Spin-correlation effects for a large-radius electron center in a magnetically mixed semiconductor

S. M. Ryabchenko

Physics Institute, Ukrainian Academy of Sciences

Yu. G. Semenov

Semiconductor Institute, Ukrainian Academy of Sciences

(Submitted 27 July 1982)
Zh. Eksp. Teor. Fiz. **84**, 1419–1421 (April 1983)

The temperature and magnetic-field dependences of the magnetic susceptibility and the positions of the spin-flip Raman scattering (SFRS) lines are studied theoretically for a large-radius electron center in magnetically mixed semiconductors. The possibility of autolocalization of a free electron and of a change in the radius of the state of the localized electron as a result of its spin correlation with the system of localized spin momenta (LSM) is also considered. The analysis is based on an approximation in which the exchange interaction of the electron and of the LSM is homogeneous over the localization region, with account taken of all the spin components of the Hamiltonian. The analysis leads to approximate analytic equations for the SFRS line shape and to formulas, exact within the framework of the model, for the partition function and the free energy. The differences between the obtained solutions and those resulting from the use of the self-consistent-field approximation are discussed. The results describe qualitatively and quantitatively the published experimental data on SFRS.

PACS numbers: 75.30.Cr, 75.10.Dg, 75.30.Et, 78.30. — j

1. INTRODUCTION

One of the accomplishment of magnetic-semiconductor physics was the prediction and observation in them of special types of autolocalized carrier states, due to the spin correlation of a free carrier or a carrier bound to a defect with the localized spin moments (LSM) of the ions making up the crystal (see, e.g., Refs. 1 and 2). In most papers dealing with the theory of such states, only one component was taken into account in the spin wave function of the carrier, and the interaction of the electron with the LSM system was described in the approximation of a self-consistent effective exchange field. The problem was as a rule made complicated by the need for taking into account the strong interaction in the LSM system. In Refs. 3 and 4, where the exchange interaction of the carrier with the LSM was considered with account taken of all the spin components, they solved the problem of an electron rigidly localized by the Coulomb interaction in such a way that the exchange interaction with the LSM was unable to change the radius of the state of the center.

Investigations were recently initiated of magnetically mixed (semimagnetic) semiconductors,[5–8] in which the interaction within the LSM system does not play a decisive role, so that the exchange interactions of free carriers or carriers in a large-radius state with the LSM manifests itself in purest form. The investigation of spin-correlated states in such objects becomes simpler both experimentally and theoretically. In particular, in Res. 9 and 10 was investigated Raman scattering with spin flip (SFRS) of shallow donors in the magnetically mixed hexagonal semiconductors $Cd_{1-x}Mn_xSe$ and CdS:Mn. It was observed that a finite energy shift of the SFRS exists in the absence of an external magnetic field; this is a direct indication of the presence of a spin-correlated bound state of the carriers in the LSM. A manifestation of this correlation was observed also in the change, with temperature, of the binding energy of an excitonlocalized on a neutral acceptor.[11]

Finite shifts ΔE_{SFRS} of the SFRS (or of the energy of a localized exciton) were observed in experiments[9–11] at temperatures higher than follow from the model of the self-consistent effective field, in which a local phase transition results in a bound spin state and in exchange fields, which are not equal to zero in the absence of an external magnetic field and are applied both by the carrier to the LSM ($\mathbf{H}_{eM}$) and by the LSM on the carrier spin ($\mathbf{H}_{Me}$). To eliminate this contradiction, the authors introduced the model of non-self-consistent effective field, described in greatest detail in Ref. 11. It was assumed that the electron spin "follows" adiabatically the direction of $\mathbf{H}_{Me}$, and that its projection on the direction of $\mathbf{H}_{Me}$ is independent of temperature but equals the maximum possible value. In this approach, the possibility of whose application is determined by the relaxation parameters of the problem, the modulus of $\mathbf{H}_{eM}$ does not depend on the temperature, there is no local phase transition, and the electron spin-state splitting, which determines ΔE_{SFRS}, is preserved at all temperatures. At not too low temperatures this splitting should be proportional to T^{-1}.

The model considered does not eliminate all the contradictions since, first, the extrapolation of the measured ΔE_{SFRS} to $T^{-1}\to 0$ yields a finite value,[10] and second, its application calls for long LSM spin-lattice relaxation times, something difficult to expect at the LSM densities discussed in the cited papers.

We develop in this paper a model of a spin-correlated state of a large-radius electron center without using the ef-

 0038-5646/83/040825-08$04.00

fective-field approximation and without taking into account all the spin components of either the electron or the LSM. The model takes into account the fact that the carrier—impurity exchange interaction forms an energy spectrum characterized by the total spin of the system and by its projection. The thermodynamic, magnetic, and spectral properties of the system are determined by the statistical distribution of the spin states in the given spectrum. The approach is close to that used in Refs. 3 and 4, except that here we consider the state of an electron center with a large but arbitrary radius, and take into account of its change as a result of spin correlations. It will be shown that this approach explains all the basic results on SFRS[9,10] and makes it possible to analyze consistently the problem of spin autolocalization of a carrier in a magnetically mixed semiconductor.

2. HAMILTONIAN AND BASIC APPROXIMATION

We consider an electron localized a crystal with N_0 unit cells, in N_{M} of which the lattice ions are replaced by ions with spin S_{M}. The interaction of these LSM with each other will be neglected for the time being.

