[19] T. Smith and S. A. Friedberg, Phys. Rev. 176, 660 (1968).

[20] B. E. Myers, L. Berger, and S. A. Friedberg, J. Appl. Phys. 40, 1149 (1969).

[21] C. A. Raquet, Ph.D. dissertation (Carnegie Institute of Technology, 1967) (unpublished).

[22] L. G. Polgar, Ph.D. dissertation (Carnegie-Mellon University, 1970) (unpublished).

[23] R. H. Sherman, S. G. Sydoriak, and T. R. Roberts, J. Res. Natl. Bur. Std. (U.S.) 68A, 579 (1964).

[24] F. G. Brickwedde, H. van Dyk, M. Durieux, J. R. Clement, and J. K. Logan, J. Res. Natl. Bur. Std. (U.S.) 64A, 1 (1960).

[25] J. R. Clement, E. H. Quinnell, M. C. Steele, R. A. Hein, and R. L. Dolecek, Rev. Sci. Instr. 24, 545 (1953).

[26] D. L. Decker and H. Laquer, Cryogenics 9, 481 (1969).

[27] K. D. Bowers and J. Owens, Rept. Progr. Phys. 18, 304 (1955).

[28] See, for example, T. Nagamiya, K. Yosida, and R. Kubo, Advan. Phys. 4, 1 (1955).

[29] E. Ishiguro, K. Kambe, and T. Usui, Physica 17, 310 (1951).

PHYSICAL REVIEW B VOLUME 6, NUMBER 9 1 NOVEMBER 1972

Low-Temperature Heat Capacity of $Ni(CH_3COO)_2 \cdot 4H_2O$[†]

L. G. Polgar[*] and S. A. Friedberg

Department of Physics, Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213

(Received 17 July 1972)

The heat capacity of $Ni(CH_3COO)_2 \cdot 4H_2O$ has been measured between 0.43 and 10.73 K revealing a Schottky anomaly with $C_{p\,max} = 1.182$ cal/mole K at $T_{max} = 1.98$ K. An octahedral crystal field with axial and rhombic distortions plus spin-orbit interaction split the triplet ground state completely, the upper components lying $3.52k$ and $8.06k$ above the lowest. The lattice contribution to C_p is estimated to be $3.69 \times 10^{-4} T^3$ cal/mole K. Comparison of the ground-state splittings with those inferred from magnetic-susceptibility data suggests the presence of a small interaction between Ni^{++} ions. This is described by an antiferromagnetic molecular-field coefficient $A/k = +0.08$ K which may be largely of dipolar origin.

INTRODUCTION

Nickel acetate tetrahydrate forms monoclinic crystals belonging[1] to the space group $P2_1/c$. The unit cell contains two formula units and has the dimensions[1,2] $a = 4.75$ Å, $b = 11.77$ Å, and $c = 8.44$ Å with $\beta = 93°36'$. Each Ni^{++} ion is octahedrally coordinated by six oxygen atoms; four of these belong to water molecules and the others to carboxyl groups.

Measurements of the magnetic susceptibility of powdered $Ni(CH_3COO)_2 \cdot 4H_2O$ between 1.3 and 20 K [3] and from 0.35 to 4.2 K [4] give no obvious evidence of significant coupling among Ni^{++} ions. The data could be well described by a single-ion model in which the octahedral environment exhibits both axial and rhombic distortions. These, together with the spin-orbit interaction, fully lift the threefold spin degeneracy of the ^3A ground state. The two upper levels were found[4] to lie $3.82k$ and $7.82k$ above the lowest. The average g factor was 2.24. Mookherji and Mathur[5] have measured the single-crystal susceptibilities of this salt between 85 and 300 K. They interpret their results by assuming only a tetragonal distortion of the crystal field and conclude that an upper doublet lies $\sim 12k$ above a lower singlet. It is not clear whether any attempt was made to include a rhombic distortion in this analysis. In any event, the effects of additional splitting of the ground state would not be readily observable at such relatively high temperatures. Apparent differences between splittings deduced from high- and low-temperature magnetic data may indicate some temperature variation of the crystal field in this system, but this is not firmly established. Preliminary results of single-crystal susceptibility measurements[6] performed in this laboratory at low temperatures confirm conclusions drawn from the powder data in that region.

