ . In the case of the transition atom impurity, $l=2$ and $E_0 = E_d^\sigma$ are the energies of the virtual d states with spin σ . We shall assume a fivefold orbital degeneracy but allow E_d^σ and $E_d^{-\sigma}$ to be different corresponding to a possible magnetic state for the impurity atom. Thus,

$$\begin{aligned} \eta_l &= \eta_l^0, & l \neq 2 \\ &= \eta_l^0 + \cot^{-1}[(E_d^\sigma - \epsilon)/\Delta(\epsilon)], & l = 2 \end{aligned} \quad (19)$$

where η_l^0 are the nonresonant phase shifts resulting from potential scattering.

As a result of the above scattering process, charge accumulates in the vicinity of the impurity and locally screens the impurity potential. Friedel has considered this screening process in detail and derived a self-consistency condition relating the phase shifts to the perturbing charge difference Z . The Friedel sum rule¹⁵ is thus generally valid and requires that

$$Z = - \sum_{\pi} \sum_{\sigma} \sum_l (2l+1) \eta_l(E_f), \quad (20)$$

where the phase shifts are to be evaluated at the Fermi energy, E_f . Using Eq. (19) for the phase shifts η_l , the sum rule becomes

$$Z = - \sum_{\pi} \sum_{\sigma l} (2l+1) \eta_l^0(E_f) + \sum_{\pi} \sum_{\sigma} \cot^{-1} \frac{E_d^\sigma - E_f}{\Delta(E_f)}. \quad (21)$$

We show in Appendix A that to a good approximation in real metals the nonresonant phase shifts are small relative to the resonant term and may be neglected. Consequently, the above reduces to

$$Z = - \sum_{\pi} \sum_{\sigma} \cot^{-1} [(E_d^\sigma - E_f)/\Delta(E_f)]. \quad (22)$$

The quantity on the right is recognized as the Anderson expression for the number of localized electrons in the orbitally degenerate case as given in Eq. (16) above, so that

$$Z = 5 \sum_{\sigma} N_{\sigma}', \quad (23)$$

where N_{σ}' is the total occupation number common to each of the virtual levels of given spin. To this approximation, the electrons in the virtual bound states at the impurity site exactly neutralize the excess charge and consistency with the Friedel sum rule is achieved.

The conclusions are therefore obvious. The total number of electrons localized near the transition atom impurity in the metal is determined only by the excess charge Z , and thus increases uniformly as one goes across the $3d$ series from Ti to Ni. The above arguments justify the intuitive expectations that the number of d -electrons is determined by charge neutrality and indicate that the Anderson resonance energies must be self-consistently calculated within the metal. The Anderson theory can in the above manner be made consistent with the Friedel sum rule despite earlier comments to the contrary.

In the case of solution of transition group atoms into simple metals where the above theory may be expected to be valid there is considerable evidence that Eq. (23) holds. In particular, when the transition atom possesses a magnetic moment, e.g., Mn in Cu or Fe in Cu, the moment is very close to the free atom spin only value¹⁶ so that $N = Z$. We shall give evidence below that the condition holds in the nonmagnetic case as well.

Examination of the Anderson theory indicates that for the Friedel self-consistency condition to hold in different host metals the unperturbed d -state energies E_m^0 must effectively track the Fermi energy. The physical mechanism by which this takes place is clearly of interest. If E_m^0 did not have the proper value, the excess charge would have to be screened by the conduction electrons. Such a process would necessarily be at the expense of the conduction electron kinetic energy. An estimate of this screening energy may be obtained from studies of vacancy energies in Cu¹⁷ which indicate that it takes approximately 1 eV per charge for such screening. The over-all energy of the system can therefore be minimized if the "atomic energies" E_m^0 are made to track the Fermi energy by a self-consistent calculation within the metal. The real part of the self-energy also shifts the d -state energies somewhat, and may contribute to this effect.

In following sections we calculate the residual resistivity, specific heat, and susceptibility due to the transition atom impurities with the above ideas in mind, and compare the results with experimental observations as described in Sec. II.

¹⁴ L. D. Landau and E. M. Lifschitz, *Quantum Mechanics* (Addison-Wesley Publishing Company, Inc., Reading, Massachusetts, 1958), p. 440.

¹⁵ C. Kittel, *Quantum Theory of Solids* (John Wiley & Sons, Inc., New York, 1963), p. 112.

