Our samples do not strictly belong to either of the above limiting cases. In principle we should use a more general analysis,[7] but the accuracy of our results does not justify it. We have made a simple numerical estimate of the ratio (slope Nb I)/(slope Nb II) at low temperature using Ref. 7 and assuming that $K_2(T=0)$ is the same for both samples. We gind a ratio of 2:5. This agrees with the experimental low-temperature ratio taken from Fig. 2. At $T=0.6T_c$ the slope is predicted to pass through zero and to become negative for $T>0.6T_c$. This important feature seems to be verified by extrapolation of the experimental points of Fig. 2. Further experiments are on the way to clarify this problem. In conclusion our experiments are in agreement with the theoretical results in the gapless region close to the upper critical field H_{c2}. In particular they show the predicted differences in behavior between the clean and the dirty limits.

We would like to thank Professor P. G. de Gennes and Professor A. Redfield for illuminating discussions.

[1]W. Fite, II, and A. G. Redfield, Phys. Rev. Letters 17, 381 (1966); B. G. Silbernagel, M. Weger, and J. H. Wernick, Phys. Rev. Letters 17, 384 (1966); K. Asayama and Y. Masuda, J. Phys. Soc. Japan 21, 1459 (1960); B. G. Silbernagel, M. Weger, W. Gilbert Clark, and J. H. Wernick, Phys. Rev. 153, 535 (1967). For a review see the Orsay Group on Superconductivity, "Nuclear Magnetic Resonance In Type-II Superconductors," in Proceedings of the Fourteenth Colloque Ampère, Ljubljana, Yugoslavia, 1966 (to be published).

[2]P. G. de Gennes, Phys. Condensed Matter 3, 79 (1964).

[3]E. Helfand and N. R. Werthamer, Phys. Rev. 147, 288 (1966).

[4]M. Cyrot, J. Phys. 27, 283 (1966).

[5]In principle $K_2(T)$ is a function of the mean free path. Here we neglect this effect and take for both samples the values given by D. K. Finnemore, T. F. Stromberg, and C. A. Swenson, Phys. Rev. 149, 231 (1966).

[6]Orsay Group on Superconductivity, Phys. Condensed Matter 5, 141 (1966).

[7]D. Eppel, W. Pesch, and L. Tewordt, Z. Physik 197, 46 (1966).

MAGNETIC POLARIZATION OF A SINGLE MAGNETIC IMPURITY IN METALS

Sang Boo Nam and James Wing Fai Woo
Department of Physics, Rutgers, The State University, New Brunswick, New Jersey
(Received 28 July 1967)

The spin polarization of a single magnetic impurity in a metal in an external magnetic field has been calculated by variational method. The results are in agreement with the measurement of the hyperfine field by the Mössbauer technique.

Recently, there has been much interest in the nature of the ground state of dilute alloys of transition elements in some metals.[1-4] It is believed that below a Kondo temperature T_K, a bound state between the localized magnetic impurity and the conduction electrons is formed. This state has a binding energy of the order of kT_K and is characterized by a long-range conduction-electron polarization cloud.[1] There is experimental evidence that this state is a singlet,[3] although the theoretical situation is not entirely clear. It had been expected that this bound state will partially break up in the presence of an external magnetic field and that it will completely dissociate when the external field reaches a value $\mu_B H_K \simeq kT_K$.[3] However, Frankel et al.[4] recently reported results of Mössbauer experiments on dilute Fe in Cu which shows that the bound state is not completely destroyed until an external field four to five times kT_K is applied. In this paper, we present results of calculations of a single magnetic impurity in an external field.