The spin part of the energy of the band (nonlocalized) electron in such a crystal is determined by the Zeeman Hamiltonian and by the interaction of the electron spin $S_e = \frac{1}{2}$ with the effective exchange field[5]

$$\mathbf{G}=-2J\frac{N_{\text{M}}}{N_0}\langle \mathbf{S}_{\text{M}}\rangle \equiv \Delta\langle \mathbf{S}_{\text{M}}\rangle, \tag{1}$$

where J is the exchange constant and $g\mu_B N_{\text{M}}\langle \mathbf{S}_{\text{M}}\rangle$ is the magnetization of the LSM system in an external magnetic field $\mathbf{H}$. For a large-radius electron center in a state with wave-function orbital part $\psi(\mathbf{r})$, the spin part of the Hamiltonian is

$$\mathcal{H}=\mathcal{H}_{\text{exc}}+\mathcal{H}_z, \tag{2}$$

where the exchange and Zeeman parts of the interaction are defined as

$$\mathcal{H}_{\text{exc}}=-2\sum_{j=1}^{N_{\text{M}}}A_j\mathbf{S}_e\mathbf{S}_{\text{M}}^j, \qquad \mathcal{H}_z=\omega_e S_{eZ}+\omega_{\text{M}}\sum_{j=1}^{N_{\text{M}}}S_{\text{M}Z}^j.$$

Here $\omega_{e\,(\text{M})}=g_{e\,(\text{M})}\mu_B H$ are the corresponding Zeeman frequencies ($\hbar=1$) and the Z axis is directed along $\mathbf{H}$. The constants A_j are connected with the carrier-impurity exchange interaction constant contained in (1) by the relation

$$A_j=J\Omega_0|\psi(\mathbf{R}_j)|^2, \tag{3}$$

where Ω_0 is the volume of the unit cell and $\mathbf{R}_j$ is the radius vector of the jth LSM.

The basic approximation used in this paper to find the spectrum of the states of the Hamiltonian (2) is the homogeneous-exchange-interaction model, i.e., replacement of the exact Hamiltonian $\mathcal{H}_{\text{exc}}$ by the approximate one

$$\mathcal{H}_{\text{exc}}^{(0)}=\mathcal{H}_{\text{exc}}-\Delta\mathcal{H}_{\text{exc}}=-2\bar{A}\sum_{j=1}^{\bar{N}}\mathbf{S}_e\mathbf{S}_{\text{M}}^j. \tag{4}$$

The parameters $\bar{A}$ and $\bar{N}$ must be determined here from the requirement that the contribution of $\Delta\mathcal{H}_{\text{exc}}$ to the system spectrum be a minimum. To solve this problem we use one more approximation based on partial diagonalization with respect to the electron spin $\mathbf{S}_e$, as proposed in Ref. 12. According to Ref. 12, the term $\Delta\mathcal{H}_{\text{exc}}$ can be represented in the form of an expansion in even powers of the operators $\mathbf{S}_M^j$. We determine $\bar{A}$ and $\bar{N}$ from the condition that the mean value of the first term of the expansion vanish and the mean value of the second be a minimum. As a result we obtain for $\bar{A}$ and $\bar{N}$ in the case of a spherically symmetrical $\psi(\mathbf{r})$ the equations

$$\bar{A}=JN_{\text{M}}/\bar{N}N_0=-\Delta/2\bar{N}, \qquad \bar{N}=N_{\text{M}}\bar{V}/N_0\Omega_0, \tag{5}$$

$$4\pi\int_0^{\bar{R}}[|\psi(r)|^2-|\psi(\bar{R})|^2]r^2\,dr-{}^1/_2=0, \tag{6}$$

where $\bar{R}$ and $\bar{V}$ are the radius and volume of the sphere inside of which the true exchange interaction of the carrier with the LSM is effectively replaced by homogeneous exchange interaction. Condition (5) is equivalent in essence to introducing in (3) a normalized plane spherical function of the form $\bar{\psi}(r)=\bar{V}^{-1/2}\theta(\bar{R}-r)$, where $\theta(x)$ is the Heaviside step function, whereas to describe all the remaining characteristics of the electron center we retain the function $\psi(r)$.

For the simplest wave functions frequently used in models of large-radius electron centers, Eq. (6) can be easily solved. The obtained $\bar{R}$ and $\bar{V}$ are given in Table I. When the approximation (4) is used, the Hamiltonian (2) is replaced by

$$\mathcal{H}^{(0)}=\frac{\Delta}{\bar{N}}\mathbf{S}_e\mathbf{S}_\Sigma+\omega_e S_{eZ}+\omega_{\text{M}}S_{\Sigma Z}, \quad \mathbf{S}_\Sigma=\sum_{j=1}^{\bar{N}}\mathbf{S}_{\text{M}}^j, \tag{7}$$

where $\mathbf{S}_\Sigma$ is the total spin of the system of $\bar{N}$ LSM. This Hamiltonian corresponds to the one used in Ref. 13 to calculate the EPR of F centers, is similar to the Hamiltonians in Refs. 3 and 4, and permits an exact solution of the problem of the energy spectrum using the Breit-Rabi formulas.

It will be shown below that $\mathcal{H}^{(0)}$ (7) likewise permits exact solutions of the problems of thermodynamic and magnetic properties of a large-radius electron center and of the problem of autolocalization of an electron as a result of carrier-impurity exchange interaction, and makes it possible to describe the experiments on SFRS.

TABLE I.

