Calculation of the Influence of the Crystalline Electric Field on the Spin-Disorder Resistivity of Rare-Earth Alloys and Comparison with Results on $CeAl_2$†

V. U. S. Rao and W. E. Wallace
Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15213
(Received 19 June 1970)

An expression is developed for the spin-disorder resistivity for metallic rare-earth systems; it takes into account the effect of the crystalline electric field. The expression, which is general, is made use of to treat the case of Ce^{+3} in $CeAl_2$; its resistivity-temperature behavior is adequately accounted for on the basis of a Γ_7 doublet ground state.

INTRODUCTION

The effect of localized magnetic moments on the electrical resistivity of rare-earth metals and alloys via the exchange scattering of conduction electrons is now well known.[1] When evaluated in the first Born approximation, this interaction gives rise, in the paramagnetic state, to a contribution which is usually termed as the spin-disorder resistivity.[2] In these calculations, if one ignores the crystal-field effects on the ground state of the rare-earth ion [i.e., effects associated with the total or partial lifting of $(2J+1)$-fold degeneracy], one obtains a temperature-independent term for the spin-disorder resistivity which is proportional to the quantity $(g_J-1)^2J(J+1)$ for the rare-earth ion. In interpreting the experimental resistivity data in the paramagnetic state of rare-earth alloys, such a temperature-independent expression for the spin-disorder resistivity is widely used[3]; indeed such a procedure is valid for temperatures sufficiently high compared to the crystal-field splitting that one may regard the different crystal-field states as being almost equally populated, as is shown below. However, recent heat-capacity measurements in this laboratory[4] have given direct evidence for the existence of sizable crystal-field splittings in a number of rare-earth intermetallic compounds. For example, the heat-capacity data on cubic $CeAl_2$ have revealed that the separation between the Γ_7 doublet and the Γ_8 quartet is of the order of 100°K.

In this paper, a method of evaluating the influence of the crystalline electric field is shown. Using this method the temperature variation of the spin-disorder resistivity is calculated for $CeAl_2$ and compared with the experimental measurements. The method, however, is of general applicability; it can readily be applied to other structures and to other rare-earth ions.

SPIN-DISORDER RESISTIVITY IN ABSENCE OF CRYSTALLINE FIELD

As a prelude to our analysis, we shall briefly review the steps involved in the derivation of the spin-disorder resistivity in the rare earths.[2] We shall assume in the usual manner that the exchange interaction between a conduction electron of spin $\mathbf{s}$ at $\mathbf{r}$ and a rare-earth atom of spin $\mathbf{S}$ at $\mathbf{R}$ can be written as

$$\mathcal{H}=-2G\delta(\mathbf{r}-\mathbf{R})\mathbf{s}\cdot\mathbf{S}, \tag{1}$$

where G is a quantity with the dimensions energy times volume. As a result of spin-orbit coupling, Eq. (1) can be rewritten in terms of the total angular momentum $\mathbf{J}$ as

$$\mathcal{H}=-2G(g-1)\delta(\mathbf{r}-\mathbf{R})\mathbf{s}\cdot\mathbf{J}$$
$$=-2G(g-1)\delta(\mathbf{r}-\mathbf{R})[s_zJ_z+\tfrac{1}{2}(s_+J_-+s_-J_+)], \tag{2}$$

where g is the Landé factor of the rare-earth ion.

In the absence of electric or magnetic fields, the $(2J+1)$ eigenstates of the ground J multiplet are degenerate in the paramagnetic state and can be labeled by the eigenvalues (m_J) of J_z. A conduction electron in a state $\mathbf{k}$ moving in the vicinity of a rare-earth atom is scattered by the potential (2) into a new state $\mathbf{k}'$. The scattering occurs without spin flip if the initial and final states are connected by the term s_zJ_z in the Hamiltonian and with spin flip if they are connected by the terms $s_\pm J_\mp$.

The scattering probability for a particular process is, in the first Born approximation, proportional to the absolute square of the matrix element $M_{ii'}(\mathbf{k}\to\mathbf{k}')$ connecting the initial (i) and final (i') states of the system. The transport properties are then discussed in terms of the relaxation times $\tau_{F\pm}$ for electrons with spin up and spin down, respectively, at the Fermi surface. The relaxation times are inversely proportional to the scattering probabilities and are given by[5]