¹⁶ J. Owen, M. E. Browne, V. Arp, and A. F. Kip, *J. Phys. Chem. Solids* 2, 85 (1957).

¹⁷ W. M. Lomer, *Progress in Metal Physics* (Pergamon Press, Ltd., London, 1959), Vol. 8, p. 284.

IV. RESIDUAL RESISTIVITY

The treatment of the impurity problem from a resonant scattering approach suggests that the transition atom impurities will strongly affect the conduction electron mean free path and thereby change the residual resistivity. For a nearly free electron metal the resistivity is given by

$$\Delta R = \frac{m^*}{ne^2} \frac{1}{\tau(E_f)}, \quad (24)$$

where n is the number of carriers per unit volume, m^* and e their effective mass and charge, and $1/\tau(E_f)$ the collision frequency at the Fermi surface. For n_i impurities, the spin-averaged collision frequency is

$$\frac{1}{\tau(E_f)} = \frac{2n_i}{\hbar} \left[\frac{1}{2} \sum_{\sigma} \text{Im} G_{kk}^{\sigma}(E_f)^{-1} \right], \quad (25)$$

where G_{kk}^{σ} is the conduction electron Green's function in the presence of an impurity and is given by Eq. (10). Equation (25) for $1/\tau(E_f)$ assumes the n_i impurities scatter independently; a good approximation at low concentrations. To lowest order,

$$G_{kk}^{\sigma}(\epsilon)^{-1} = (\epsilon - E_k) - \sum_m |V_{mk}|^2 G_{mm}^{\sigma}(\epsilon) \quad (26)$$

from which the residual resistivity is determined as

$$\Delta R = \frac{n_i}{n} \left(\frac{2m^*}{\pi e^2 \hbar \rho} \right) \sum_{m,\sigma} \sin^2 \pi N_{m\sigma}'. \quad (27)$$

ρ is the host metal density of states at the Fermi level. In the case of a free-electron approximation for the host metal the above result reduces to that of the Friedel partial-wave analysis.⁵ For the nonmagnetic case $N_{m\sigma}' = N/10$ and Eq. (27) reduces to

$$\Delta R = \frac{20n_i}{n} \left(\frac{m^*}{\pi e^2 \hbar \rho} \right) \sin^2 \left(\frac{\pi N}{10} \right). \quad (28)$$

Substitution of the host metal parameters n , m^* , and ρ into this expression allows a determination of $\sin^2(\pi N/10)$ from the measured residual resistivity.

In the present case of Be as the host metal, it is clear that a free-electron treatment is a very crude and inaccurate approximation. The two s electrons per atom lead to a filled s band, and were it not for a small amount of overlap with higher bands, divalent Be would be an insulator. Detailed band structure calculations¹⁸ confirm these expectations and give a Fermi surface in close agreement with experiment. In addition Hall effect measurements¹⁹ give a large positive Hall coefficient

¹⁸ T. Loucks and P. H. Cutler, Phys. Rev. **133**, A819 (1964); **134**, A1618 (1964).

¹⁹ C. Kittel, *Introduction to Solid State Physics* (John Wiley & Sons, Inc., New York, 1961), p. 298.

indicating that the conductivity arises from holes at the top of the s band, and that only of the order of 10% of the total number of valence electrons are effective in conductivity. Using this information together with the measured density of states and an effective mass equal to the thermal mass, one finds from the measured value of $10 \mu\Omega\text{-cm}$ per at. % N_i

$$\sin^2 \left(\frac{\pi N}{10} \right) \approx 0.14$$

corresponding to $N = 8.7$. The resistivity measurements therefore indicate that the number of d electrons per nickel atom is between 8 and 9 in rough agreement with the Friedel sum rule and that the anomalously large resistivity due to Ni in Be is the result of the small number of carriers in the Be conduction band.

We take special note of the fact that to within the experimental accuracy the residual resistivity is a linear function of the Ni concentration. This strongly suggests that the addition of the small concentrations of Ni does not significantly change the number of carriers, but only affects their relaxation time. This is not surprising in view of the above result for N which indicates that each nickel atom contributes between one and two conduction electrons to the Be conduction band. Since the number of carriers is thus almost unchanged we may expect that the host metal contribution to the specific heat and susceptibility will be unaltered, so that any changes observed in these quantities may be attributed to the localized states on the impurity atoms.