$\psi(r)$	$\bar{R}/a$	$\gamma=\bar{V}/a^3$
$(3/4\pi a^3)^{1/2}\theta(a-r)$	1	$4\pi/3$
$(2/\pi a^2)^{3/4}\exp\{-(r/a)^2\}$	1.043	4.753
$(\pi a^3)^{-1/2}\exp(-r/a)$	1.836	25.93

3. SPECTRUM OF SYSTEM STATES, PARTITION FUNCTION

As a simpler but inessential simplification we assume in (7) that $\omega_e=\omega_{\text{M}}\equiv\omega_0$. In this case the exact quantum numbers of the problem are the total spin $\mathbf{F}=\mathbf{S}_\Sigma+\mathbf{S}_e$ and its projection μ on the quantization axis. We introduce a quantum number equal to $+$ or $-\frac{1}{2}$ for states with parallel and antiparallel $\mathbf{S}_\Sigma$ and $\mathbf{S}_e$, respectively. The energies of the states with given S_Σ, μ, and f are equal to ($f=F-S_\Sigma$)

$$E_{S_\Sigma,\mu,f}=\Delta\bar{N}^{-1}f(S_\Sigma+{}^1/_2)+\omega_0\mu-\Delta/4\bar{N}, \tag{8}$$

and the corresponding wave functions are defined as linear combinations of the LSM states $|S_\Sigma, M\rangle$ with given S_Σ and its projection M and of the eigenvectors of the operator of the electron spin $|+\rangle, |-\rangle$:

$$\psi_{S_\Sigma,\mu,f} = \left(\frac{1}{2}+\frac{f\mu}{S_\Sigma+1/2}\right)^{1/2}\left|S_\Sigma, \mu-\frac{1}{2}\right\rangle\left|+\right\rangle + \left(\frac{1}{2}-\frac{f\mu}{S_\Sigma+1/2}\right)^{1/2}\left|S_\Sigma, \mu+\frac{1}{2}\right\rangle\left|-\right\rangle. \quad (9)$$

In what follows it is necessary to find the statistical weights of the states with energies (8) and the SFRS transitions between them. We determine first the partition function Z of the system in question.

For N identical noninteracting spins S_M, whose Zeeman energy is $\omega_0 S_{MZ}$, the partition function is defined as

$$Z_0 = \left[\frac{\operatorname{sh}\beta\omega_0(S_M+1/2)}{\operatorname{sh}\beta\omega_0/2}\right]^N \quad (10)$$

($\beta = 1/T$ is the reciprocal temperature; $k_B = 1$). It is determined by the sum of the populations of the states over the specified projection M of the total spin of the system:

$$Z_0 = \sum_{M=-NS_M}^{NS_M} X_N(M)\exp(-\beta\omega_0 M) = \sum_{M=\sigma}^{NS_M}(2-\delta_{M,0})\operatorname{ch}\beta\omega_0 M, \quad (11)$$

where $X_N(M)$ is the statistical weight of the states with given M; $\sigma = 0$ or $\frac{1}{2}$ depending on the parity of $2NS_M$.

The partition function of a system described by the Hamiltonian (7) is, by definition,

$$Z = \sum_{f=-1/2,1/2}\sum_{S_\Sigma=\sigma}^{\bar{N}S_M}\sum_{u=-S_\Sigma}^{S_\Sigma+f} X_{\bar{N}}^{S_\Sigma}(M) \times\exp\left\{-\beta\left[\frac{\Delta}{\bar{N}}f\left(S_\Sigma+\frac{1}{2}\right)+\omega_0\mu-\frac{\Delta}{4\bar{N}}\right]\right\}, \quad (12)$$

where the statistical weight $X_{\bar{N}}^{S_\Sigma}(M)$ of the states of the system of $\bar{N}$ spins with fixed S_Σ and M is independent of M and is expressed in terms of the $X_N(M)$ introduced above:

$$X_N^S(M) = X_N(S) - X_N(S+1). \quad (13)$$

Comparison of (12) with (10) and (11) yields after summing over μ and taking (13) into account

$$Z = \frac{e^{\beta(\bar{A}+\omega_0)}-1}{2\operatorname{sh}(\beta\omega_0/2)}\left\{\frac{\operatorname{sh}[\beta(\bar{A}+\omega_0)(S_M+1/2)]}{\operatorname{sh}[\beta(\bar{A}+\omega_0)/2]}\right\}^{\bar{N}} + \frac{1-e^{\beta(\bar{A}-\omega_0)}}{2\operatorname{sh}(\beta\omega_0/2)}\left\{\frac{\operatorname{sh}[\beta(\bar{A}-\omega_0)(S_M+1/2)]}{\operatorname{sh}[\beta(\bar{A}-\omega_0)/2]}\right\}^{\bar{N}}. \quad (14)$$

This expression is the exact partition function for the investigated problem.

4. SPIN AUTOLOCALIZATION OF FREE ELECTRON AND POSSIBILITY OF LOCAL SPIN ORDERING IN A LARGE-RADIUS ELECTRON CENTER

We consider first the properties of a large-radius electron center, disregarding the possible change of the radius of its state on account of spin correlation with the LSM. The longitudinal magnetic susceptibility $\chi_\parallel$ of such a center and the spin part of its free energy F_M can be obtained on the basis of (14) from the known relations

$$\chi_\parallel = \frac{T}{\bar{N}}\frac{\partial^2 \ln Z}{\partial H^2}, \quad (15)$$

$$F_M = -T\ln Z. \quad (16)$$

It is convenient to transform (14) by introducing the notation

$$x_\pm = \beta\left(\frac{\Delta}{2\bar{N}}\pm\omega_0\right), \quad x_0 = \frac{\beta\Delta}{2\bar{N}}, \quad Y(x) = (1-e^{-x})\left[\frac{\operatorname{sh}x(S_M+1/2)}{\operatorname{sh}(x/2)}\right]^{\bar{N}}. \quad (17)$$