We have measured the heat capacity of $Ni(CH_3COO)_2 \cdot 4H_2O$ at low temperatures in order to get an independent determination of the zero-field splitting of the ground state of the Ni^{++} ion. Since the splitting evidently leaves a singlet as the lowest state, the possibility arises that there might be significant interionic interaction in this material which could be "subcritical" in the sense that it would be too small relative to the splitting to produce cooperative long-range spin order at any temperature.[7] In the simplest molecular-field picture, subcritical interactions contribute to the effective magnetic field at a Ni^{++} ion when an external field is applied. While in first approximation both the initial susceptibility and zero-field heat capacity would appear to be those of a system of single Ni^{++} ions, the ground-state splittings inferred from the two sets of data would differ since the susceptibility directly exhibits the influence of subcritical coupling. This effect appears to explain differences in ground-state splittings observed by magnetic and thermal means in α-$NiSO_4 \cdot 6H_2O$ [8-10] and $Ni(NO_3)_2 \cdot 6H_2O$.[11]

EXPERIMENTAL DETAILS

The measurements to be reported were made on a specimen of $Ni(CH_3COO)_2 \cdot 4H_2O$ crystallized from an aqueous solution of Fisher Certified Reagent Grade material. The sample consisted of 16.5583 g (0.36654 mole) of clear green needle-like crystals with typical dimensions ~7×2×1.5 mm and was sealed, together with a small amount (5 Torr at 77 K) of He^3 gas, in a copper capsule. Details of the liquid-He^3-cooled calorimeter and its mechanical heat switch have been given elsewhere.[12,13] The heat capacity of the unfilled capsule and other addenda was determined in separate experiments and amounted to 2.5% of the total measured heat capacity at 0.5 K, 1% at 2.0 K, and 5% at 4.2 K. An ac bridge[13] operating at 38 Hz and employing phase-sensitive detection was used to measure the resistance of a germanium thermometer attached to the capsule. This thermometer was calibrated against the vapor pressures of He^3 (1962 scale),[14] He^4 (1958 scale),[15] and H_2 (1948 NBS standard).[16] The interpolation formula[17]

$$T^{-1} = A(\ln R)^{-1} + B + C\ln R + D(\ln R)^2$$

yielded a better description of the behavior of the thermometer than did other schemes. We estimate the accuracy of our temperature scale to be ±0.005 K for $T < 4.2$ K and ±0.01 K above 4.2 K.

RESULTS AND DISCUSSION

The measured heat capacity of $Ni(CH_3COO)_3 \cdot 4H_2O$ between 0.4 and 10.7 K is shown in Fig. 1 and summarized in Table I. Except perhaps at the upper end of this temperature interval where the capsule correction to the total heat capacity is large (30% at 10.7 K) and the uncertainty in the interpolated temperature scale most troublesome, we believe systematic errors to be quite small. Thus the accuracy of the data is adequately represented by their scatter. The most obvious feature of the results is, of course, the rounded Schottky anomaly which reaches its maximum value of 1.182 cal/mole K at a temperature $T_{max} = 1.98 \pm 0.03$ K. The form of this anomaly shows that any interaction occurring between Ni^{++} ions must be subcritical. The magnitude of $C_p(\max)$ indicates, furthermore, that the ground-state triplet of the Ni^{++} ion is fully split.