V. SPECIFIC HEAT AND MAGNETIC SUSCEPTIBILITY

A. Specific Heat

The increased density of states at the Fermi level resulting from the added impurity atoms will clearly alter the low-temperature specific heat of the metal. In the following paragraphs we calculate the alloy specific heat when the host metal density of states is energy-dependent.

The internal energy associated with the nearly free electrons of the host metal, since they are assumed non-interacting, is

$$\bar{\epsilon}_h = \int_0^{\infty} \epsilon f(\epsilon) \rho(\epsilon) d\epsilon,$$

where $f(\epsilon)$ is the Fermi-Dirac distribution function. The internal energy associated with the " d " electrons is more complex because of the interaction term. One must take care not to include this interaction energy twice. To see how the contribution to the internal energy from the d -electron part of the Hamiltonian must be calculated we assume, initially, that there is no s - d mixing; i.e., $V_{kd} = 0$, and consider the simple case of a nondegenerate orbital. Under these conditions the

d states are exact and there is no problem in calculating the internal energy. The d -state density is a δ function,

$$\rho_d = 2\delta[\epsilon - (E_0 + UN)],$$

where the factor of 2 arises from spin degeneracy and $N = N_+ = N_-$. We compute the term

$$\int_0^\infty \epsilon f(\epsilon) \rho_d(\epsilon) d\epsilon.$$

Assuming $E_d = (E_0 + UN) < E_F$ so that the d levels are occupied,

$$\int_0^\infty \epsilon f(\epsilon) \rho_d d\epsilon = 2(E_0 + UN) = 2(E_0 + U),$$

since in this case $N_+ = N_- = 1$. However, since the d states are exact in this limit, it is clear that the *actual* d -state energy is $2E_0 + U$. In other words, we have counted the interaction energy twice in the above prescription. To correct this consider the integral

$$\int_0^\infty (\epsilon - \frac{1}{2}UN) f(\epsilon) \rho_d(\epsilon) d\epsilon = 2(E_0 + U) - U = 2E_0 + U.$$

This clearly is the correct expression for the d -state internal energy in the absence of the s - d mixing interaction. Thus, when $V_{kd} = 0$ the total internal energy may be written

$$\bar{\epsilon} = \int_0^\infty \epsilon f(\epsilon) (\rho + \rho_d) d\epsilon - UN^2. \quad (29)$$

The effect of turning on the s - d admixture is to broaden the d level into a virtual level and to locally perturb the conduction electron charge density. Under these conditions the exact states of the system are not host band states and simple d states as above, and the argument is no longer rigorous. However, one physically expects that the s - d mixing will not affect the internal energy other than to allow the virtual d electrons to occupy a band of energies as described by Anderson's d -state density and possibly to alter the conduction-electron state density near the resonance energy. This will not affect the interaction energy, and one expects the above expression for $\bar{\epsilon}$ to be valid. To justify this argument, it is necessary to explicitly calculate the internal energy in terms of the exact energy states of the system. This has been done by Scalapino, Schrieffer, and Kjollerstrom,²⁰ and they obtain results equivalent to the above in the Hartree-Fock limit. This argument is easily generalized to the orbitally degenerate case

²⁰ D. Scalapino, J. R. Schrieffer, and B. Kjollerstrom (to be published).

where

$$\bar{\epsilon} = \int_0^\infty \epsilon f(\epsilon) (\rho + \rho_i) d\epsilon - (U - J) \sum_{m < n, \sigma} N_{m\sigma} N_{n\sigma} - U \sum_{m, n} N_{m\sigma} N_{n-\sigma}. \quad (30)$$

In the above expression ρ_i is the change in the density of states due to the impurities present, and may be obtained from the Green's functions given in Eqs. (9) and (10).

$$\rho_i = -\frac{1}{\pi} \text{Im} \sum_{m\sigma} \left[\frac{1 - (d/d\epsilon)\Sigma(\epsilon)}{\epsilon - E_{m\sigma} - \Sigma(\epsilon)} \right]. \quad (31)$$

Using the usual low-temperature expansion,²¹ the mean energy becomes

$$\bar{\epsilon} = \int_0^{E_f} \epsilon (\rho + \rho_i) d\epsilon + \frac{\pi^2}{6} (kT)^2 \left[\epsilon \frac{d}{d\epsilon} (\rho + \rho_i) + (\rho + \rho_i) \right]_{E_f} - (U - J) \sum_{m < n, \sigma} N_{m\sigma} N_{n\sigma} - U \sum_{m, n} N_{m\sigma} N_{n-\sigma}. \quad (32)$$

