EQUIVALENCE OF LOCALIZED SPIN FLUCTUATIONS AND THE KONDO-NAGAOKA SPIN-COMPENSATED STATE

N. Rivier
Cavendish Laboratory, University of Cambridge, Cambridge, England

and

M. J. Zuckermann
Department of Physics, Imperial College, London S.W. 7, England

The physical equivalence between the Kondo-Nagaoka spin-compensated state and localized spin fluctuations in a dilute "nonmagnetic" alloy is demonstrated. The Kondo temperature is shown to be equal to τ_0^{-1}, the width of the spin fluctuations, and determines the boundary between magnetic and nonmagnetic behavior of dilute alloys.

The nature of the Nagoaka condensed state in a dilute magnetic alloy is not yet fully understood, although experimentalists and theorists agree fairly well on how the measureable quantities should behave as a function of the temperature.[1] We suggest in this Letter that the Nagaoka condensation or spin-compensated state is equivalent to the state of a dilute alloy, nonmagnetic in the sense of Friedel and Anderson,[2] but where localized spin fluctuations[3] are important and at low temperatures ($kT \ll \tau_0^{-1}$, where τ_0 is the lifetime of the localized spin fluctuation). Such a description includes both a conjecture by Schrieffer[4] that some dilute alloys (like transitional impurities in Al), traditionally viewed as nonmagnetic, are in fact Kondo compensated magnetic impurities, and Anderson's[5] view of the Kondo temperature as the boundary between the nonmagnetic and magnetic behavior of dilute alloys.

A localized spin fluctuation is the repeated scattering between an electron and a hole of opposite spin on the impurity site.[3] It has a lifetime τ_0 which is given by

$$\tau_0 = \pi\rho_d(0)[1-U\rho_d(0)]^{-1}, \tag{1}$$

where U is the Coulomb repulsion between localized d electrons in the Anderson model[2] and $\rho_d(0)$, the density at the Fermi level of a d electron state of position E_d and width Δ,

$$\rho_d(0) = \Delta[\pi(E_d^2+\Delta^2)]^{-1}. \tag{2}$$

In the Hartree-Fock sense, the alloy is nonmagnetic (i.e., $U\rho_d(0) < 1$) and will exhibit at low temperatures ($kT \ll \tau_0^{-1}$) nonmagnetic transport properties, susceptibility and specific heat, with some weak additional contribution of the spin fluctuations (correlation effects). This is the spin-compensated state. However, as soon as the temperature reaches the degeneracy temperature (which is τ_0^{-1} rather than Δ as in the case of a virtual bound state), the spin fluctuations behave classically as would a well-defined spin (i.e., Curie paramagnetism). In other words, when the temperature becomes of the order τ_0^{-1}, the spin fluctuations are slower than the thermal fluctuations of the temporary moment that they describe. At this temperature and above, there is no physical difference between a spin fluctuation and a genuine spin; the system behaves as if it were magnetic (resistance minimum, Curie law for the susceptibility, and giant thermopower). The transition is smooth, as it should be in a system involving a limited number of degrees of freedom, and occurs at the Kondo temperature.[5] We postulate that the Kondo temperature obtained from the spin-fluctuation theory is given by

$$kT_K^{sf} = \tau_0^{-1}. \tag{3}$$

This result agrees with the experimental and theoretical values deduced from the resistivity in the spin-compensated state and from the susceptibility both at high temperatures and at $T = 0$, as will be shown below.

T_K^{sf} indicates only a change of regime; analytically, it is not the well-defined temperature of Abrikosov (divergence of the series of dominant diagrams)[6] or of Suhl (appearance of inadmissible complex poles).[7] The Kondo temperature according to Abrikosov,

$$kT_K^{A} = D\exp(-1/N(0)J), \tag{4}$$

usually quoted in the literature for T_K, is formally associated with the maximum in the high-temperature expression for the reisitivity,[8] i.e., the unitarity limit of the high-temperature T matrix. For the localized spin fluctuations, one

finds that $kT_K^A \ll \tau_0^{-1}$ lies outside the validity range of the high-temperature resistivity formula. The true resistance maximum does not occur at the Kondo temperature, as appears in the results of Suhl and Wong.[7] Moreover, while Eq. (4) is independent of the ordinary (spin-nonflip) potential, T_K^A is modified by potential scattering in the curves of the latter authors. It is also the case of T_K^{sf}, where $\rho_d(0)$, via E_d, is affected by the potential.