$$\frac{1}{\tau_{F\pm}}=\frac{mk_F}{\pi\hbar^3}\Bigg(\sum_{i,i'}N_i\,|\,M_{ii'}(\mathbf{k}_\pm\to\mathbf{k}_\pm')\,|^2\frac{2}{1+\exp(-E_{ii'}/k_BT)}$$
$$+\sum_{j,j'}N_j\,|\,M_{jj'}(\mathbf{k}_\pm\to\mathbf{k}_\mp')\,|^2\frac{2}{1+\exp(-E_{jj'}/k_BT)}\Bigg), \tag{3}$$

where $E_{ii'}$ and $E_{jj'}$ are the energies gained by the electrons in the particular scattering processes. N_i and N_j are the numbers of scattering centers per unit volume producing the respective collision processes. The conductivities $\sigma_{e\pm}$ are then related to $\tau_{F\pm}$ through the well-known formula

$$\sigma_{e\pm}=(n_\pm e^2/m)\tau_{F\pm}, \tag{4}$$

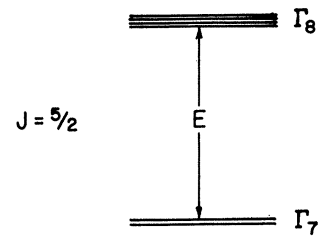

FIG. 1. Cubic crystal-field splitting of the ground state ($J=\frac{5}{2}$) of Ce^{3+} ion into doublet (Γ_7) and quartet (Γ_8) levels. The sign of the crystal field establishes whether Γ_7 or Γ_8 is lower lying.

where $n_{\pm}$ are the numbers of conduction electrons with spin up or spin down, respectively. In the absence of electric and magnetic fields, all the m_J substates of the rare-earth ion are equally probable, since they are degenerate, and all $E_{ii'}=E_{jj'}=0$, since all collisions are elastic. The spin-disorder resistivity ρ_{s1}^0 under these conditions becomes

$$\rho_{s1}^0=(3\pi Nm/2\hbar e^2E_F)G^2(g-1)^2J(J+1), \quad (5)$$

where N is the number of scattering centers per unit volume. From Eq. (5) it is seen that ρ_{s1}^0 is independent of temperature. Here, as in the rest of this paper, the subscript $s1$ denotes that the resistivity has been obtained correct to the first Born approximation. ρ_{s2} will represent the additional contribution when the resistivity is evaluated in the second Born approximation.

SPIN-DISORDER RESISTIVITY IN PRESENCE OF CRYSTAL FIELD

When the effect of the crystal-field interaction is included, the above procedure has to be modified in the following manner. First, the eigenstates are no longer pure m_J states but are admixtures of them. The matrix elements $M_{ii'}$ and $M_{jj'}$ in Eq. (3) should now be taken between the crystal-field states. Second, the probability p_i of a rare-earth atom being in a certain crystal-field state i of energy E_i depends on the extent of the crystal-field splitting and on the temperature through the Boltzmann relation

$$p_i=\frac{N_i}{N}=\frac{\exp(-E_i/k_BT)}{\sum_j \exp(-E_j/k_BT)}. \quad (6)$$

Finally, some of the collisions will be inelastic, and the $E_{ii'}$ and $E_{jj'}$ in Eq. (3) will not all be zero.

With these modifications, and using Eqs. (3) and (4), the expression for the resistivity at a temperature T becomes

$$\rho_{s1}(T)=\frac{3\pi Nm}{\hbar e^2E_F}G^2(g-1)^2 \times \sum_{m_s,m_s',i,i'} \langle m_s', i' \mid \mathbf{s}\cdot\mathbf{J} \mid m_s, i\rangle^2 p_i f_{ii'}, \quad (7)$$

where m_s and m_s' are the spins of the conduction electron in the initial and final states and the matrix elements are between the simultaneous eigenstates for the local-moment–conduction-electron system. The $f_{ii'}$ in Eq. (7) are given by

$$f_{ii'}=\frac{2}{1+\exp(-E_{ii'}/k_BT)}. \quad (8)$$

APPLICATION TO CERIUM IN CUBIC CRYSTAL FIELD; COMPARISON WITH EXPERIMENT

It is well known that a cubic crystal field splits the ground multiplet ($J=\frac{5}{2}$) of the $Ce^{3+}(f^1)$ ion into a Γ_7 doublet and a Γ_8 quartet (Fig. 1). These states are described by the following linear combinations of the pure m_J states[6]:

$$\mid \Gamma_7\rangle = a \mid \pm\tfrac{5}{2}\rangle - b \mid \mp\tfrac{3}{2}\rangle,$$

$$\mid \Gamma_8\rangle = b \mid \pm\tfrac{5}{2}\rangle + a \mid \mp\tfrac{3}{2}\rangle,$$