The specific heat is then

$$C = \frac{d\bar{\epsilon}}{dT} = \frac{dE_f}{dT} (\rho + \rho_i) + \int_0^{E_f} \epsilon \frac{d\rho_i}{dT} d\epsilon + \frac{\pi^2}{3} k^2 T \left[\epsilon \frac{d}{d\epsilon} (\rho + \rho_i) + (\rho + \rho_i) \right]_{E_f} - (U - J) \sum_{m \neq n, \sigma} N_{m\sigma} \frac{dN_{n\sigma}}{dT} - U \sum_{m, n, \sigma} N_{m\sigma} \frac{dN_{n-\sigma}}{dT}. \quad (33)$$

The total number of electrons is conserved.

$$N_{\text{tot}} = \int_0^{E_f} (\rho + \rho_i) d\epsilon + \frac{\pi^2}{6} (kT)^2 \frac{d}{d\epsilon} (\rho + \rho_i) \Big|_{E_f}. \quad (34)$$

$$\frac{dN_{\text{tot}}}{dT} = 0 = \frac{dE_f}{dT} (\rho + \rho_i) + \int_0^{E_f} \frac{d\rho_i}{dT} d\epsilon + \frac{\pi^2}{3} k^2 T \frac{d}{d\epsilon} (\rho + \rho_i) \Big|_{E_f}. \quad (35)$$

Substitution into the specific-heat expression yields

$$C = \frac{\pi^2}{2} k^2 T (\rho + \rho_i) + \int_0^{E_f} (\epsilon - E_f) \frac{d\rho_i}{dT} d\epsilon - (U - J) \sum_{m \neq n, \sigma} N_{m\sigma} \frac{dN_{n\sigma}}{dT} - U \sum_{m, n, \sigma} N_{m\sigma} \frac{dN_{n-\sigma}}{dT}. \quad (36)$$

The second term on the right may be integrated using

²¹ F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), p. 150.

Eq. (31) for ρ_i

$$\begin{aligned} & \int_0^{E_f} (\epsilon - E_f) \frac{d\rho_i}{dT} d\epsilon \\ &= -\frac{1}{\pi} \text{Im} \sum_{m\sigma} \left[\int_0^{E_f} (\epsilon - E_f) \frac{(1 - (d/d\epsilon)\Sigma(\epsilon)) dE_{m\sigma}}{(\epsilon - E_{m\sigma} - \Sigma(\epsilon))^2} d\epsilon \right] \\ &= -\frac{1}{\pi} \text{Im} \sum_{m\sigma} \frac{dE_{m\sigma}}{dT} \left[\int_0^{E_f} (\epsilon - E_f) \frac{d}{d\epsilon} \left(\frac{1}{\epsilon - E_{m\sigma} - \Sigma(\epsilon)} \right) d\epsilon \right] \\ &= \sum_{m\sigma} \frac{dE_{m\sigma}}{dT} \left[\int_0^{E_f} \epsilon \frac{d}{d\epsilon} \left(\frac{\rho_d}{10} \right) d\epsilon - E_f \int_0^{E_f} \frac{d}{d\epsilon} \left(\frac{\rho_d}{10} \right) d\epsilon \right] \\ &= \sum_{m\sigma} \frac{dE_{m\sigma}}{dT} \frac{N_d}{10}, \end{aligned}$$

where N_d is the number of occupied d states on the impurity. Noting Eq. (11) for $E_{m\sigma}$, one finds for the specific heat the particularly simple result

$$C = C_{\text{host}} + \frac{\pi^2}{3} k^2 T \rho_i(E_f), \quad (37)$$

with ρ_i as defined in Eq. (31) given by

$$\rho_i = \rho_d(E_f) \left[1 - \frac{(E_f - E_d)}{\rho(E_f)} \frac{d\rho(E_f)}{d\epsilon} \right]. \quad (38)$$

It is to be noted that the above expression differs from Anderson's² Eq. (59) for the specific heat. The anomalous term in the Anderson expression arises from improper handling of the interaction terms in the Hamiltonian.