In the new notation, Eq. (14) takes the form

$$Z = [Y(x_+)-Y(x_-)]/2\operatorname{sh}(\beta\omega_0/2). \quad (18)$$

Using (18), the expression for the susceptibility becomes

$$\chi_\parallel = \frac{(g\mu_B)^2}{\bar{N}T}\left[\frac{Y''(x_+)-Y''(x_-)}{Y(x_+)-Y(x_-)} - \left(\frac{Y'(x_+)+Y'(x_-)}{Y(x_+)-Y(x_-)}\right)^2 + \frac{1}{4\operatorname{sh}^2(\beta\omega_0/2)}\right], \quad (19)$$

where $Y'(x)$ and $Y''(x)$ are the corresponding derivatives of $Y(x)$ with respect to x. Interest attaches to the expression for the susceptibility in a zero external magnetic field

$$\chi_0 = \lim_{\omega_0\to 0}\chi_\parallel = \frac{(g\mu_B)^2}{\bar{N}T}\frac{Y'''(x_0)-Y'(x_0)/4}{3Y'(x_0)}, \quad (20)$$

or, introducing the Planck factor $n(x) = [\exp(x)-1]^{-1}$ and the renormalized Brillouin function

$$b_S(x) \equiv SB_S(Sx) = (S+1/2)\operatorname{cth}\left[x\left(S+\frac{1}{2}\right)\right] - 1/2\operatorname{cth}\frac{x}{2},$$

$$\chi_0 = \frac{(g\mu_B)^2}{\bar{N}T}\frac{1}{\bar{N}b_{S_M}(x_0)+n(x_0)}\{1/3\bar{N}^3 b_{S_M}^3(x_0) + \bar{N}^2 b_{S_M}(x_0)[b_{S_M}(x_0)n(x_0)+b_{S_M}'(x_0)] + \bar{N}[1/3(b_{S_M}''(x_0)-1/4 b_{S_M}(x_0)) + n(x_0)(b_{S_M}'(x_0)-b_{S_M}(x_0))] + 1/4 n(x_0)\}, \quad (21)$$

where $b_S'(x)$ and $b_S''(x)$ are the first and second derivatives of $b_S(x)$ with respect to x.

Analysis of this expression shows that χ_0 has no singularities at any temperature and saturates at $x_0 > 1$. Thus, in the system there is no phase transition into a locally magnetically ordered state with $\langle S_{\Sigma Z}\rangle \neq 0$, a state obtained in the model of the self-consistent effective field for the analogous problem. The complete expression for the crystal susceptibility contains, besides (21), also a contribution from $N_M - \bar{N}$ LSM which do not enter in the effective localization region of the electron.

We obtain now the free energy of the system. At fixed $\bar{N}$, only the spin part of the system can change because of spin correlation. For the sake of completeness we add to the expression (18) for Z also the contribution of the LSM located outside the electron localization region. Then the complete partition function for $H = 0$ ($\omega_0 = 0$) is

$$Z_{\text{м}}=2Y'(x_0)\,(2S_{\text{м}}+1)^{N_{\text{м}}-\bar{N}}. \tag{22}$$

Calculations of (16) and (22) yield

$$F_{\text{м}}=-\bar{N}T\ln\left\{\frac{\operatorname{sh}[x_0(S_{\text{м}}+1/2)]}{(2S_{\text{м}}+1)\operatorname{sh}(x_0/2)}\right\}$$

$$-T\ln\{e^{-x_0}+\bar{N}(1-e^{-x_0})b_{S_{\text{м}}}(x_0)\}. \tag{23}$$

The additive constant is chosen here such that $F_{\text{M}}\to 0$ as $\bar{N}\to\infty$, in accord with the physical gist of the problem.

It can be seen that $F_{\text{M}}=F_{\text{M}}(\bar{N})$ is always negative, corresponding to spin correlation, regardless of $\langle S_{\Sigma Z}\rangle=0$ at any temperature. An analysis of the spin part of the free energy (16) with allowance for (18) as $H\to 0$ confirms the absence of a local phase transition into a state with $\langle S_{\Sigma Z}\rangle\neq 0$. Nonetheless, autolocalization or a change of the radius of the electron center turns out to be possible if it is assumed that $\bar{N}$ changes as a result of spin correlation.

We consider first an electron in the absence of attraction centers (free electron). We assume that as a result of autolocalization, owing to the interaction with the LSM, a state sets in with an electron wave function $\psi(r)$ characterized by a radius a connected with $\bar{N}$ by the expression

$$a=\gamma^{-1/3}\bar{R}=(\bar{N}N_0\Omega_0/\gamma N_{\text{м}})^{1/3}, \tag{24}$$

where γ is a factor that depends on the concrete form of $\psi(r)$ (typical values of γ are given in Table I). The kinetic part of the free energy is then

$$F_{\text{к}}=\alpha\gamma^{2/3}\frac{\hbar^2}{m^*}\left(\frac{N_{\text{м}}}{N_0\Omega_0}\right)^{2/3}\bar{N}^{-2/3}, \tag{25}$$

where m^* is the effective mass, and $\alpha=2$ and $\frac{1}{2}$ for the Gaussian and hydrogenlike approximation of $\psi(r)$, respectively. The total free energy (23) and (25), $F_{\text{Mk}}=F_{\text{M}}+F_{\text{k}}$, is positive at high temperatures and decreases monotonically with increasing N, having a minimum $F_{\text{Mk}}=0$ at $\bar{N}=\infty$, i.e., the electron remains delocalized. With decreasing temperature, starting with a certain T_1, a local minimum appears on the plot of $F_{\text{Mk}}=F_{\text{Mk}}(\bar{N})$ (at finite $\bar{N}=\bar{N}_m$ and $F_{\text{Mk}}(N_m)>0$); this minimum becomes absolute starting with a temperature $T_c<T_1$ and drops below zero. At this temperature there should occur in the system a first-order phase transition into an autolocalized state with $\bar{N}=\bar{N}_m$. With further decrease of the temperature, $\bar{N}_M$ increases to $\bar{N}_m\to\infty$ as $T\to 0$. The dependence of F_{Mk} on $\bar{N}$, numerically calculated for the parameters of the CdS:Mn crystal investigated in Ref. 10, is shown in Fig. 1. Also investigated was the dependence of T_c on the LSM concentration and on the value of the exchange integral (Fig. 2). It follows from the presented plots that

$$T_c=T_c(N_{\text{м}}/N_0)\sim(N_{\text{м}}/N_0)^{1/2}, \tag{26}$$

$$T_c=T_c(J)\sim|J|^{5/2}. \tag{27}$$

The last relations agree with the result obtained in Ref. 1 for autolocalization of a fluctuon in an ideal paramagnet. It follows from the numerical analysis illustrated in Figs. 1 and 2 that the values of T_c and $\bar{N}_m$ corresponds to a situation wherein an electron interacts with one LSM and $\Delta/\bar{N}_m$ becomes of the order of T_c. In this case only the lowest states of the spectrum of the eigenvalues (8) are populated, and the differences between the approach of the present paper and