Our method is a variational approach similar to that of Heeger and Jensen[2] for the corresponding problem in the absence of the magnetic field. Our results are in agreement with the data of Frankel et al.[4]

We assume a one-orbital impurity, an antiferromagnetic s-d interaction, a large intraatomic Coulomb interaction so that the impurity is never doubly occupied, and the equality of g factor of the d electron and of the con-

duction electron. The Hamiltonian for our model is

$$H=\sum_{k,\sigma}\epsilon_k n_{k\sigma}+\tfrac{1}{2}|J|\sum_{k,q}\{(C_{k\uparrow}{}^{\dagger}C_{q\uparrow}-C_{k\downarrow}{}^{\dagger}C_{q\downarrow})S_z+C_{k\uparrow}{}^{\dagger}C_{q\downarrow}S_-+C_{k\downarrow}{}^{\dagger}C_{q\uparrow}S_+\}-\gamma[S_z+\tfrac{1}{2}\sum_k(\eta_{k\uparrow}-\eta_{k\downarrow})]. \quad (1)$$

Here ϵ_k is the kinetic energy of the conduction electron of the kth mode measured from the chemical potential, and $C_{k\sigma}{}^{\dagger}$, $C_{k\sigma}$, and $\eta_{k\sigma}$ are the usual conduction-electron operators. $\gamma=g\mu_B H_z$, where H_z is the external magnetic field. The d-electron spin operator S is given by

$$S_z=\tfrac{1}{2}(C_{d\uparrow}{}^{\dagger}C_{d\uparrow}-C_{d\downarrow}{}^{\dagger}C_{d\downarrow}),\quad S_{+(-)}=C_{d\uparrow(\downarrow)}{}^{\dagger}C_{d\downarrow(\uparrow)}.$$

Since there is only one impurity, we expect the wave function to be almost the same as in the absence of the s-d interaction. Thus, we choose as our wave function

$$|\psi\rangle=\sum_k\{C_{d\uparrow}{}^{\dagger}(a_k+\beta_k C_{k\downarrow}{}^{\dagger}+\bar{\alpha}_k C_{k\uparrow}{}^{\dagger})+C_{d\downarrow}{}^{\dagger}(\bar{a}_k+\alpha_k C_{k\uparrow}{}^{\dagger}+\bar{\beta}_k C_{k\downarrow}{}^{\dagger})\}$$

$$\times\prod_{\substack{\epsilon_p>\frac{1}{2}\gamma\\ p\neq k}}(U_p)\prod_{\substack{|\epsilon_p|<\frac{1}{2}\gamma\\ p\neq k}}(f_p C_{p\uparrow}{}^{\dagger})\prod_{\substack{\epsilon_p<-\frac{1}{2}\gamma\\ p\neq k}}(V_p C_{p\uparrow}{}^{\dagger}C_{p\downarrow}{}^{\dagger})|0\rangle, \quad (2)$$

where $V_k=\theta(-\frac{1}{2}\gamma-\epsilon_k)$, $U_k=\theta(-\frac{1}{2}\gamma+\epsilon_k)$, $f_k=1-V_k-U_k$, $\theta(x)=1$ for $x>0$, and $\theta(x)=0$ for $x<0$. Upon minimization of the energy, it is found that all the bar quantities are zero; henceforth, we neglect them. The normalization condition for $|\psi\rangle$ is

$$\sum_k[\alpha_k{}^2+\beta_k{}^2+a_k{}^2]=1. \quad (3)$$

The energy of the system in the state $|\psi\rangle$ is

$$E=\sum_k\{\epsilon_k[\alpha_k{}^2+\beta_k{}^2+(f_k{}^2+2V_k{}^2)(1-\alpha_k{}^2-\beta_k{}^2-a_k{}^2)]-\tfrac{1}{2}\gamma[a_k{}^2+f_k{}^2(1-a_k{}^2-\alpha_k{}^2-\beta_k{}^2)]\}$$

$$+\sum_{k,q}|J|\{[\alpha_k\beta_q-\tfrac{1}{4}(\alpha_k\alpha_q+\beta_k\beta_q)](U_kU_q+V_kV_q)+(\alpha_k-\tfrac{1}{2}\beta_k)a\ V_kf_q+\tfrac{1}{4}a_ka_qf_kf_q\}. \quad (4)$$