In order to draw quantitative conclusions about the zero-field splitting of the ground state, we assume that the magnetic and lattice contributions to the total heat capacity are additive and that the lattice part varies as T^3 in the region of interest. Thus we write

$$C_p = C_{mag} + aT^3 . \tag{1}$$

The expression for C_{mag} is that for a system of single Ni^{++} ions whose ground state is described by the spin Hamiltonian[18]

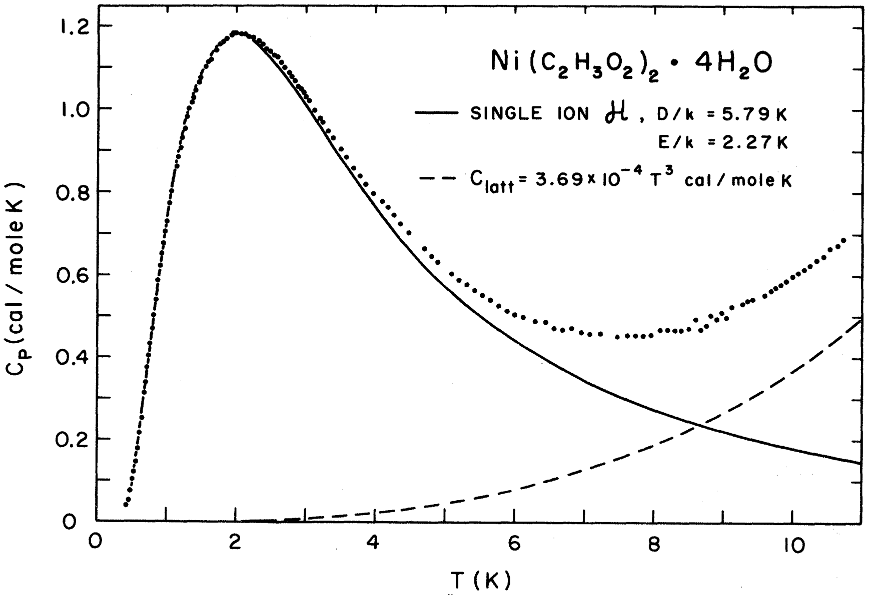

FIG. 1. Heat capacity C_p of $Ni(CH_3COO)_2 \cdot 4H_2O$ as a function of temperature. Experimental data are shown as dots, the magnetic contribution, fitted with a single-ion model, as a solid curve, and the estimated lattice contribution as a dashed curve. Those data for $T < 4.2$ K were used in the fitting process.

$$\mathcal{H} = DS_z^2 + E(S_x^2 - S_y^2) + g\mu_B \vec{S}\cdot\vec{H} \ , \tag{2}$$

where the constants D and E arise, respectively, from axial and rhombic contributions to the crystal field and $S=1$. For $H=0$, the corresponding energy levels are 0, $D-E$, and $D+E$. In the simplest molecular-field approximation these levels are not affected by possible subcritical interaction. The corresponding magnetic heat capacity may be shown to be

$$\frac{C_{\text{mag}}}{R} = \frac{2\{2E^2 + e^{D/kT}\ [(E^2+D^2)\cosh(E/kT) - 2DE\sinh(E/kT)]\}}{(kT)^2[e^{D/kT} + 2\cosh(E/kT)]^2} \ . \tag{3}$$

Letting

$$C(D,E,a;T) = C_{\text{mag}}(D,E;T) + aT^3 \ , \tag{4}$$

the data were fitted by minimizing[19] the function

$$f = \tfrac{1}{2}\textstyle\sum_i \ [C(x_j;T_i) - C_{\text{expt}}(T_i)]^2 \tag{5}$$

with respect to the parameters x_j. In this process we have used only those data taken below 4.2 K. Not only are systematic errors most likely to be negligible in this region but also the simplifying assumption that the lattice heat capacity may be represented by a single term in T^3 is more apt to be satisfied. We find the best set of parameters to be $D/k = 5.79$ K, $E/k = 2.27$ K, and $a = 3.69\times10^{-4}$ cal/mole K^4. The magnetic and lattice contributions to the heat capacity calculated with these parameters for the whole range covered by the experiments are shown in Fig. 1 by solid and dashed lines, respectively. The fit of the data given by the sum of these two curves is quite good up to about 9 K. Discrepancies at the highest temperatures may reflect inadequacy of the simple T^3 expression for the lattice heat capacity. However, undetected systematic errors may also be present in this region.

