Equation of State from a Phenomenological Model for the Kondo System Cu:Fe†

A. S. Edelstein
University of Illinois, Chicago, Illinois 60680, and Argonne National Laboratory, Argonne, Illinois 60439
(Received 14 August 1972)

Susceptibility measurements are used to fit the two parameters of a phenomenological model based upon a nearly Lorentzian density of states. The model is then employed to calculate the single-impurity contribution to the specific heat of Cu:Fe as a function of temperature and magnetic field. The model is also briefly applied to Au:V.

The original work[1,2] on the Kondo problem is valid only for $T > T_K$. Recently, scaling techniques have been applied to develop a theory[3-6] which is valid also for $T \ll T_K$. Qualitatively, this theory can be interpreted in terms of a Lorentzian density of states with a width Δ of order T_K. At low temperatures in the special case of the resonant-level model[6] (RL) ($U=0$, $E_0=0$ in the Anderson model) $\chi_{RL}^{-1} \approx \pi\Delta + \pi^3 T^2/3\Delta$ while at high temperatures $\chi_{RL}^{-1} \approx 4(T+\Delta/1.85)$. Despite this progress, there are not firm quantitative theoretical predictions even for the case $S=\frac{1}{2}$ for the low-temperature susceptibility and specific heat. Essentially, no theoretical work has been done for other values of S. Hence there is some merit in a model which can be used to treat real systems even if this model must, necessarily, be largely heuristic. Such a phenomenological model[7,8] has been employed previously to fit the susceptiblity $\chi(T,H)$ of the Kondo system La:Ce. This model was based upon a density of states

$$N(E) = N_0(E^2+\Delta^2)^{-\beta}, \tag{1}$$

where E is measured from the Fermi level E_F. The susceptibility was calculated by assuming that the magnetic field has only the effect of shifting the up and down spin densities of states by an amount $g\mu S_z H$. For La:Ce, the best fit was obtained with $\beta \approx \frac{1}{4}$ and $\Delta/k < 0.1$ K. For $\beta = 1$, one has a Lorentzian distribution and the form of $\chi(T,0)$ is identical to χ_{RL}.

The purpose of this Letter is to apply Eq. (1) to calculate the single-impurity contribution to the specific heat C of Cu:Fe as a function of temperature and magnetic field. We will use $\beta \approx 1$ so that we have an approximately Lorentzian distribution for $N(E)$. This is the distribution theorists believe may be correct. All the parameters in the model except β will be determined either from susceptibility measurements or from a natural *a priori* normalization condition. After this is done, the model will be used to predict the specific heat. This is not trivial since there is no relation that allows one to predict the specific heat directly from the susceptibility. The fact that the predictions of the model agree with experiment lends important support to the notion of a Lorentzian-like singularity of width T_K at the Fermi surface.

The character of the high-temperature susceptibility depends upon whether $\beta > \frac{1}{2}$ or not. For $\beta > \frac{1}{2}$, one can normalize $N(E)$. In this case at high temperatures, $\chi \propto 1/T$, whereas for $\beta < \frac{1}{2}$, $\chi \propto 1/T^{2\beta}$. Thus if we require that the model be qualitatively correct at high temperatures, susceptibility data[9] for Cu:Fe require that $\beta > \frac{1}{2}$. For $\beta > \frac{1}{2}$, if we require (1) that the peak occur at E_F,[5,6,10] and (2) that there be one entity of spin S per impurity atom, then normalization requires that

$$N_0 = 2A\Delta^{2\beta-1}/(2S+1)B(\tfrac{1}{2}, \beta-\tfrac{1}{2}), \tag{2}$$

where B is the beta function and A is Avogadro's number. It should be noted that in order to have the correct number of states under the distribution for $S > \frac{1}{2}$, one must have more states at high energy than are given by Eq. (2). Because the model is phenomenological, there is no valid criterion for choosing between possible alternative methods of doing the normalization. Because it is a natural *a priori* choice, is simple, and agrees with experiment, we shall use the normalization given by Eq. (2).