The above discussion of the mechanism of the condensation is a conjecture which we now intend to prove. In the rest of this paper, we calculate the transport properties, the susceptibility, and the influence of the valence of the impurity on T_K in the spin-fluctuating state, and show how they compare both with the experimental results in dilute alloys and with the theoretical predictions for the Nagoaka condensation.[9] In what follows, T_K refers to the experimental value of the Kondo temperature whereas T_K^x with a superscript is the theoretical value of the Kondo temperature appropriate to the physical quantity under consideration (e.g., T_K^S is appropriate to the thermopower S). The various expressions of T_K^x thus obtained are different in value due to the difference in weighting factors in the relevant physical expressions.[1] The spin-compensated state and the spin fluctuations are not mathematically equivalent. Conceptually, the former is a magnetic state while the latter is nonmagnetic. Physically, however, their effect on observable quantities like the transport coefficients or the susceptibility is the same. It is also much easier to visualize a nonmagnetic alloy with spin fluctuations looking magnetic at high temperatures than the condensation at low temperatures of a magnetic impurity with the surrounding conduction electrons.

(A) Resistivity.—An expression for the d electron's self-energy $\Sigma_d(\omega)$ valid in the limits of $|E_d| \ll \Delta$, $\omega \approx kT \ll \Delta$, and $\tau_0 \ll \Delta$, i.e., the condition for the existence of a localized spin fluctuation (Δ^{-1} is the lifetime of a single conduction electron), was derived elsewhere by the authors.[5] At low temperatures, the Sommerfeld expression can be used to evaluate the Fermi and Bose integrals with the following result:

$$\Sigma_d(\omega \pm i\delta) = (U/\pi)[(\omega/\Delta - \eta)\ln(\tau_0\Delta) + \eta \mp i\ln(1 \mp i\tau_0\omega) - \tfrac{1}{3}(\pi kT\tau_0)^2[(\eta \pm \tfrac{3}{2}i) + O(kT)^4], \quad (5)$$

where $\eta = E_d/\Delta$. This demonstrates that the low-temperature limit means $kT \ll \tau_0^{-1}$, a result which was predicted physically above. From Σ_d the electronic contribution to the transport properties is derived in the usual way [Ref. 2, Eqs. (9)-(13)]. One obtains the resistivity

$$\rho = \rho_0[1 - A\tau_0^2(kT)^2], \quad (6)$$

where $A = \frac{1}{3}\pi^2(U/\pi\Delta)[1 + 2U/\pi\Delta]$ is a coefficient of order 10. Equation (6) is to be compared with the theoretical[10,11] and experimental[12] results for the resistivity in the spin-compensated state, i.e.,

$$\rho = \rho_0[1 - (T/T_K^{\rho})^2]. \quad (7)$$

T_K^{ρ} is a characteristic temperature, approximately equal to T_K. This is the case with our result

$$kT_K^{\rho} = A^{-\frac{1}{2}}\tau_0^{-1} \quad (8)$$

when it is referred to Eq. (3).

The high-temperature resistivity was derived elsewhere[5] and exhibits the magnetic character predicted above.

(B) Thermopower.—The first term in the Sommerfeld expression (the $d\ln\Sigma$ formula) gives the following result for the thermopower at low temperatures:

$$S = -\frac{\pi^2}{3}\frac{k^2T}{|e|}\tau_0\frac{U}{\pi\Delta}\sin\left(\frac{\pi N}{S}\right). \quad (9)$$

N is the valence of the impurity, i.e., the amount of charge in the screening cloud around the impurity, determined by the Friedel sum rule. Although Eq. (9) accounts for the large thermopower of nearly magnetic alloys, it does not exhibit the observed asymmetry between impurities on the left and on the right of Mn, diluted in Al.[13] In the same way as for the resistivity, one defines a characteristic temperature

$$kT_K^S = \pi\Delta/U\tau_0, \quad (10)$$

which is approximately equal to T_K^{sf} though larger than T_K^{ρ}. This is not surprising since it is the peak of the thermopower, not the slope at low temperature which is usually associated with T_K^{ρ}.[1]

(C) Susceptibility.[9]—The susceptibility of a dilute nonmagnetic alloy with spin fluctuations can be derived from the particle-hole T matrix,[5] using a formula due to Spencer.[8] At all temperatures one obtains for χ as a function of temperature

$$\chi = (g\mu_B)^2 n_I (2\pi^2 kT)^{-1} \psi'[\tfrac{1}{2} + 1/2\pi kT\tau_0], \quad (11)$$

where ψ is the logarithmic derivative of the gamma function. When $\Delta \gg kT \gg \tau_0^{-1}$, the susceptibility (11) follows a Curie-Weiss law,

$$\chi \simeq n_I (g\mu_B)^2 / [4kT + \pi\tau_0^{-1}], \quad (12)$$

while at low temperatures, i.e., $\tau_0^{-1} \gg kT$, it reads

$$\chi \simeq n_I (g\mu_B)^2 (\tau_0/\pi)[1 - \tfrac{1}{3}\pi^2(1-3\eta^2)(\tau_0 kT)^2]. \quad (13)$$