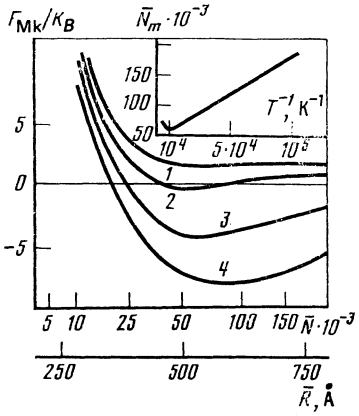

FIG. 1. Free energy F_{Mk} vs the effective radius $\bar{R}$ of the localization region at various temperatures $T=20\times10^{-5}$; 15×10^{-5}; 8×10^{-5} and 4×10^{-5} respectively for curves 1–4. The remaining parameters correspond to the CdS:Mn crystal investigated in Ref. 10: $N_{\text{M}}/N_0\Omega_0=10^{20}$ cm^{-3}; $\Delta=-12$ cm^{-1}; $m^*/m_0=0.43$. The values $\alpha=2$ and $\gamma=4.75$ were used. The inset shows the dependence of $\bar{N}_m$ on the reciprocal temperature.

the effetive-field model used in Ref. 1 vanish. Therefore the values of T_c themselves, obtained with the aid of (23) and (25) become close to those estimated from the equations of Ref. 1. The obtained autolocalized state is nevertheless not accompanied by the onset of local magnetization, and this distinguishes it from those considered in Refs. 1 and 2 using the effective-field model. We note that the foregoing analysis is based on the exact expression (23) for the free energy of the model system with the Hamiltonian (7), and requires no further allowance for fluctuations.

The numerical analysis reflected in Figs. 1 and 2 shows that autolocalization of a free electron as a result of carrier-impurity exchange interaction can take place in real magnetically mixed (semimagnetic) semiconductors[6,7] only at milikelvin temperatures.

The situation changes qualitatively for an electron localized in the Coulomb field of a defect. Here the state radius is finite also without allowance for the spin interactions. It is now necessary to take into account in the free energy the contribution from the attraction potential energy in the Coulomb field

$$F_p=-\frac{e^2}{\varkappa}\gamma^{1/3}\left(\frac{N_{\text{м}}}{N_0\Omega_0}\right)^{1/3}\bar{N}^{-1/3}, \tag{28}$$

which leads together with F_{k} (25) without allowance for F_{M}

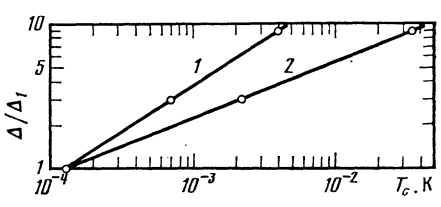

FIG. 2. Dependence of T_c on Δ/Δ_1. A value 12 cm^{-1}, corresponding to the data of Ref. 10, was used for Δ_1. The variation of Δ was introduced by varying N_{M} with J constant (line 1 corresponding to $T_c\sim\Delta^{3/2}$) or by varying J at fixed N_{M} (line 2 corresponding to $T_c\sim\Delta^{5/2}$).

(23) to a minimum of the energy at

$$\bar{N}=\bar{N}_{\text{K}}=\gamma a_B^3 \frac{N_{\text{M}}}{N_0\Omega_0}, \tag{29}$$

where a_B is the Bohr radius of a shallow donor, as might be expected from (24), and $\gamma = 25.93$ (Table I).

The problem of the change of the localization region because of the spin correlation of the electron with the LSM should be solved in the general case with allowance for the possible change of the form of the wave function of the Coulomb localized state. We, however, shall not take this change into account, but consider the possible change of only the localization region radius [or of $\bar{N}$ connected with it by expression (5)] from the solution of the equation for the minimum of $F_{\text{Mkp}} = F_{\text{M}} + F_{\text{k}} + F_{\text{p}}$.

In the general case the analytic solution of this problem is complicated, so that it makes sense to consider a number of limiting case. First, when $\bar{N}_{\text{K}} > \bar{N}_m$, where $\bar{N}_m$ is determined by F_{Mk}, it can be assumed that as $T \to T_c$ the system will be localized in a volume corresponding to $\bar{N}_m$, and this localization can have for certain parameters the character of a local phase transition. For real magnetically mixed II-VI semiconductors with Mn^{2+} the inverse relation holds, $\bar{N}_{\text{K}} < \bar{N}_m$. In this case there is no phase transition, the radius of the state varies continuously with temperature, and the dependence of the equilibrium $\bar{N} = \bar{N}_{\text{eq}}$ on the temperature is represented by a curve with a minimum in the region $T \sim T_c$ with $\bar{N}_{\text{eq}} \to N_{\text{k}}$ as $T \to 0$ or $T \to \infty$. For comparison with experiment, the important temperature region is the one corresponding to $x_0 \ll 1$. In this case

$$\frac{\partial F_{\text{M}}}{\partial \bar{N}} = T x_0^2 \left[\frac{S_{\text{M}}(S_{\text{M}}+1)}{2} - \frac{2T}{\Delta} \right] + O(x_0^2) \tag{30}$$

and the minimum of $F_{\text{Mkp}}(\bar{N})$ corresponds to

$$\bar{N}_{\text{p}} = \bar{N}_{\text{K}} \left\{ 1 - \frac{3}{4T} \left[\frac{S_{\text{M}}(S_{\text{M}}+1)}{2} - \frac{2T}{\Delta} \right] \frac{m^* \Delta^2}{\gamma^{2/3} \hbar^2 \bar{N}_{\text{p}}^{1/3}} \left(\frac{N_0\Omega_0}{N_{\text{M}}} \right)^{2/3} \right\}. \tag{31}$$