The low-temperature form of the susceptibility predicted by the model is

$$\chi = [N_0 \textstyle\sum (g\mu S_z)^2/\Delta^{2\beta}][1 - \frac{1}{3}\beta(\pi kT/\Delta)^2], \tag{3}$$

where S_z is summed from $-S$ to $+S$. We use $S = \frac{3}{2}$ and $g = 1.76$ to obtain the Tholence-Tournier[9] value of $\mu = 3.4\mu_B$. Taking these values and using Eqs. (2) and (3), we can determine N_0 and Δ for different values of β from the experimental value[9] for the low-temperature susceptibility $\chi(0) = 4.98 \times 10^{-2}$ emu/mole. For example if $\beta = 1$, we find $N_0 = 2.46 \times 10^{8}$ states erg/mole and $\Delta = 18.6$ K. In this case the model predicts $\chi = 4.98 \times 10^{-2}(1$

$-0.0095T^2$) emu/mole while the experimental result[11] is $\chi = 4.98\times10^{-2}(1-AT^2)$, where $A<0.018$. Further, the model predicts, in agreement with experiment, that χ is independent of H for $g\mu H \ll \Delta$.

We can calculate the specific heat in zero magnetic field from

$$C = (2S+1)(\partial/\partial T)\int_{-E_F}^{\infty} Ef(E/kT)N(E)\,dE, \qquad (4)$$

where f is the Fermi function. In writing this expression, we have assumed that the different multiplets are degenerate in zero magnetic field. The low-temperature form of the specific heat given by Eq. (4) is $(2S+1)\pi^2k^2TN_0/3\Delta^{2\beta}$. The result of a numerical calculation of C/T using the above parameters for $\beta=1$ is shown in Fig. 1(b) and is compared with the measurements of Triplett and Phillips.[12] From the low-temperature form of C and Eq. (3) we see that

$$\lim_{T\to 0}\frac{C}{T\chi} = \frac{(k\pi)^2}{(\mu g)^2 S(S+1)}. \qquad (5)$$

Since the model has been fitted to $\chi(0)$, one sees from Fig. 1(b) that the ratio of $C/T\chi$ predicted for Cu:Fe holds to within 6%. The calculated results at low temperatures only depend weakly on the value of β employed. This is demonstrated in Fig. 1(a) where the values $\beta=\frac{1}{3}$, $\Delta=7.8$ K, and $N_0=3.95\times10^{27}$ states/erg$^{1/3}$ mole have been employed. We have chosen $\beta=\frac{1}{3}$ to emphasize the insensitivity to β at low temperatures. In this case since $N(E)$ is not normalizable, the upper bound of the quadratic term in χ was used to determine the parameters uniquely. At higher temperatures $\beta=\frac{1}{3}$ gives a very poor fit. It is appropriate to note that work based upon trying to guess the correct ground state gives low-temperature specific-heat curves which vary as $(T/T_k)\ln(T/T_k)$,[13] or as T/T_k.[14]

A comparison between the experimental specific heat[12] and the prediction of the model at higher temperatures for different values of β is shown in Fig. 2. Since $C\propto T^{1-2\beta}$ for $T\gg\Delta$ and $\beta<\frac{3}{2}$, one expects the weak temperature dependence of C for $\beta=0.6$. In all cases the normalization given by Eq. (2) has been used along with $\chi(0)$ to determine N_0 and Δ. Also shown in Fig. 2 is the prediction of the theory of Bloomfield and Hamann[15] (BH). The BH curve has been adjusted to agree with the data at the peak. Notice that on adjusting β by 20% to 0.8 the model correctly agrees with the data at low temperatures and BH at high temperatures. This is interesting since BH should be correct at high temperatures. For β