and

$$\mid \pm\tfrac{1}{2}\rangle,$$

where $a=0.4083$ and $b=0.9129$. The matrix elements in Eq. (7) are taken between the above crystal-field eigenstates. In this particular case, Eq. (7) can then be written

$$\rho_{s1}(T)=(3\pi Nm/\hbar e^2E_F)G^2(g-1)^2 \times[2a^2(3a^2-1)(p_1+p_2-p_1f_1-p_2f_2) +(9/4)p_1+11p_2+\tfrac{13}{2}(p_1f_1+p_2f_2)], \quad (9)$$

where p_1 and p_2 are the probabilities that a given state in the Γ_7 and Γ_8 manifolds, respectively, is occupied. If E, the separation between the two levels, is taken to be positive when the Γ_7 doublet is lower and negative when the Γ_8 quartet is lower, we have, with $x=\exp(-E/k_BT)$, $p_1=(2+4x)^{-1}$ and $p_2=xp_1$. f_1 and f_2

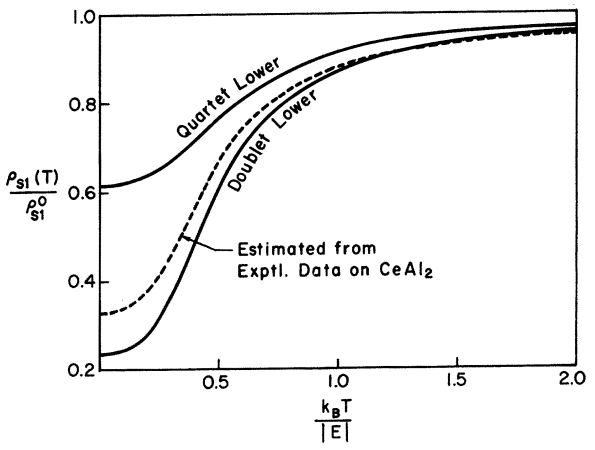

FIG. 2. Theoretical curves for the variation of spin-disorder resistivity of $CeAl_2$ with temperature under the influence of a cubic crystal field for (a) doublet lower and (b) quartet lower are shown by the solid lines. $\rho_{s1}(T)$ and ρ_{s1}^0 are given by Eqs. (7) and (5). The dotted curve is the experimental curve estimated from data on $CeAl_2$ (see Fig. 3).

in Eq. (9) are given by $f_1=2(1+x^{-1})^{-1}$ and $f_2=2(1+x)^{-1}$.

It is easily seen from Eq. (9) that at temperatures high compared to $|E|$, i.e., as $x\rightarrow 1$, the quantity inside the square brackets in Eq. (9) tends to the value 35/8. Thus Eq. (9) in this limit becomes identical to the Eq. (5) for ρ_{s1}^0 with $J=\frac{5}{2}$.

Expression (9) was evaluated for different temperatures with (a) doublet lying lower and (b) quartet lying lower. The variation of $\rho_{s1}(T)/\rho_{s1}^0$ with $k_BT/|E|$ is shown in Fig. 2. It is seen that $\rho_{s1}(T)$ tends to a much lower value as $T\rightarrow 0$ when the doublet is lower than when the quartet is lower.

The experimental ρ-versus-T curve for $CeAl_2$ was first obtained by van Daal and Buschow.[7] Measurements on this compound made in this laboratory were in satisfactory agreement with those of these authors. The measured resistivity (from which the residual resistivity of about 20 $\mu\Omega$ cm has been subtracted) is plotted as a function of temperature between 6 and 290°K as the solid curve in Fig. 3. In other words, the solid curve in Fig. 3 is the sum of two contributions

$$\rho(T)=\rho_l(T)+\rho_s(T),$$

where $\rho_l(T)$ is the lattice part and $\rho_s(T)$ is the spin-disorder part. The second-order contribution to ρ_s is included, i.e., $\rho_s(T)=\rho_{s1}(T)+\rho_{s2}(T)$.

$CeAl_2$ has the cubic Laves structure and the environment of the Ce atoms is also cubic so that our theory is applicable to this compound. The upturn in the ρ-T curve below 15°K is now regarded as a Kondo anomaly.[8] The point of interest to us is the unusual broad "knee" in the ρ-T curve at about 70°K. We ascribe this behavior to the influence of the crystal field on the spin-disorder resistivity. The only other contribution strongly dependent on temperature in this region is the lattice or phonon part, $\rho_l(T)$. The isomorphous but nonmagnetic compounds $LaAl_2$, $YbAl_2$, and YAl_2, where the lattice contribution to resistivity might be expected to be similar to that of $CeAl_2$, do not show this behavior.[7]