The extremal condition of the energy, subject to the constraint of Eq. (3), leads to the following equation for α_k, β_k, and a_k:

$$\alpha_k=(\delta_2-2\delta_1-2\delta_3)\bar{V}_k+(\delta_5-2\delta_4)\bar{U}_k,\quad \beta_k=(\delta_1-2\delta_2+\delta_3)\bar{V}_k+(\delta_4-2\delta_5)\bar{U}_k,$$

$$a_k=(\delta_1-2\delta_2-\delta_3)\bar{f}_k, \quad (5)$$

where

$$\bar{V}_k=V_k/4(\lambda-\epsilon_k),\quad \bar{U}_k=U_k/4(\lambda+\epsilon_k),\quad \bar{f}_k=f_k/4(\lambda-\epsilon_k),\quad \delta_1=\sum_k|J|\beta_kV_k,$$

$$\delta_2=\sum_k|J|\alpha_kV_k,\quad \delta_3=\sum_k|J|a_kf_k,\quad \delta_4=\sum_k|J|\beta_kU_k,$$

$$\delta_5=\sum_k|J|\alpha_kU_k. \quad (6)$$

The Lagrange multiplier λ is determined by the above self-consistent equations (5), (6), and (3). The binding energy is given by $\lambda-\frac{1}{2}\gamma$. This is the difference in energy between our state and that with $\alpha_k=0=\beta_k$ in the presence of an external magnetic field. The results of λ, α_k, β_k, and a_k are[5]

$$\alpha_k=\kappa(2-3\delta)\bar{V}_k,\quad \beta_k=-2\kappa\bar{V}_k,\quad a_k=\kappa(2-11\delta+2\delta^2)\bar{f}_k, \quad (7)$$

$$\tfrac{1}{4}|J|N_0\ln[(\lambda+\tfrac{1}{2}\gamma)/(\lambda-\tfrac{1}{2}\gamma)]=(4\delta-3\delta^2)/(2-11\delta^2+6\delta^2),$$

$$\delta=\tfrac{1}{4}|J|N_0\ln[(\lambda+\tfrac{1}{2}\gamma)/\gamma_0],$$

$$(\tfrac{1}{4}\kappa)^2|J|N_0[8-12\delta+9\delta^2+(2-11\delta+6\delta^2)^2\gamma/(\lambda-\tfrac{1}{2}\gamma)]=\lambda+\tfrac{1}{2}\gamma.$$

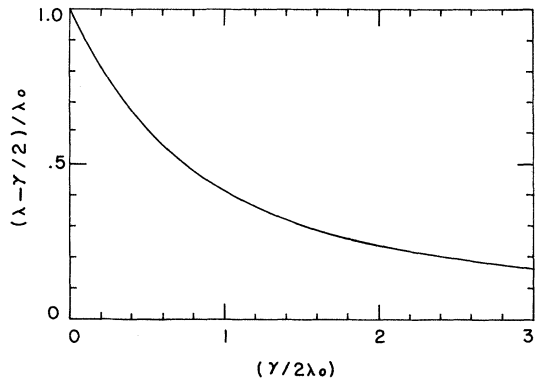

FIG. 1. The binding energy as a function of $\gamma = g\mu_B H$.

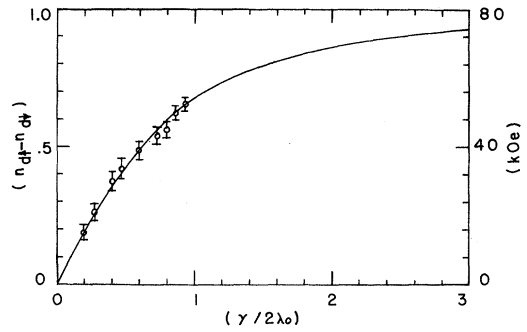

FIG. 2. d-electron polarization and zero-temperature hyperfine field as functions of γ. The hyperfine field curve is from Frankel et al., Ref. 4.

Here N_0 is the density of states at the Fermi surface and λ_0 is the binding energy when $H_z = 0$.[6] A graph of the binding energy as function of γ is shown in Fig. 1.