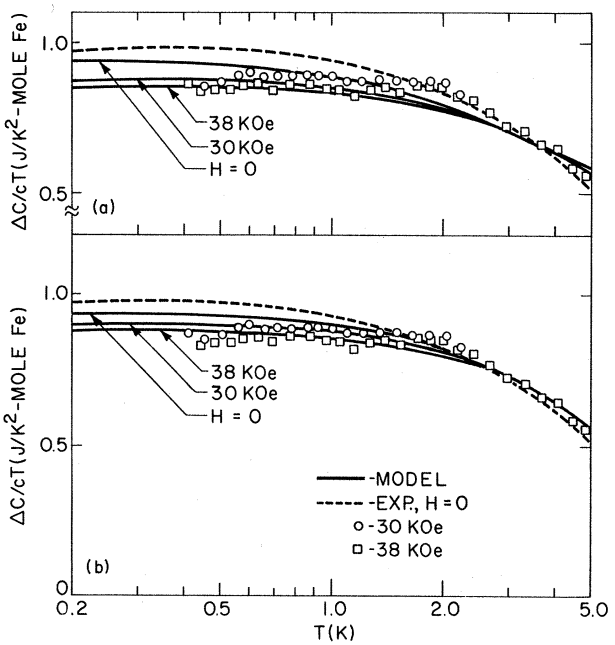

FIG. 1. Comparison of the predicted values of C/T based upon the model with experimental values in the dilute limit. For (a) $\beta=\frac{1}{3}$, $\Delta=7.8$ K, $N_0=3.95\times10^{27}$ states/erg$^{1/3}$ mole, and $g=1.76$; for (b) $\beta=1.0$, $\Delta=18.75$ K, $N_0=2.46\times10^{8}$ states erg/mole, and $g=1.76$.

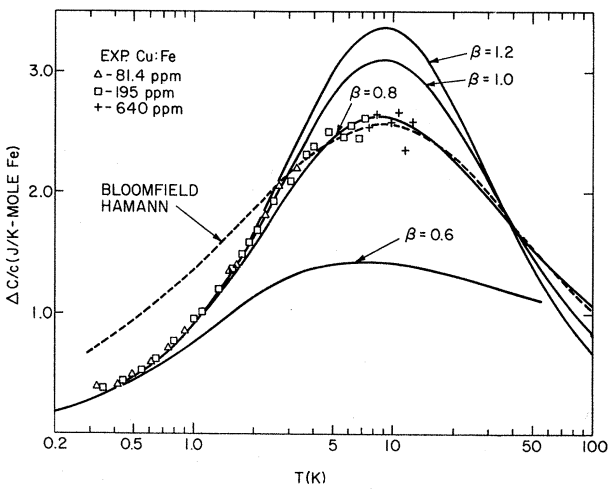

FIG. 2. Comparison of the predicted values of C based upon the model with experimental values in the dilute limit. The dashed curve based upon the theory of Bloomfield-Hamann (Ref. 13) has been adjusted to fit at the peak. The values of Δ and N_0 used with the various values of β are as follows: for $\beta=1.2$, $\Delta=23.27$ K, $N_0=6.160\times10^{2}$; for $\beta=1.0$, $\Delta=18.57$ K, $N_0=2.457\times10^{3}$; for $\beta=0.8$, $\Delta=12.80$ K, $N_0=9.401\times10^{13}$; and for $\beta=0.6$, $\Delta=5.148$ K, $N_0=2.485\times10^{19}$. Given β these values follow uniquely from Eqs. (2) and (3).

$= 0.8$ the coefficient in the quadratic term in the susceptibility is 0.016 which is less than the experimental upper bound. The fact that $\beta = 0.8$ provides a better fit than $\beta = 1.0$ probably is not significant since in principle Δ may be temperature and/or energy dependent.

The model can also be used to calculate the specific heat in the presence of an applied magnetic field. The specific heat in a magnetic field H is given by

$$C(T,H) = C(T,0) + T\frac{\partial^2}{\partial T^2}\int_0^H M(T,H')\,dH', \qquad (6)$$

$$M = \int_{-E_F}^{\infty}\sum_{S_z} g\mu S_z f(E/kT)N(E + g\mu S_z H)\,dE. \qquad (7)$$

Note that in Eq. (7) we have assumed[16] that the only effect of a magnetic field is to rigidly shift the bands. Using the values of the parameters quoted above in connection with Fig. 1, we have calculated the magnetic field dependence of C/T and in Fig. 1 compared these results with experiment.[12] One sees that the model automatically incorporates the correct magnetic field dependence for $\mu H < \Delta$. A magnetic field reduces C at low temperatures while the model predicts that above 5 K the specific heat will be increased in a magnetic field.