The general shape of the ρ-T curve in the temperature range (i.e., above 20°K) of interest is satisfactorily accounted for by our analysis as may be seen by a comparison of Figs. 2 and 3. To make a quantitative comparison between theory and experiment, one would have to subtract the lattice contribution $\rho_l(T)$ as well as the contribution $\rho_{s2}(T)$ described earlier from the measured resistivity. It can be seen from Fig. 3 that at high temperatures ($T>100$°K) the ρ-T curve is linear with a slope of 0.091 $\mu\Omega$ cm °K^{-1}, which may be compared with the value of about 0.12 $\mu\Omega$ cm °K^{-1} observed in nonmagnetic $YbAl_2$ and YAl_2. The temperature dependence of ρ in this region arises almost entirely from the variation of $\rho_l(T)$ with T. An estimation of $\rho_l(T)$ for $CeAl_2$ was made by scaling the entire $\rho_l(T)$-versus-T curve of $YbAl_2$[7] by a constant factor in such a way that the slope of the curve at high temperatures (above 100°K) was equal to that of the

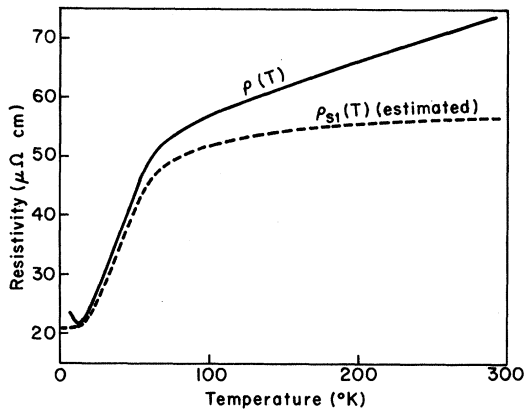

FIG. 3. Solid curve gives the measured resistivity of $CeAl_2$ from which the residual resistivity has been subtracted. The dotted curve shows the estimated spin-disorder resistivity $\rho_{s1}(T)$.

experimental $\rho(T)$-versus-T curve of $CeAl_2$ shown in Fig. 3. $\rho_{s2}(T)$ has also been estimated by noting that this term is solely responsible for the upturn in the ρ-versus-T curve (the Kondo phenomenon) below about 15°K and that above this temperature its contribution is quite negligible. Subtracting these estimated values of $\rho_l(T)$ and $\rho_{s2}(T)$ from the measured resistivity, one obtains the estimated $\rho_{s1}(T)$-versus-T curve, which is shown as the dotted line in Fig. 3 and also in Fig. 2, for a comparison with the theoretical curves. To plot the latter curve, the crystal-field separation in $CeAl_2$ has been taken to be 100°K which is the value given by neutron-scattering measurements.[9] It is apparent from Fig. 2 that the curve of $\rho_{s1}(T)$ versus T for $CeAl_2$ estimated from the experimental data is in much better agreement with the theoretical curve when the Γ_7 doublet is the lower-lying level than when the Γ_8 quartet is the lower-lying level. From heat-capacity measurements in the temperature range 0.5–15°K, Hill and da Silva[10] have also come to the conclusion that the Γ_7 level is the lower-lying level.

CONCLUSIONS

The influence of the crystalline electric field on the spin-disorder resistivity has been shown to be of importance at temperatures lower than the crystal-field splitting of the rare-earth ions in rare-earth alloys and intermetallic compounds. A method of quite general applicability has been put forward for the calculation of the spin-disorder resistivity as a function of temperature in the presence of a crystal field. The method has been illustrated by a calculation for Ce^{3+} ion in a cubic crystal field and is found to yield results in substantial agreement with the measured resistivity of $CeAl_2$.

The crystal field should also have interesting consequences on a calculation of the resistivity in the second Born approximation. This aspect is presently being investigated and will be reported later.

† Work assisted by a grant supplied by the National Aeronautics and Space Agency.

[1] See, e.g., T. Kasuya, Progr. Theoret. Phys. (Kyoto) **16,** 58 (1956); **22,** 227 (1959); P. G. deGennes and J. Friedel, J. Phys. Chem. Solids **4,** 71 (1958); P. G. deGennes, J. Phys. Radium **23,** 510 (1962).

[2] See A. J. Dekker, J. Appl. Phys. **36,** 906 (1965), for a review of this problem.

[3] See, e.g., Ref. 7.

[4] W. E. Wallace, R. S. Craig, A. Thompson, C. Deenadas, M. Dixon, M. Aoyagi, and N. Marzouk, *The Rare-Earth Elements* (Centre National de la Recherche Scientifique, Paris, 1970), p. 427.