The correction to $\bar{N}_{\text{K}}$ for real objects is small, so that to solve (31) we can replace $\bar{N}_{\text{eq}}$ in the right-hand side by $\bar{N}_{\text{K}}$ (29). Numerical estimates for the experimental situations[9,10] using $\gamma = 25.93$ yiled a change $(\bar{N}_{\text{K}} - \bar{N}_{\text{eq}})/\bar{N}_{\text{K}}$ at $T = 1$ K amounting to 4% (10^{20} cm^{-3}) for CdS:Mn (Ref. 10) and 7% for $Cd_{0.95}Mn_{0.05}Se$ (Ref. 9). We note that these estimates are possibly too low, since the shrinking of the radius of the state because of the spin correlation alters also the form of the wave function (the value of γ). The role of the magnetic field in this effect reduces to a decrease of the shrinking, so that at $|\omega_0/\bar{A}| \gtrsim 1$ we have $a \to a_B$ ($\bar{N}_{\text{eq}} \to \bar{N}_{\text{K}}$).

5. RAMAN SCATTERING WITH ELECTRON SPIN FLIP

To consider SFRS in this model we must find the possible transitions between the states (9) in the course of the SFRS and obtain the envelope of the spectrum of the SFRS transitions. The last proble, cannot be solved by knowing the partition function of the system, since its solution calls for a determination, in explicit form, of the statistical weights of the spectrum (8).

The SFRS transition occur when the electron center interacts with a virtual electron-hole pair.[14] The operator part of Hamiltonian, which describes the SFRS transitions, is determined in the electron-spin basis by S_{ex}. Accordingly, the SFRS frequency shifts and quantities proportional to the transition probabilities were obtained for the energy spectrum (8) with the eigenvectors (9). The calculation results are given in Table II. We see that there are two types of transition, one with a shift of the SFRS, equal to $\pm\omega_0$ (if the approximation $\omega_e = \omega_{\text{M}}$ is not used, it can be established that these shifts are proportional to the Zeeman frequency ω_{M} of the LSM), and with a shift $\sim 2f\Delta/(S_\Sigma + \frac{1}{2})/\bar{N}$. The latter transitions were the ones observed in Refs. 10 and 11, whereas the transitions of the first type were apparently observed in Ref. 15. We note that the selection rules for SFRS and EPR of an electron center formally coincide, therefore the question of the SFRS shift is fully equivalent to the question of EPR of a shallow donor.

The SFRS spectrum contains in accord with the data of Table II a set of discrete closely-lying transitions (they merge into a single line in the experiment) with intensities

$$I(\omega) = d \sum_{S_\Sigma, f} \sum_{\mu=-S_\Sigma-f}^{S_\Sigma+f} \sum_{i=1}^{4} \delta(\omega-\omega_i) W_i^{S_\Sigma, f}(\mu) n_{S_\Sigma, f}(\mu), \tag{32}$$

where

$$n_{S_\Sigma, f}(\mu) = Z^{-1} P_{S_\Sigma, f}(\mu) \exp\left\{ -\beta \left[\frac{\Delta}{\bar{N}} f\left(S_\Sigma + \frac{1}{2}\right) + \omega_0 \mu \right] \right\}. \tag{33}$$

Z is the partition function (14), and the statistical weight $P_{S_\Sigma, f}(\mu)$ of the states of the system with a fixed set of quan-

TABLE II.

	Selection rules	SFRS frequency shifts ω_i	Transition probabilities W_i (in arbitrary units)
1	$\lvert S_\Sigma, \mu, f\rangle \to \lvert S_\Sigma, \mu-1, f\rangle$	$-\omega_0$	$\dfrac{(S_\Sigma + f + 1/2)^2 - (\mu - 1/2)^2}{(2S_\Sigma+1)^2}$
2	$\lvert S_\Sigma, \mu, f\rangle \to \lvert S_\Sigma, \mu+1, f\rangle$	ω_0	$\dfrac{(S_\Sigma + f + 1/2)^2 - (\mu + 1/2)^2}{(2S_\Sigma+1)^2}$
3	$\lvert S_\Sigma, \mu, f\rangle \to \lvert S_\Sigma, \mu-1, -f\rangle$	$-2f\dfrac{\Delta}{\bar{N}}\left(S_\Sigma + \dfrac{1}{2}\right) - \omega_0$	$\dfrac{(2f\mu + S_\Sigma + 1/2 - f)^2 - 1/4}{(2S_\Sigma+1)^2}$
4	$\lvert S_\Sigma, \mu, f\rangle \to \lvert S_\Sigma, \mu+1, -f\rangle$	$-2f\dfrac{\Delta}{\bar{N}}\left(S_\Sigma + \dfrac{1}{2}\right) + \omega_0$	$\dfrac{(-2f\mu + S_\Sigma + 1/2 - f)^2 - 1/4}{(2S_\Sigma+1)^2}$

tum numbers S_Σ, f, and μ coincides with the statistical weight $X^{S_\Sigma}_{\bar N}(M)$ (13) introduced above and is thus independent of μ; expressions for ω_i and W_i are given in Table II, and d is a dimensional coefficient that reflects the experimental conditions and the connection of the SFRS probabilities with W_i.