It is appropriate at this point to consider whether Eq. (1) can be used to interpret the high-concentration data as well. The susceptibility of Cu:Fe measured by Hirschkoff *et al.*,[17] has a component which is given by $A_0 c^2/T^{2/3}$, where $A_0 = (92 \pm 5)\times 10^{-12}$ K$^{2/3}$/ppm^2. This is believed to be the contribution of isolated pairs of impurities which are in close proximity to one another. For $T \gg \Delta$ and $\beta < \frac{1}{2}$, the model predicts

$$\chi = 2g^2\mu^2(\textstyle\sum S_z^2)N_0(1 - 2^{1+2\beta}) \times \Gamma(1-2\beta)\zeta(-2\beta)/(kT)^{2\beta}, \qquad (8)$$

where ζ is the Riemann ζ function. Comparing Eq. (8) with experiment gives $\beta = \frac{1}{3}$ and $\Delta < 0.01$ K. The model would predict that these spins contribute a term to the specific heat proportional to $T^{1/3}$. There are uncertainties connected with trying to separate the two contributions to the specific heat,[12] but the additional contribution appears to be different from this. Apparently this is one of a number[8,18,19] of cases in which interaction effects manifest themselves differently in different measurements. For example, in measurements on La:Ce the incremental resistivity[18,20] departs from being proportional to concentration at a much lower concentration than the susceptibility.[7,8]

The model is also useful in making predictions for other systems. For Au:V using $g = 1.86$ and $S = \frac{3}{2}$ in Eq. (5), one finds $C/T\chi = 1.68\times 10^8$ erg/emu K^2 while the experimental ratio[21,22] is 1.5×10^8 erg/emu K^2; i.e., the ratio $C/T\chi$ is correctly predicted by the model and is similar to that of Cu:Fe even though the individual values are more than an order of magnitude different.

If $\beta \approx 1$ permits a good fit for the single-impurity contribution in Cu:Fe, what is the significance of the $\beta = \frac{1}{3}$ fit for the pair contribution to the susceptibility and of the $\beta = \frac{1}{4}$ fit for Ce-La? These fits may be just numerical, and a more complete theory of $N(E)$ treating nonisolated impurities and/or crystalline-field effects[23] may establish some other form such as a sum of Lorentzians of different widths. In these cases if $N(E)$ were a sum of Lorentzians, the original idea of singularities at E_F would remain.

In summary, the values of the parameters in the model were determined either as *a priori* choices or from high- and low-temperature susceptibility measurements. The model then correctly predicts $\chi(T,H)$ for kT and $g\mu H \ll \Delta$. The model was then used to calculate the specific heat as a function of temperature and magnetic field. The model also correctly predicts the low-temperature value for $C/T\chi$ of Au:V. The model is being applied to other systems and other properties.

The author wishes to acknowledge helpful discussions with B. B. Triplett, N. E. Phillips, D. R. Hamann, T. Arai, and J. W. Garland.

---

†Work performed under the auspices of the U. S. Atomic Energy Commission.

[1]J. Kondo, Progr. Theor. Phys. 32, 37 (1964).

[2]For a review of the theory, see J. Kondo, in *Solid State Physics*, edited by F. Seitz, D. Turnbull, and H. Ehrenreich (Academic, New York, 1969), Vol. 23, p. 183; A. J. Heeger, *ibid.*, p. 283.

[3]G. Yuval and P. W. Anderson, Phys. Rev. B 1, 1522 (1970).

[4]P. W. Anderson, G. Yuval, and D. R. Hamann, Phys. Rev. B 1, 4464 (1970).

[5]D. R. Hamann, Phys. Rev. B 2, 1373 (1970).

[6]K. D. Schotte and U. Schotte, Phys. Rev. B 4, 2228 (1971).

[7]A. S. Edelstein, L. R. Windmiller, J. B. Ketterson, G. W. Crabtree, and S. P. Bowen, Phys. Rev. Lett. 26, 516 (1971).

[8]A. S. Edelstein, L. R. Windmiller, J. B. Ketterson, and H. V. Culbert, in *Magnetism and Magnetic Materials–1971*, AIP Conference Proceedings No. 5 (American