The hyperfine field at nucleus measured by the Mössbauer technique is mainly due to the polarization of the inner s electrons caused by the polarization of the d electrons. Thus, we expect the hyperfine field at zero temperature to be roughly proportional to the d-electron polarization:

$$\eta_{d\uparrow} - \eta_{d\downarrow} = \sum_k (\beta_k^2 - \alpha_k^2 + a_k^2) = \sum_k (n_{k\downarrow} - n_{k\uparrow} + f_k^2)$$

$$= |J| N_0 (\tfrac{1}{4}\kappa)^2 [(2 - 11\delta + 6\delta^2)^2 \gamma / (\lambda - \tfrac{1}{2}\gamma) - 12\delta + 9\delta^2] / (\lambda + \tfrac{1}{2}\gamma). \quad (8)$$

The magnetic susceptibility at zero field is[7]

$$\chi(0) = \mu_B^2 (1 - \tfrac{3}{8}|J| N_0) / \lambda_0. \quad (9)$$

In Fig. 2 we display the polarization of the d electron as a function of the external field assuming $|J| N_0 = 0.1$. We note that this polarization is a most insentive function of $|J| N_0$. In comparing our results with the experiment, we determine λ_0 from the slope of the polarization at zero field. λ_0 is about 150 kOe from Ref. 4.[8] By choosing this value of λ_0, the experimental data shown in Fig. 2 agree with our calculation.

In conclusion, we found that the bound state does not break up completely until the external magnetic field is many times the Kondo temperature. It seems that the reason for this is that in the presence of an external magnetic field, the expectation value of the s-d interaction is enhanced because of the presence of singly occupied (i.e., only spin-up state is occupied) conduction-electron states.

We would like to acknowledge discussions with Professor E. Abrahams and Professor D. Langreth.

---

*This work was supported by the Office of Naval Research and the National Science Foundation.

[1]J. Kondo, Phys. Rev. 154, 644 (1967); Y. Nagaoka, Phys. Rev. 138, A1112 (1965); K. Yosida, Phys. Rev. 147, 223 (1966).

[2]A. J. Heeger and M. A. Jensen, Phys. Rev. Letters 18, 488 (1967).

[3]M. A. Jensen, A. J. Heeger, L. B. Welsh, and G. Gladstone, Phys. Rev. Letters 18, 997 (1967).

[4]R. B. Frankel, N. A. Blum, Brian B. Schwartz, and Duk Joo Kim, Phys. Rev. Letters 18, 1051 (1967).

[5]With the condition of Eq. (7), the wave function of Eq. (2) is the same as the one being constructed by destroying a conduction electron and creating a d-electron from the ground state of the noninteracting Fermi gas in the presence of the external field, i.e.,

$$|\psi\rangle = \sum_k \{C_{d\uparrow}^\dagger (\beta_k C_{k\uparrow} + \beta_k C_{k\downarrow}) + C_{d\downarrow}^\dagger (\alpha_{d\downarrow} C_{k\downarrow} + \alpha_k C_{k\uparrow})\} \prod_{\epsilon_P > \frac{1}{2}\gamma} (U_P) \prod_{|\epsilon_P| < \frac{1}{2}\gamma} (f_P C_{P\uparrow}^\dagger) \prod_{\epsilon_P < -\frac{1}{2}\gamma} (V_P C_{P\uparrow}^\dagger C_{P\downarrow}^\dagger) |0\rangle$$

$$= \sum_k \{C_{d\uparrow}^\dagger (\beta_k f_k + \beta_k V_k C_{k\downarrow}^\dagger - \bar{\beta}_k V_k C_{k\uparrow}^\dagger) + C_{d\downarrow}^\dagger (\alpha_k f_k + \bar{\alpha}_k V_k C_{k\uparrow}^\dagger - \alpha_k V_k C_{k\downarrow}^\dagger)\}$$

$$\times \prod_{\substack{\epsilon_P > \frac{1}{2}\gamma \\ p \neq k}} (U_P) \prod_{\substack{|\epsilon_P| < \frac{1}{2}\gamma \\ p \neq k}} (f_P C_{P\uparrow}^\dagger) \prod_{\substack{\epsilon_P < -\frac{1}{2}\gamma \\ p \neq k}} (V_P C_{P\downarrow}^\dagger C_{P\downarrow}^\dagger) |0\rangle.$$

This state is clearly an eigenstate of the total number of electrons, and so is that of Eq. (2) with Eq. (7). When $\gamma = 0$, this state is equivalent to that of Yosida by replacing the electron operator by the hole operator.