For $S_M = \frac{1}{2}$, the statistical weight $X_{\bar N}(M)$ is equal to the number of combinations of $C^{(\bar N + 2M)/2}_{\bar N}$. For arbitrary S_M this problem becomes more complicated and in a number of cases[3,4,13] it is solved by direct numerical calculation using, e.g., the recurrence relation

$$X_{N+1}(M) = \sum_{m=-S_M}^{S_M} X_N(M+m)$$

and the "initial condition" $X_1(M) = 1$ at $|M| \leqslant S_M$ and $X_1(M) = 0$ at $|M| > S_M$. For sufficiently large $\bar N$ one can use in place of the exact values of $X_n(M)$ the approximate formula

$$\tilde X_{\bar N}(M) = (2S_M+1)^{\bar N}(\pi\sigma_{\bar N})^{-1/2}\exp(-M^2/\sigma_{\bar N}), \tag{34}$$

$$\sigma_{\bar N} = {}^2/_3 S_M(S_M+1)\bar N. \tag{35}$$

It can be easily verified that in the case $S_M = \frac{1}{2}$ the approximation (34) coincides with the standard asymptotic ($\bar N \to \infty$) representation of $C^{(\bar N + 2M)/2}_{\bar N}$. For $S_M = 5/2$ this approximation is good enough already at $N = 5$, but for $|M|$ substantially smaller than $\bar N S_M$. As $|M| \to \bar N S_M$ this approximation is poor, and moreover gives an incorrect dependence of $\tilde X_{\bar N}(M)$ on M for $|M| \approx \bar N S_M$, and this leads to errors in the region where the Brillouin function for $\langle S_{MZ}\rangle$ differs substantially from the linear approximation. However, in that region of external fields and temperatures where only the lowest states are populated in the spectrum (8), the experimental situation is described in the mean-field approximation (1). The vital region of weak external fields, however, corresponds to validity of the approximation (34). We note that approximation (34) for the region $|M| \sim \bar N S_M$ can be easily improved, but this complicates substantially the form of the analytically obtained results.

We consider below only transitions corresponding to a giant shift of the SFRS ($i = 3$ and 4 in Table II). Substituting in (33) in place of $P_{S_\Sigma, f}(\mu)$ the derivative of $\tilde X_{\bar N}(M)$ (34) with respect to M at $M = S_\Sigma + \frac{1}{2}$, taken with a minus sign [this approximation is obvious from (13)], and substituting next in (32), we obtain after summing over μ:

$$I(\omega) = I_+(\omega) + I_-(\omega). \tag{36}$$

Here

$$I_\pm(\omega) = C\sum_{S_\Sigma, f}\delta\left(\omega \mp \omega_0 + 2f\frac{\Delta}{\bar N}\left(S_\Sigma + \frac{1}{2}\right)\right)\left(S_\Sigma + \frac{1}{2}\right)$$

$$\times\exp\left\{-\frac{(S_\Sigma + {}^1/_2)^2}{\sigma_{\bar N}} - \frac{\beta\Delta}{\bar N}f\left(S_\Sigma + \frac{1}{2}\right) \pm \left(f + \frac{1}{2}\right)\beta\omega_0\right\}$$

$$\frac{\mathrm{sh}(\beta\omega_0 S_\Sigma)}{\mathrm{sh}(\beta\omega_0/2)}\left\{1 + \frac{b_{S_\Sigma - 1/2}(\beta\omega_0)}{2(S_\Sigma + {}^1/_2)^2}\left[\pm 4f(S_\Sigma + 1) - \mathrm{cth}\frac{\beta\omega_0}{2}\right]\right\}, \tag{37}$$

where $C = d(2S_M + 1)^{\bar N} Z^{-1}(\pi\sigma^3_{\bar N})^{-1/2}$.

For sufficiently large $\bar N$, the set of levels (9) is quasicontinuous, so that we can consider a continuous envelope $\tilde I(\omega)$ of the SFRS spectrum. Recognizing, in addition, that in actual cases ω_0 is much less than the SFRS shifts, the transition to the continuous spectrum is effected in (37) by replacing $S_\Sigma + \frac{1}{2}$ by $-2f\bar N\omega/\Delta$. It must be stipulated here that $\tilde I(\omega) = 0$ outside the interval $|\bar A| \leqslant |\omega| \leqslant (2\bar N S_M + 1)|\bar A|$. Within the limits of this interval, the SFRS line is of the form

$$\tilde I(\omega) = 2C\frac{|\omega|}{\Delta^2}\bar N^2\exp\left(-\frac{\omega^2}{\delta^2} + \frac{\beta\omega}{2}\right)\frac{\mathrm{sh}[\beta\omega_0(|\omega\bar N/\Delta| - {}^1/_2)]}{\mathrm{sh}(\beta\omega_0/2)}$$

$$\times\mathrm{ch}\left[\beta\omega_0\left(\lambda + \frac{1}{2}\right)\right]D(\omega);$$

$$D(\omega) = 1 + \frac{b_{|\omega\bar N/\Delta| - 1}(\beta\omega_0)}{2\omega^2\bar N^2/\Delta^2}\left\{4\lambda\left(\left|\frac{\omega\bar N}{\Delta}\right| + \frac{1}{2}\right)\right.$$

$$\left.\times\mathrm{th}\left[\beta\omega_0\left(\lambda + \frac{1}{2}\right)\right] - \mathrm{cth}\frac{\beta\omega_0}{2}\right\}, \tag{38}$$

where $\lambda = -\omega\Delta/2|\omega\Delta|$. In the case of a zero external field ($\omega_0 = 0$) the SFRS envelope is described by the expression