Institute of Physics, New York, 1972), p. 558.
[9]J. L. Tholence and R. Tournier, Phys. Rev. Lett. 25, 867 (1970).
[10]D. R. Hamann, private communication.
[11]B. B. Triplett, private communication.
[12]B. B. Triplett and N. E. Phillips, Phys. Rev. Lett. 27, 1001 (1971); B. B. Triplett, to be published; J. C. F. Brock, J. C. Ho, G. P. Schwartz, and N. E. Phillips, Solid State Commun. 8, 1139 (1970).
[13]J. A. Appelbaum and J. Kondo, Phys. Rev. Lett. 19, 906 (1967).
[14]V. Celli and M. J. Zuckermann, Phys. Lett. 25A, 305 (1967); A. P. Klein, Phys. Lett. 26A, 57 (1967).
[15]P. E. Bloomfield and D. R. Hamann, Phys. Rev. 164, 856 (1967).
[16]For large fields and $\beta \leq 1/2$, the model will not lead to saturation.
[17]E. C. Hirschkoff, M. R. Shanabarger, C. G. Symko, and J. C. Wheatley, J. Low Temp. Phys. 5, 545 (1971).
[18]A. S. Edelstein, Phys. Lett. 27A, 614 (1968).
[19]H. Claus, Phys. Rev. B 5, 1134 (1972).
[20]J. J. Wollan and D. K. Finnemore, Phys. Lett. 33A, 299 (1970), and Phys. Rev. B 4, 2996 (1971); T. Sugawara and H. Eguchi, J. Phys. Soc. Jap. 26, 1322 (1969).
[21]J. E. van Dam and P. C. M. Gubbens, Phys. Lett. 34A, 185 (1971).
[22]B. M. Boerstoel and W. M. Star, Phys. Lett. 29A, 97 (1969).
[23]B. Cornut and B. Coqblin, Phys. Rev. B 5, 4541 (1972).

Anticentrifugal Stretching in ^{20}Ne

H. C. Lee
Atomic Energy of Canada Limited, Chalk River Nuclear Laboratories, Chalk River, Ontario, Canada

and

R. Y. Cusson
Physics Department, Duke University, Durham, North Carolina 27706
(Received 31 August 1972)

A variation-after-projection Hartree-Fock calculation shows that the rms radius of ^{20}Ne decreases with increasing spin in the ground-state band. This decrease is consistent with the significant reduction in α width between the 6^+ and the 8^+ states. It also leads to the theoretical $B(E2)$ values reproducing the measured values exceedingly well.

The atomic nucleus ^{20}Ne has provided one of the classic manifestations of collective rotational motion in light nuclei.[1] The low-lying members of its ground-state band have energy spacings proportional to $J(J+1)$ and have the strong intraband $E2$ transitions characteristic of the rigid rotor. However, higher-lying members of the band, especially the recently observed 8^+ state at 11.95 MeV,[2,3] have properties which are markedly different from those of the simple rotational model. Thus in the rigid rotor the 8^+ state is predicted to be at a considerably higher energy than 12 MeV, and the ratio of the $E2$ γ-decay strengths, $\mathcal{R} = B(E2; 6^+ \rightarrow 4^+)/B(E2; 8^+ \rightarrow 6^+)$, which is predicted to be 0.96, is measured[3] to be $2.7^{+1.9}_{-0.9}$. On the other hand both the j-j coupled[4] and the SU(3)[5] shell-model calculations predict $\mathcal{R} = 1.6$ and level spacings close to those observed. In these models an (additional) effective charge of $\sim 0.5e$ per nucleon is needed to reproduce the absolute $B(E2)$ values.

The α decay of excited states is another interesting facet of the structure of ^{20}Ne. Among members of the ground band the 6^+ and 8^+ states are α-particle unbound, and the α widths of these states have recently been measured,[2] the result being $\Gamma_{6^+}{}^{\alpha} = 110 \pm 25$ eV and $\Gamma_{8^+}{}^{\alpha} = 35 \pm 10$ eV. As usual one analyzes the experimental width Γ_l in terms of the product of a spectroscopic factor S_l and a single-particle width $\Gamma_l{}^{s.p.}$, or $\Gamma_l{}^{exp} = S_l \Gamma_l{}^{s.p.}$. Here the "single particle" has reduced mass number $\frac{16}{5}$, and its motion is the relative motion of the departing α particle and the residual ^{16}O. Arima and Yoshida[6] calculated $\Gamma_l{}^{s.p.}$ using the Coulomb potential plus a real Woods-Saxon potential of appropriate depth, radius R, and diffusivity a; these parameters are chosen in such a way that the wave function has maximum overlap with the wave function obtained in the cluster model[6] and that the resonance energy coincides with the observed energy. The following results[6] were then obtained: (a) Assuming $R_{6^+} = R_{8^+}$, then one must have $S_{6^+} = 2S_{8^+} = 0.24$ in order to reproduce the experimental α widths; (b) if one demands that $S_{6^+} = S_{8^+} = 0.24$ then $R_{6^+} - R_{8^+} \cong 0.25$ F. Neither (a) nor (b) is