From Eq. (37) for the specific heat we see that the addition of dilute impurities to the host metal will result in a change in the linear term in the alloy specific heat. In the simple case where

$$\left| \frac{(E_f - E_d)}{\rho(E_f)} \frac{d\rho(E_f)}{d\epsilon} \right| \ll 1, \quad (39)$$

the increase in the linear term of the specific heat measures directly the total d -state density at the Fermi energy, $\rho_d(E_f)$ as defined in Eq. (17). This inequality will hold for simple metals where the density of states is slowly varying as a function of energy. For the noble metals as hosts the above inequality will surely hold. In the particular case of interest here, the host metal density of states does vary with energy as a result of the nearly filled s band of Be.¹⁸ Detailed band-structure calculations have been performed with the result that the Fermi energy occurs almost precisely at a minimum in the density of states.¹⁸ The value of the Fermi energy determined by these calculations is quite accurate as a result of using the equality of the number of electrons

and holes as the criterion for determining the Fermi energy. Thus, if the gross features of the calculated density of states curve are correct for Be, it would appear that the inequality (39) holds. In what follows we shall assume this to be the case, so that the specific heat becomes

$$C = C_{\text{host}} + c \frac{\pi^2}{3} k^2 T \rho_d(E_f), \quad (40)$$

where c is the impurity concentration. We have argued above in connection with resistivity results that the host metal contribution to the linear term in the specific heat will be unchanged by the addition of small concentrations of nickel impurity atoms. The experimental results were described in Sec. II. From Fig. 4 we see that there is experimentally an easily observable increase in the density of states. Attributing this increase to the added d -state density one finds, using Eq. (40)

$$\rho_d = 1.15 \text{ states per eV per Ni atom.}$$

The accuracy of the specific-heat measurements is quite good ($<2\%$) and judging from the scatter of the data points about the straight line of Fig. 4, the over-all accuracy of the above value for ρ_d is of 10%. Applying Eq. (17) for ρ_d

$$\rho_d = 10 \frac{\sin^2(\pi N/10)}{\pi \Delta}$$

and taking the value for $\sin^2(\pi N/10)$ determined from the residual resistivity one finds

$$\Delta \simeq 0.4 \text{ eV.}$$

Furthermore, using the expression for the level width $\Delta = \pi \langle V^2 \rangle_{av} \rho / 2$ one finds $\langle V^2 \rangle_{av} \simeq 3(\text{eV})^2$, a somewhat small, but not unreasonable, value.

B. Magnetic Susceptibility

The magnetic susceptibility of the system may be calculated directly from the occupation numbers of the localized up and down d electrons. The orbital moment is found to be quenched by the s - d mixing interaction rather than the crystal field as discussed in detail by Yosida *et al.*¹² However, there will in general be an induced orbital moment due to the spin-orbit coupling which comes in second order and can be expressed as a change in g value, Δg . Δg has been estimated by Yosida *et al.*¹² to be of the order of 0.2 and therefore constitutes a negligibly small correction to the susceptibility. We shall assume that the host electron susceptibility is not altered by the addition of the transition atom impurities. As argued above, this assumption appears to be valid at low Ni concentrations since each Ni contributes between one and two electrons to the Be conduction band and leaves the number of carriers unchanged to within the experimental accuracy. The change in the population resulting from the application

of a magnetic field H in the nonmagnetic case is, for a single impurity,

$$\delta N_+ - \delta N_- = -\frac{1}{\pi} \sum_m (\delta E_{m+} - \delta E_{m-}) \times \int_0^{E_f} \text{Im} \frac{1 - (d/d\epsilon)\Sigma(\epsilon)}{[\epsilon - E_m - \Sigma(\epsilon)]^2} d\epsilon. \quad (41)$$

The corresponding energy shifts are

$$\delta E_{m\pm} = \mp \mu H + (U - J) \sum_{n \neq m} \delta N_{n\pm} + U \sum_n \delta N_{n\mp}. \quad (42)$$

Then

$$\delta N_+ - \delta N_- = \mu H \rho_d + (U + 4J) \frac{\rho_d}{10} (\delta N_{d+} - \delta N_{d-}). \quad (43)$$

Because of the Anderson compensation effect $\delta N_+ - \delta N_- = \delta N_{d+} - \delta N_{d-}$ [see Anderson's Eq. (47)] and the d -state contribution to the susceptibility is

$$\chi_d = \frac{\mu}{H} (\delta N_{d+} - \delta N_{d-}) = \frac{\mu^2 \rho_d}{1 - (U + 4J)\rho_d/10} = \eta \mu^2 \rho_d(E_f), \quad (44)$$

where η is the enhancement factor defined by the above equation. The total susceptibility for a concentration c of impurities is therefore

$$\chi = \chi_{\text{host}} + c\eta\mu^2\rho_d. \quad (45)$$

Note that in the degenerate case the Anderson criterion for formation of a magnetic state is equivalent to requiring that the denominator of Eq. (44) vanish, at which point the zero-temperature susceptibility diverges as expected on physical grounds.