At $T = 0$, one can picture the susceptibility due to spin fluctuation as the Pauli susceptibility, which is enhanced in the usual way[2,14]:

$$\chi = \chi_d^P = n_I (g\mu_B)^2 \rho_d(0)[1 - U\rho_d(0)]^{-1}$$

$$= n_I (g\mu_B)^2 \tau_0 \pi^{-1}. \quad (14)$$

The connection between the enhancement of the susceptibility and the T^2 coefficient of the resistivity was first pointed out by Caplin and Rizzuto[15] in their measurement of the resistivity of Al:Mn and Al:Cr alloys. They quote $\tau_0^{-1} = (9.0 \pm 0.2) \times 10^{-2}$ eV for Al:Mn and $(1.5 \pm 0.1) \times 10^{-1}$ eV for Al:Cr, from Flynn's data,[14] in good agreement with their resistivity results and our Eq. (6). The enhancement is maximum when the virtual bound state is half full, i.e., $E_d = 0$. In Al, this occurs between Cr and Mn, in agreement with the susceptibility,[14] residual resistivity,[16] and thermopower[13] measurements.

A Curie-Weiss law for the susceptibility of a dilute magnetic alloy below and above T_K has been suggested on experimental[1,12,17] and theoretical[11,18] grounds, with an antiferromagnetic Weiss temperature approximately equal to T_K. Our value for the Weiss temperature, derived from Eq. (12),

$$kT_K^{\chi} = \tfrac{1}{4}\pi\tau_0^{-1}, \quad (15)$$

is in good agreement with these results. The slight departure from a Curie-Weiss behavior at low temperature predicted by Eq. (13) has possibly been observed in Cu:Fe.[19] It might be masked by a Curie-Weiss behavior due to Ruderman-Kittel-Yosida interaction between impurities[20]—with a concentration-dependent Weiss temperature—but should have been seen in Au:V at very low concentration, where $T_K \approx 290°K$.[12] At very high temperatures ($T_K \gtrsim 500°K$ in Al:Mn), the increase of the susceptibility due to the effect of thermal expansion on the band structure [it effects the k-d overlap, i.e., τ_0 via $\rho_d(0)$], can mask a Curie-Weiss behavior. In Flynn's results,[14] for instance, the two contributions have opposite sign and are of the same order of magnitude.

It has been shown in this paper that the spin fluctuations in a nonmagnetic alloy describe qualitatively and even quantitatively the nonmagnetic to magnetic transition as the temperature is raised. The Kondo temperature has been introduced as the smooth boundary between the two regimes. The theory does not rely on the fact that the unitarity limit of the scattering is reached at $T = 0$, as in Schrieffer's work.[3] The alloys considered need not be close to the Hartree-Fock condition for the existence of localized spin fluctuations being $\tau_0^{-1} \ll \Delta$. As Schrieffer and Mattis[21] pointed out, electron correlations decrease the effective value of the Coulomb interaction U thus making a static localized moment very difficult to obtain, at least for a transitional impurity. What the present theory provides is a very simple picture of the spin-compensated state and a model for the Nagaoka condensation. It gives a physical value for the Kondo temperature. The demonstration of its physical equivalence with the Nagaoka condensation relies on the justification of the experimental notion of characteristic temperature and in the agreement of our results with the experimental and theoretical curves.[22] Therefore, the correct way of looking at the magnetic properties of dilute alloys is to understand how a nonmagnetic alloy with spin fluctuations exhibits magnetic properties at high temperatures rather than to find how a well-defined spin can be bound to the surrounding electrons to form a nonmagnetic entity at low temperatures.

We would like to thank Professor P. W. Anderson, B. R. Coles, and Dr. A. D. Caplin for stimulating discussions. The results of Dr. Caplin and Dr. Rizzuto were the starting point of the research described in this paper. One of us (N.R.) wishes to thank Atomic Energy Research Establishment (Harwell) for a research grant.