Subtracting the lattice correction aT^3 obtained above from the measured heat capacity one gets an "experimental" value of C_{mag}. As a check on the consistency of the separation process one may calculate the entropy change $\Delta S = \int_0^\infty (C_{\text{mag}}/T)\,dT$ which should be just $R\ln 3$ if only the ground triplet enters and if the zero-field splitting leaves a single level lowest. Between 0.426 and 10.732 K this integral has been evaluated numerically from the corrected C_p data yielding $1.061R$. The theoretical expression (2) with the fitted values of D and E has been used to extrapolate the integration to $T=0$ and $T=\infty$, giving contributions of $0.002R$ and $0.043R$, respectively. The total, $1.106R$, is in excellent agreement with $\Delta S = R\ln 3 = 1.098R$.

From the analysis of the observed Schottky anomaly we conclude that each Ni^{++} ion in $Ni(CH_3COO)_2 \cdot 4H_2O$ has access at low temperatures to three levels, the upper two being $3.52k$ and $8.06k$ above the lowest. The powder susceptibility data above 0.35 K have been analyzed previously[4] on the assumption that interionic coupling may be neglected. On this basis, it was concluded that the upper components of the triplet occurred at $3.82k$ and $7.82k$. These values are really quite close to the calorimetric results and indicate that interionic interaction is indeed very small in this salt. It is interesting, however, to

TABLE I. Specific heat of $Ni(CH_3COO)_2 \cdot 4H_2O$. C_p is given in cal/mole K and T is given in K.

T	C_p	T	C_p	T	C_p	T	C_p	T	C_p
0.426	0.038	1.479	1.074	2.750	1.090	4.806	0.643	9.422	0.539
0.448	0.052	1.543	1.102	2.795	1.077	4.899	0.630	9.591	0.551
0.475	0.076	1.574	1.112	2.834	1.068	5.099	0.602	9.668	0.564
0.504	0.103	1.623	1.118	2.877	1.054	5.200	0.588	9.746	0.572
0.520	0.118	1.700	1.140	2.917	1.049	5.306	0.578	9.825	0.576
0.536	0.135	1.724	1.145	2.957	1.039	5.416	0.562	9.906	0.585
0.551	0.146	1.749	1.156	2.994	1.028	5.530	0.542	9.988	0.599
0.580	0.178	1.778	1.161	3.036	1.019	5.649	0.539	10.073	0.606
0.610	0.216	1.803	1.163	3.121	0.996	5.765	0.525	10.160	0.616
0.637	0.251	1.829	1.168	3.161	0.986	5.880	0.513	10.249	0.625
0.686	0.316	1.856	1.170	3.200	0.977	5.996	0.503	10.339	0.635
0.704	0.343	1.887	1.175	3.237	0.968	6.118	0.499	10.432	0.646
0.727	0.375	1.917	1.179	3.275	0.959	6.284	0.488	10.531	0.666
0.748	0.403	1.943	1.184	3.315	0.946	6.443	0.487	10.632	0.673
0.771	0.435	2.004	1.180	3.354	0.945	6.565	0.471	10.732	0.688
0.796	0.470	2.032	1.182	3.390	0.929	6.695	0.468		
0.821	0.504	2.060	1.181	3.429	0.918	6.824	0.471		
0.850	0.543	2.087	1.179	3.467	0.920	6.953	0.459		
0.881	0.586	2.115	1.182	3.502	0.903	7.092	0.457		
0.909	0.621	2.141	1.177	3.538	0.893	7.227	0.458		
0.933	0.650	2.173	1.175	3.575	0.884	7.483	0.452		
0.955	0.677	2.206	1.180	3.614	0.875	7.611	0.454		
0.977	0.705	2.233	1.173	3.653	0.874	7.729	0.454		
1.006	0.732	2.283	1.173	3.695	0.857	7.840	0.451		
1.042	0.770	2.308	1.164	3.738	0.850	7.961	0.455		
1.071	0.800	2.338	1.157	3.780	0.837	8.085	0.468		
1.104	0.833	2.367	1.157	3.823	0.827	8.193	0.469		
1.138	0.861	2.395	1.152	3.866	0.818	8.296	0.467		
1.164	0.884	2.422	1.145	3.911	0.808	8.395	0.465		
1.190	0.906	2.450	1.150	3.967	0.796	8.492	0.471		
1.220	0.929	2.476	1.140	4.021	0.784	8.584	0.492		
1.256	0.951	2.502	1.130	4.098	0.778	8.668	0.468		
1.292	0.978	2.528	1.128	4.140	0.767	8.749	0.477		
1.322	0.999	2.553	1.128	4.182	0.759	8.812	0.503		
1.352	1.015	2.579	1.126	4.222	0.752	8.889	0.494		
1.381	1.026	2.605	1.116	4.265	0.743	8.965	0.510		
1.410	1.044	2.631	1.111	4.314	0.732	9.042	0.496		
1.461	1.064	2.658	1.104	4.377	0.715	9.120	0.525		
1.489	1.080	2.685	1.099	4.456	0.709	9.275	0.532		
1.516	1.093	2.711	1.093	4.711	0.664	9.350	0.538		