[5] T. van Peski-Tinbergen and A. J. Dekker, Physica **29,** 917 (1963).

[6] K. R. Lea, M. J. M. Leask, and W. P. Wolf, J. Phys. Chem. Solids **23,** 1381 (1962).

[7] H. J. van Daal and K. H. J. Buschow, Solid State Commun. **7,** 217 (1969).

[8] K. H. J. Buschow and H. J. van Daal, Phys. Rev. Letters **23,** 408 (1969).

[9] B. D. Rainford, D. Phil. thesis, Oxford, 1969 (unpublished), quoted in Ref. 10.

[10] R. W. Hill and J. M. Machado da Silva, Phys. Letters **30A,** 13 (1969).

PHYSICAL REVIEW B VOLUME 2, NUMBER 11 1 DECEMBER 1970

Generalization of Conditions due to Domb for Reducing the Number of Unknown Terms in the Ising Fugacity Expansion*

M. FERER†

Department of Physics, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801

(Received 4 May 1970)

The derivation of low-temperature series for the Ising model is simplified by a high-temperature symmetry condition, a general proof of which does not exist in the open literature. The magnetic linked-cluster expansion provides an elementary and general proof.

BACKGROUND

We present the proof in detail for the free energy F of the nearest-neighbor $S=\frac{1}{2}$ Ising model. The straightforward generalization to $S>\frac{1}{2}$, longer-range interactions, and physical quantities other than F is indicated in conclusion. The Hamiltonian of the model is

$$-\beta\mathcal{H}=v\sum_{\langle ij\rangle}\sigma_i\sigma_j+h\sum_i\sigma_i, \tag{1}$$

where $\sigma_i=1\,(-1)$ for spin up (down), the indices range over lattice sites, and the sum in the first term is over nearest-neighbor pairs. The free energy is given by $-\beta F=\ln \mathrm{Tr}e^{-\beta\mathcal{H}}$.

At low temperatures (1) can usefully be rewritten in terms of operators measuring the deviation from complete alignment, $n_i\equiv\frac{1}{2}(1-\sigma_i)$,

$$-\beta\mathcal{H}=N(\tfrac{1}{2}qv+h)+4v\sum_{\langle ij\rangle}n_in_j-2(h+qv)\sum_i n_i, \tag{2}$$

where q is the number of nearest neighbors. The low-temperature (high-field) series for F is[1] just the Yvon-Mayer expansion with chemical potential $-2(h+qv)$. The free energy can be written as

$$-\frac{\beta F}{N}=\tfrac{1}{2}qv+h+\sum_{n=1}^{\infty}\mu^n L_n(u), \tag{3}$$

where $\mu=e^{-2h}$, $u=e^{-4v}$, and the $L_n(u)$ are finite polynomials[2] in u,

$$L_n(u)=u^{nq/2}\sum_{r=0}^{\frac{1}{2}n(n-1)}[n,r]u^{-r}.$$

The coefficients $[n, r]$ may be determined from the Mayer graphs. The quantity $(1-u)$ is a high-temperature variable, so high-temperature series can be derived from (3),

$$-\frac{\beta F}{N}=\tfrac{1}{2}qv+h+\sum_{n=1}^{\infty}\sum_{r=0}^{\infty}(-1)^r\mu^n \times\frac{(1-u)^r}{r!}\frac{\partial^r L_n(u)}{\partial u^r}\bigg|_{u=1}. \tag{4}$$

SYMMETRY CONDITION AND ITS USE

It is easy to see from (1) that the free energy F has the symmetry $F(v, h)=F(v, -h)$. This symmetry, which is explicit in the high-temperature series, is lost at low temperatures, where series converge only for $\mu\leq 1$. The high-temperature symmetry condition is

$$-\frac{\beta F}{N}=\tfrac{1}{2}qv+h+\ln(1+\mu)+\sum_{r=1}^{\infty}(1-u)^r\frac{\varphi_r(\mu)}{(1+\mu)^{2r}}, \tag{5}$$

with the specification that

$$\varphi_r(\mu)\equiv\sum_{n=1}^{2r-1}\varphi_r^{(n)}\mu^n$$

is a finite polynomial having the symmetry $\varphi_r(\mu)=\mu^{2r}\varphi_r(1/\mu)$. Note that this incorporates invariance under $h\leftrightarrow -h$. Equation (5) was first conjectured by Domb[3] and has subsequently been proved for various cases.[4] To our knowledge there is no proof in the open literature which is applicable to close-packed lattices and spins greater than $\frac{1}{2}$.