The experimental results for dilute solutions of N_i in Be were described in some detail in Sec. II. Figure 4 shows that the increase in susceptibility due to the addition of Ni impurities is enhanced by comparison with the true change in density of states as obtained from specific heat. From this figure, assuming the Anderson model as described above, one finds

$$\eta^{-1} = 1 - (U + 4J)(\rho_d/10) = 0.16,$$

with $\rho_d = 1.15$ states per eV per atom of Ni. Combining these results one obtains

$$U + 4J \simeq 7.3 \text{ eV}.$$

The limits of error on the above value for $(U + 4J)$ seem to be set by the homogeneity of the samples themselves rather than on the susceptibility and specific-heat measurements as indicated by the deviations of the experimental points from the indicated straight lines. However, the above value appears to be accurate to about 10%; or in the range 6 to 8 eV.

VI. DISCUSSION

One concludes from the interpretation of the experimental results in terms of the Anderson model that the quantity

$$(U + 4J)/\Delta \gg 1$$

in the system Be:Ni with the magnitudes of the individual quantities as given above. This conclusion rests on two fundamental assumptions:

(i) The host-metal density of states is slowly varying at the Fermi level.

(ii) The host-metal specific heat and susceptibility are unchanged when a small concentration of nickel impurities is added.

Both of these assumptions appear to be valid as argued above, and small effects will not alter the final conclusion. The most serious error undoubtedly arises from assumption (ii) since the large diamagnetic susceptibility of pure Be may be sensitive to small changes in the number of electrons or holes. In fact, one possible indication of this may be the disappearance of the small temperature dependence of the average susceptibility found in pure Be with the addition of Ni. It is impossible to be quantitative in this regard, but we note that an error in the d -state contribution to the susceptibility and consequently the enhancement factor η , by as much as a factor of 2 only reduces the value of $(U + 4J)$ to 6.1 eV which is within the estimated limits. Furthermore, we shall see that analysis of data for the Cu:Ni system leads one to the same conclusion concerning the magnitudes of $(U + 4J)$ and Δ .

A similar experimental study of dilute Cu:Ni alloys was made some time ago.^{22,23} In connection with ideas of this paper copper is a simple host in that the density of states at the Fermi level is certainly slowly varying, and the host susceptibility is insensitive to small changes in the number of electrons. One clear disadvantage is the partial d character of the conduction electrons at the Fermi surface resulting from the filled Cu d band which lies of the order of 3.5 eV below the Fermi energy. Measurements of residual resistivity²² for Ni in Cu give $\Delta\rho = 1.25 \mu\Omega\text{-cm/at.}\%$ Ni. If one substitutes the appropriate parameters for Cu ($m^* \sim 1$, $n = 1/\text{atom}$ and the measured density of states) into Eq. (28), the result is

$$\sin^2(\pi N/10) = 0.1$$

or $N = 9$ electrons again in agreement with the Freidel sum rule. Unfortunately, specific-heat data at Ni concentrations below 10% Ni in Cu are not available making an estimate of ρ_d somewhat difficult. Analysis of the existing data²³ indicates a value for ρ_d of about 1 state/eV per Ni atom which applying Eq. (17) gives a value for Δ of about 0.3 eV. Finally, the enhancement factor is estimated from susceptibility and specific-heat

²² Linde, Ann. Physik **15**, 219 (1932).

²³ E. Pugh and F. M. Ryan, Phys. Rev. **111**, 1038 (1958).

data to be about²³ 3 yielding a value of $(U+4J)$ of about 6 eV. The results for Cu:Ni are thus fully consistent with those obtained from the Be alloys.

The resulting value of $(U+4J)$ is to be compared with a free-atom value of more than 20 eV.²⁴ However, a significant reduction in the metal is not surprising. In particular, there are two obvious mechanisms by which the Coulomb and exchange integrals may be reduced in the metal: firstly, simple screening by the nearby conduction electrons, and secondly, by many-body correlation effects. Although a detailed estimate is difficult, a reduction by a factor of 3 to the observed value due to screening alone does not seem unreasonable. The role of correlation awaits further theoretical work although recent attempts to include two-body effects in the localized moment theory²⁵ as well as the theory of ferromagnetic metals²⁶ predict a relatively large reduction of the effective U and apparently overestimate the correlation.