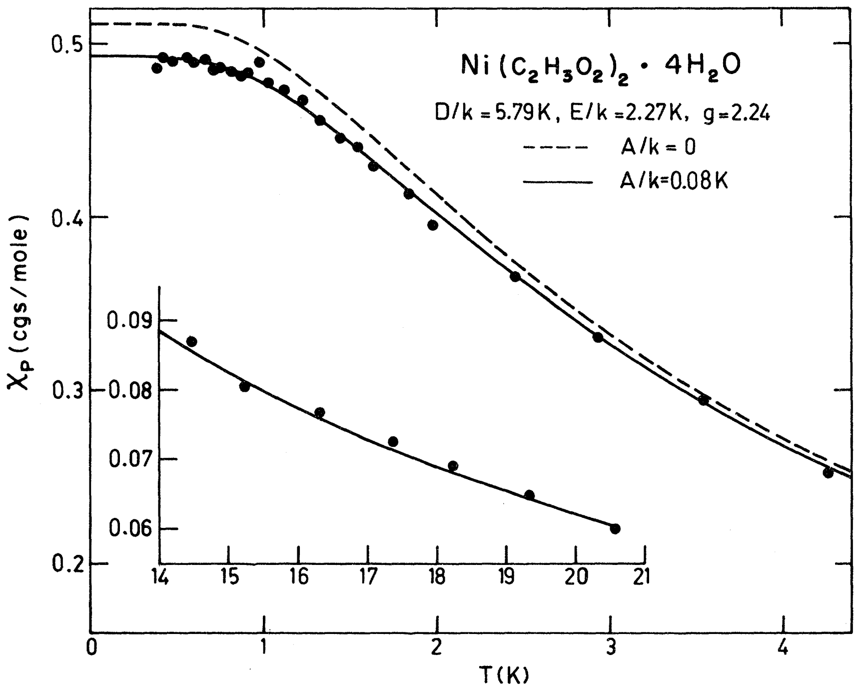

FIG. 2. Magnetic susceptibility of powdered $Ni(CH_3COO)_2 \cdot 4H_2O$ as a function of temperature. The data (dots) are from Refs. 3 and 4. The curves have been calculated using the zero-field splittings deduced from C_p data with (solid line) and without (dashed line) molecular-field coupling. Above 14 K (inset), the calculated curves are indistinguishable.

pursue further the possibility that the small discrepancies between the ground-state splittings deduced from magnetic and thermal data are real. We have refitted the powder susceptibility data, adding to the single-ion spin Hamiltonian (2) a molecular-field term of the usual form, $A\langle\vec{S}\rangle\cdot\vec{S}$. The appropriate formula for χ_p in this case has been given in Ref. 7. Assuming the g factor to be isotropic and equal to 2.24 and constraining D and E to have the values determined calorimetrically, one finds a small antiferromagnetic coupling constant $A/k = +0.08$ K. Figure 2 shows the susceptibility data and the fitted theoretical curve (solid line). Note that the small molecular-field term is of negligible consequence in the liquid-H_2 region (inset). Also shown (dashed curve) is the calculated result for the same D and E values without interaction, i.e., with $A \equiv 0$.