[1]For a review, see M. D. Daybell and W. A. Steyert,

Rev. Mod. Phys. 40, 380 (1968).
[2]P. W. Anderson, Phys. Rev. 124, 41 (1961).
[3]N. Rivier, M. J. Zuckermann, and M. Šunjić, to be published.
[4]J. R. Schrieffer, J. Appl. Phys. 38, 1143 (1967).
[5]P. W. Anderson, to be published.
[6]A. A. Abrikosov, Physics 2, 5 (1965).
[7]H. Suhl and D. Wong, Physics 3, 17 (1967).
[8]Y. Nagaoka, Progr. Theoret. Phys. 37, 13 (1967); H. J. Spencer, Phys. Rev., to be published.
[9]The concept of replacing a localized spin by localized spin fluctuations was first introduced by H. Suhl, Phys. Rev. Letters 19, 442 (1967). Computer calculations of the susceptibility and resistivity were reported in the above reference as well as in M. J. Levine and H. Suhl, Phys. Rev. 171, 567 (1968), and M. J. Levine, T. V. Ramakrishnan, and R. A. Weiner, Phys. Rev. Letters 20, 1370 (1968). They exhibit the change of regime discussed above and agree qualitatively with our results.
[10]Y. Nagaoka, Phys. Rev. 138, 1112 (1965), and J. Phys. Chem. Solids 27, 1139 (1966).
[11]J. Kondo, to be published.
[12]K. Kume, to be published.
[13]G. Boato and J. Vig, Solid State Commun. 5, 649 (1967).
[14]C. P. Flynn, D. A. Rigney, and J. A. Gardner, Phil. Mag. 15, 1255 (1967).
[15]A. D. Caplin and C. Rizzuto, to be published.
[16]E. Daniel and J. Friedel, in Proceedings of the Ninth International Conference on Low Temperature Physics, Columbus, Ohio, 1964, edited by J. G. Daunt (Plenum Press, New York, 1965) p. 933.
[17]J. A. Careaga, B. Dreyfus, R. Tournier, and L. Weil, in Proceedings of the Tenth International Conference on Low Temperature Physics, Moscow, U.S.S.R., 31 August-6 September 1966 (Vimiti Publishing House, Moscow, U.S.S.R., 1967).
[18]L. Dworin, Phys. Rev. 164, 818, 841 (1967). Dworin's high temperature results are formally similar to ours (Ref. 3). His "nonanalytic part" $\Gamma(T)$ is our spin fluctuation width τ^{-1} which is also nonanalytic in Δ (see the condition for the existence of a spin fluctuation). As Dworin considers an alloy in the Schrieffer-Wolff limit ($U \gg \Delta$), his $[\Gamma(T)]^{-1}$ might well be the suitably renormalized lifetime of the present theory. [See N. Rivier, thesis, University of Cambridge, (1968).]
[19]M. D. Daybell and W. A. Steyert, Phys. Rev. 167, 536 (1958).
[20]K. Yosida, Phys. Rev. 106, 893 (1957).
[21]J. R. Schrieffer and D. C. Mattis, Phys. Rev. 140, A1412 (1965).
[22]Our results agree with the predictions of Nagaoka. An exact solution of Nagaoka's approximate equations however, gives different results but leads to physical difficulties. [P. E. Bloomfield and D. R. Hamann, Phys. Rev. 164, 856 (1967); J. Zittartz and S. Müller-Hartmann, to be published.]

EVIDENCE OF COUPLING BETWEEN ONE- AND TWO-PHONON EXCITATIONS IN QUARTZ

J. F. Scott
Bell Telephone Laboratories, Holmdel, New Jersey
(Received 8 July 1968)

We have extended earlier work on the Raman spectrum of quartz to both higher and lower temperatures (6-900°K), and find evidence for the assignment of features in the 130- to 200-cm^{-1} region as second order. Anomalies in the temperature dependence and selection rules exhibited by several features are fully reconciled by an anharmonic interaction between a "soft" zone-center optical phonon and an excitation consisting of two oppositely directed zone-edge acoustic phonons.

The α-β phase transition in quartz has been approached by several investigators in terms of lattice dynamics. The analyses of Ginzburg and Levanyuk,[1] of Elcombe,[2] and of Kleinman and Spitzer[3] are similar, and each elaborates on the basic conclusion of Saksena's early force-constant calculation[4]: that the frequency of the 207-cm^{-1} mode (in this paper vibrations will be labeled by their frequencies at 300°K) at the Brillouin zone center should approach zero as the transition temperature T_0 is approached from below. Phenomenologically this behavior is not different from that of the ferroelectric mode in Cochran's theory,[5] except that the phonon in question is infrared inactive and does not directly contribute to the dielectric response of the crystal. The difficulty encountered by those who have attempted to apply existing theories to the quartz transition is that the experimental data simply do not confirm the predictions. First, the 207-cm^{-1} mode softens but does not approach zero as $T \to T_0$,[4] in contradiction to Ginzburg's requirement for second-order transitions.[6] Second, there is an extra Raman feature[7] in the α_{xx} and α_{zz} scattering in addition to the four predicted by group theory and assigned by means of force-constant models.[2,3] Third, the frequency of this "extra" feature does approach zero frequency as T approaches T_0 from