Finally we return to the basic question of the applicability of the Anderson model and its solution in the Hartree-Fock limit to real alloys. The model, although admittedly schematic, contains the essential physics of the problem, and provided that it is interpreted in a manner consistent with the Friedel sum rule should be applicable to alloys where the host metal is not a transition metal. For transition metal hosts, where the band electrons are d -like, the situation is undoubtedly more complex as evidenced by the recent work of Jaccarino and Walker.²⁷ However, even assuming the basic model, the Hartree-Fock approximation must be examined, for in the limit of large U/Δ a self-consistent average Coulomb interaction may be a poor approximation. Attempts to take many-body effects into account²⁵ indicate that correlation may significantly alter the theoretical conclusions. However, until a solution of the correlation problem including the full d -state degeneracy is achieved, the effect of correlation in the real system will remain unclear.

APPENDIX A

The potential scattering phase shifts at the Fermi energy arising from a central potential $V(r)$ of range a are given by²⁸

$$e^{2i\eta_l^0} = -(j_l - in_l)/(j_l + in_l),$$

²⁴ R. E. Watson, Phys. Rev. **118**, 1036 (1960).

²⁵ J. R. Schrieffer and D. C. Mattis, Phys. Rev. **140**, A1412 (1965).

²⁶ J. Kanemori, Progr. Theoret. Phys. (Kyoto) **30**, 275 (1963).

²⁷ V. Jaccarino and L. R. Walker, Phys. Rev. Letters **15**, 258 (1965).

²⁸ E. Merzbacher, *Quantum Mechanics* (John Wiley & Sons, Inc., New York, 1961), p. 234.

where the spherical Bessel functions j_l and n_l are to be evaluated at the argument $k_F a$. Here k_F is the Fermi momentum. Solving for η_l^0 one finds

$$\tan\eta_l^0 = j_l/n_l.$$

For a Thomas-Fermi potential, $V(r) = (Z/r)e^{-r/a}$, and most metals $k_F a \ll 1$. In copper, for example, $k_F = 0.4 \times 10^8 \text{ cm}^{-1}$ and $a = 0.55 \times 10^{-8} \text{ cm}$. When $k_F a \ll 1$

$$\tan\eta_l^0 = -\frac{(k_F a)^l (k_F a)^{l+1}}{(2l+1)!!(2l-1)!!},$$

$$\eta_l^0 = -\frac{(k_F a)^{2l+1}}{(2l+1)!!(2l-1)!!}.$$

Substituting into the Friedel sum rule we find

$$Z = -\frac{2}{\pi} \sum_l \frac{(k_F a)^{2l+1}}{[(2l-1)!!]^2} + \sum_\sigma \cot^{-1} \frac{E_{d\sigma} - E_f}{\Delta(E_f)}$$

or

$$Z = -\frac{5}{\pi} \sum_\sigma \cot^{-1} \frac{E_{d\sigma} - E_f}{\Delta(E_f)} - \frac{2}{\pi} (k_F a) - \frac{2}{\pi} (k_F a)^3 - \dots$$

Since $k_F a$ is small

$$Z \simeq -\frac{5}{\pi} \sum_\sigma \cot^{-1} \frac{E_{d\sigma} - E_f}{\Delta(E_f)}.$$

ACKNOWLEDGMENTS

One of us (A. J. H.) would like to thank the Solid State Physics Group at the Atomic Energy Research Establishment, Harwell, England for their hospitality and cooperation during the period in which this work was begun. Particular thanks are due to Dr. Walter Marshall, Dr. W. M. Lomer, A. D. Leclair, and Dr. H. Montgomery for many stimulating discussions; and to J. Penfold for help with the susceptibility measurements. We gratefully acknowledge the help of Dr. J. White of Atomic Weapons Research Establishment Aldermaston, England who prepared the samples. We wish to thank Professor J. R. Schrieffer and Professor D. J. Scalapino for many discussions on the localized moment problem, and in particular for help in understanding the effect of the Coulomb-exchange interactions on the specific heat. We thank Arnold Marder of Curtis Wright Corporation for providing us with the Be-Ni wires used in the resistivity measurements. Finally, we thank Professor K. Atkins and the U. S. Office of Naval Research for making many of the basic elements of the specific-heat apparatus available to us for these experiments.