While the difference between these curves is close to the uncertainty in the experimental susceptibility result, the implied magnitude of A is plausible. Noting that the nearest-neighbor Ni^{++} ions in this crystal are separated by a distance $a = 4.75$ Å, we may estimate the magnetic dipolar interaction energy to be of order $S^2 g^2 \mu_B^2 / a^3 \approx 0.03k$. This is comparable in magnitude to the fitted value of A $(= 0.08k)$ and would be present even in the absence of significant exchange interaction. A detectable nonzero molecular-field coupling constant is thus not unreasonable in this system although it may be largely dipolar in origin. Evidently the superexchange interaction in $Ni(CH_3COO)_2 \cdot 4H_2O$ is quite small in comparison with that in other transition-metal compounds containing the carboxyl group, e.g., $Cu(CH_3COO)_2 \cdot H_2O$ [20,21] or $Cu(HCOO)_2 \cdot 4H_2O$.[22–24] This presumably reflects the fact that in $Ni(CH_3COO)_2 \cdot 4H_2O$ the acetate group does not serve as a bridge linking two paramagnetic ions so that its full possibilities as a superexchange intermediary are not realized.

ACKNOWLEDGMENT

We wish to thank B. E. Myers for kindly providing the specimen material used in this work.

[†] Work supported by the National Science Foundation and the Office of Naval Research. Based on part of a thesis submitted by L. G. Polgar to Carnegie-Mellon University in partial fulfillment of the requirements for the Ph.D. degree.

[*] Present address: The Research Corporation of New England, Hartford, Conn.

[1] J. N. van Niekerk and F. R. L. Schoening, Acta Cryst. 6, 609 (1953).

[2] T. C. Downie, W. Harrison, E. S. Raper, and M. A. Hepworth, Acta Cryst. B27, 706 (1971). Some of the structural parameters reported here are different from those of Ref. 1.

[3] R. B. Flippen and S. A. Friedberg, Phys. Rev. 121, 1591 (1961).

[4] J. T. Schriempf and S. A. Friedberg, J. Chem. Phys. 40, 296 (1964).

[5] A. Mookherji and S. A. Mathur, Physica 31, 1540

(1965).

[6] B. E. Myers and S. A. Friedberg (unpublished).

[7] T. Moriya, Phys. Rev. 117, 635 (1960).

[8] T. Watanabe, J. Phys. Soc. Japan 17, 1856 (1962).

[9] J. W. Stout and W. B. Hadley, J. Chem. Phys. 40, 55 (1964).

[10] R. A. Fisher and E. W. Hornung, J. Chem. Phys. 48, 4284 (1968).

[11] A. Herweijer and S. A. Friedberg, Phys. Rev. B 4, 4009 (1971).

[12] C. A. Raquet, doctoral dissertation (Carnegie Institute of Technology, 1967) (unpublished).

[13] L. G. Polgar, doctoral dissertation (Carnegie-Mellon University, 1970; University Microfilms, Ann Arbor, 1971) (unpublished).

[14] R. H. Sherman, S. G. Sydoriak, and T. R. Roberts, J. Res. Natl. Bur. Std. (U.S.) 68A, 579 (1964).

[15] F. G. Brickwedde, H. van Dijk, M. Durieux, P. R. Clement, and J. K. Logan, J. Res. Natl. Bur. Std. (U.S.) 64A, 1 (1960).

[16] H. W. Woolley, R. B. Scott, and F. G. Brickwedde, J. Res. Natl. Bur. Std. (U.S.) 41, 379 (1948).