[6]Using our wave function, $\lambda_0 = \mu \exp[-4/3N_0|J|]$, where μ is the usual cutoff energy (of order of the Fermi energy). This same expression was obtained by Heeger and Jensen (Ref. 2).

[7]We define the susceptibility as $\chi(H) = (\partial/\partial H)\{\mu_B\langle n_{d\uparrow} - n_{d\downarrow}\rangle\}$ for all fields. At low field, a similar result is obtained by Takano and Ogawa [Progr. Theoret. Phys. 35, 343 (1966)] by the usual Green's function method. However, their result is different from ours by the factor π^{-1}.

[8]This critical field corresponding to the critical temperature of 10°K is twice that of Ref. 3. The reason for this discrepancy between the two experiments is unclear.

EVIDENCE FOR A TRIPLET STATE OF THE SELF-TRAPPED EXCITON IN ALKALI-HALIDE CRYSTALS

M. N. Kabler and D. A. Patterson
U. S. Naval Research Laboratory, Washington, D. C.
(Received 7 August 1967)

The lifetimes and polarizations of intrinsic recombination radiation from alkali-halide crystals at low temperature are interpreted in terms of two self-trapped exciton states, one predominantly singlet, the other triplet in character. This is the first strong evidence for the triplet assignment. The variation with crystal of the triplet-state lifetime is attributed to effects of the different halogen spin-orbit couplings and the varying degrees of axial relaxation in the self-trapped configuration.

Under high-energy excitation at low temperature, pure alkali-halide crystals luminesce with high efficiency. This luminescence has been shown to arise primarily from intrinsic radiative recombination of electrons and self-trapped holes (V_k centers).[1-3] The emission spectra are closely related to those resulting from excitation with light in the exciton absorption bands.[4] The term "self-trapped exciton" appropriately describes the luminescent center, which may be regarded simply as a halide-ion pair in a bonding excited state. The $\langle 110 \rangle$ bond axis is evident from the polarization of the luminescence.[5]

Table I shows data obtained in this laboratory and elsewhere[2,3,6] on peak energies, polarizations, and lifetimes for self-trapped exciton emission bands at liquid-helium temperature (LHeT). Although extensive data exist on intrinsic luminescence excited by ultraviolet light,[4,7] we have for consistency included in Table I only data obtained with x-ray and high-energy-electron excitation. Both σ and π transitions occur in general, the former with short (allowed) lifetimes τ_{lm}, the latter, at lower energy, with longer (apparently forbidden) lifetimes τ_{km}. This lifetime correlation was evident in previous experiments on KI.[8] The σ transition has not been observed in four of the crystals. Only RbI exhibits a third, possibly intrinsic, band of any consequence, and it is relatively weak at LHeT.[3] The half-widths of the bands in Table I range from 0.3 to 0.7 eV.

The experimental methods have been described,[1] except for the lifetime measurements; these employed standard electronic techniques to detect luminescent decay after excitation by a 15-MeV electron pulse (≈20 nsec duration) from the Naval Research Laboratory Linac. The accuracy of τ_{lm} was limited by instrumental resolution. Since the radiative efficiencies are high at LHeT, the lifetimes will be identified with the reciprocals of radiative-transition probabilities.

We shall discuss states of the self-trapped exciton in terms of those of a diatomic rare-gas molecule. This analogy is appropriate because of the close similarities between the electronic configurations of a free rare-gas atom and a free (unrelaxed) exciton,[9] and because of the close experimental relationship of the self-trapped exciton to the V_k center (diatomic molecular ion).[1] The ground state is then $(\sigma_g np)^2(\pi_u np)^4(\pi_g np)^4(\sigma_u np)^2\,{}^1\Sigma_g^+$, which is unstable; the lowest self-trapped exciton states are $\cdots(\sigma_u np)[\sigma_g(n+1)s]^{3,1}\Sigma_u^+$, which are bound.[10] It is evident that the τ_{lm} and the polarization of the σ transition are consistent with ${}^1\Sigma_u^+ \rightarrow {}^1\Sigma_g^+$. For the π transition, the variation of τ_{km} with anion appears consistent with ${}^3\Sigma_u^+ \rightarrow {}^1\Sigma_g^+$, for which multiplicity forbiddenness is broken by mixing due to the halo-