[17] We are grateful to Dr. W. B. Yelon for pointing out the useful properties of this formula.

[18] A. Abragam and M. H. L. Pryce, Proc. Roy. Soc. (London) A205, 135 (1951).

[19] R. Fletcher and M. J. D. Powell, Comp. J. 6, 163 (1963).

[20] B. Bleaney and K. D. Bowers, Proc. Roy. Soc. (London) A214, 451 (1952).

[21] J. N. van Niekerk and F. R. L. Schoening, Acta Cryst. 6, 227 (1953).

[22] R. L. Martin and H. Waterman, J. Chem. Soc. 1359 (1959).

[23] R. B. Flippen and S. A. Friedberg, J. Chem. Phys. 38, 2652 (1963).

[24] H. Kobayashi and T. Haseda, J. Phys. Soc. Japan 18, 541 (1963).

PHYSICAL REVIEW B VOLUME 6, NUMBER 9 1 NOVEMBER 1972

Breakdown of Matthiessen's Rule in Gold Alloys[*]

T. E. Whall,[†] P. J. Ford,[‡] and J. W. Loram
School of Mathematical and Physical Sciences, University of Sussex, Brighton, United Kingdom

(Received 10 January 1972)

The resistivities of alloys of gold with magnetic (Fe, Mn, Co) and nonmagnetic (Ni, Ti) impurities have been measured in the temperature range 0.5–60 °K. Using suitable extrapolation formulas for the impurity resistivity, it is found that large departures from Matthiessen's rule occur in these alloys. At low temperatures the deviations are shown to be proportional to the phonon resistivity, or T^n, where $4<n<5$, in contrast to a recent theory which predicts an initial T^3 temperature dependence. The results are interpreted in terms of the differing anisotropies of the relaxation times for phonon and impurity scattering over the Fermi surface.

I. INTRODUCTION

In the course of investigations into the Kondo effect in dilute alloys[1-4] we have observed that large departures $\Delta(c, T)$ from Matthiessen's rule occur in many of the alloys studied. The total resistivity $\rho(T)$ of an alloy (or nominally pure metal) at temperature T may be written as the sum of three contributions:

$$\rho(c, T)=\rho_p(T)+\rho_i(c, T)+\Delta(c, T), \tag{1}$$

where $\rho_p(T)$ is the phonon resistivity of an ideally pure metal, ρ_i is the impurity resistivity in the absence of phonon scattering, and c is the concentration of solute.

Experimental results are often discussed in terms of the excess resistivity $\Delta\rho$, which is the difference in the resistivities of the alloy ρ_a and a nominally pure metal ρ_m,

$$\begin{aligned}\Delta\rho &= \rho_a-\rho_m \\ &= (\rho_{ia}-\rho_{im})+(\Delta_a-\Delta_m)\ .\end{aligned} \tag{2}$$

The subscripts a and m refer to the values for the alloy and metal, respectively. Hereafter, Δ will refer to the difference $(\Delta_a-\Delta_m)$.

Large values of Δ have been observed in both magnetic and nonmagnetic alloys and there is an extensive literature on the subject.[5-11] A positive value of Δ_a may be predicted on quite general grounds, as shown by Kohler.[12] He concludes that Δ_a is finite if the ratio of the relaxation times for phonon and impurity scattering depends on the electron wave vector k. Sondheimer and Wilson[13] assume that electrons in two bands contribute to the conductivity, and obtain an expression of the form

$$1/\Delta_a=1/\gamma\rho_p+1/\beta\rho_{ia}\ , \tag{3}$$

where γ and β may be functions of temperature. At low temperatures, $\beta\rho_{ia}\gg\gamma\rho_p$ and

$$\Delta_a\sim\gamma\rho_p\ . \tag{4}$$

Different parts of the Fermi surface of the host metal may be considered in this context to be equivalent to different bands. Following Ziman,[14] Dugdale and Baszinski[6] divide the electrons into two groups, those on the "necks" and those on the