$$\tilde I_0(\omega) = \frac{3}{4}\frac{C\bar N}{\Delta}\left(\frac{\omega^2\bar N^2}{\Delta^2} - \frac{1}{4}\right)\exp\left(-\frac{\omega^2}{\delta^2} + \frac{\beta\omega}{2}\right),$$

$$\delta^2 = \frac{\sigma_{\bar N}\Delta^2}{\bar N^2}. \tag{39}$$

Positive and negative values of ω in (38) and (39) correspond respectively to a Stokes and anti-Stokes line. The position of the maximum for the Stokes component is defined as the positive root of the equation

$$\omega^2 - \beta\omega\frac{\delta^2}{4}\left(1 + \frac{\omega_0}{|\bar A|}\right) - \frac{\delta^2}{2}$$

$$\times\left[1 + \frac{\beta\omega_0\omega/|\bar A|}{\exp[\beta\omega_0(\omega/|\bar A| - {}^1/_2)] - 1} + \frac{\omega}{D(\omega)}\frac{\partial D(\omega)}{\partial\omega}\right] = 0. \tag{40}$$

It can be seen that, in contrast to the effective-field model, the SFRS line has a finite width $\sim\sigma^{1/2}_{\bar N}|\Delta|/\bar N$, the splitting of the SFRS is preserved at $\omega_0 = 0$ and this initial splitting does not vanish in the limit as $T \to \infty$. At low temperatures the shifts ω_{St} and anti-Stokes ω_{aSt} components at $\omega_0 = 0$ are not symmetrical, with $\omega_{st}(T \to 0, \omega_0 = 0) \to S_M|\Delta|, \omega_{aSt}(T \to 0, \omega_0 = 0) \to 0$.

At high temperatures, $\bar N = \bar N_K = \mathrm{const}(T)$ according to (29). At low T it is necessary to take into account in (38), (39), and (40) the temperature dependence of $\bar N = \bar N_{eq}(T)$ (31), which is due to the change of the localization-region radius.

We note that the results show that EPR of shallow electron centers in magnetically mixed semiconductors should broaden and shift in frequency, becoming practically observable in accord with Eqs. (38) and (40).

The results cited were obtained assuming noninteracting LSM. At sufficient concentration of the latter ($\gtrsim 1\%$) the interaction between them becomes noticeable, and for the investigated magnetically mixed semiconductors in the interaction between the LSM is antiferromagnetic, and the high temperature of an LSM system can be described in the molecular-field approximation

$$\langle S_{MZ}\rangle = -\frac{1}{3}S_M(S_M+1)\frac{g\mu_B H}{T+\Theta}, \tag{41}$$

where Θ is the Curie-Weiss parameter for the magnetization.

In the model considered, this behavior of the LSM magnetization can be obtained by introducing a rough approximation of the spin-spin interaction inside a system of $\bar{N}$ LSM:

$$\mathcal{H}_{MM}=-\sum_{i\neq j} J_{ij}S_M^{\,i}S_M^{\,j}\to\frac{\Theta}{\sigma_{\bar{N}}}S_\Sigma S_\Sigma. \tag{42}$$

Inclusion of this interaction changes the system energies by $\Theta[(S_\Sigma+1/2)^2-1/4]/\sigma_{\bar{N}}$. Allowance for this contribution in (8) reduces to replacing $\sigma_{\bar{N}}$ in all the expressions that describe the SFRS by

$$\tilde{\sigma}_{\bar{N}}=\sigma_{\bar{N}}(1+\Theta/T)^{-1}. \tag{43}$$

6. COMPARISON WITH EXPERIMENT

The comparison with the experimental data[9,10] was made in the following manner. For the data of Ref. 9, starting from the results given there, we chose $\Delta=70\pm5\ \mathrm{cm}^{-1}$ and $\Theta=1.9\pm0.1$ K. Next, using (43), an iteration solution of Eq. (40) was sought for a definite $\bar{N}$. The value of $\bar{N}$ that describes best the experimental data was obtained for each temperature. The calculated SFRS shifts together with the experimental results of Ref. 9 are shown in Fig. 3. The optimal $\bar{N}$ are cited in the figure caption. These values should be compared with $\bar{N}_K$ for a neutral donor in CdSe ($a_B\approx39$ Å) with the LSM density equal to 9×10^{20} cm^{-3} for $Cd_{0.95}Mn_{0.05}Se$. According to (29), $\bar{N}_K=1380$, much higher than the obtained values. The following should be noted in this connection: first, the effective LSM concentration should be lower than the value that follows from the crystal composition, since part of the LSM are bound into antiferromagnetic pairs, triads, etc; second, the obtained $\bar{N}$ have a substantial temperature dependence that agrees qualitatively with (31) but is quantitatively stronger, so that the $\bar{N}=800$ obtained for $T=4.2$ seems still to differ from the high-temperature $\bar{N}=\bar{N}_K$.

In the comparison with the data of Ref. 10, we chose for each of the H-dependences given there for the shift of the SFRS Stokes component, besides $\bar{N}$, also the temperature (inasmuch as in this experiment was determined from the magnetic-field dependence of the SFRS shift, and this dependence is modified by the zero-field splitting). The results of the calculations together with the data of Ref. 10 are shown in Fig. 4. We used in the calculation the values $\Delta=-12\ \mathrm{cm}^{-1}$ and $\Theta=0$. For CdS with Mn (10^{20} cm^{-3}) we have $a_B=23$ Å, hence $\bar{N}_K=31$, in very good agreement with $\bar{N}=30$ for $T=14.7$ K. The temperature dependence of $\bar{N}$ also agrees qualitatively that expected from (31), and is quantitatively somewhat higher. This difference, just as in the case of the experiment of Ref. 9, seems to reflect a variation of γ in the course of the shrinking of the electron localization region on account of the spin correlation. The variation of γ within the range of the values in Table I overlaps the discrepancy between the calculation and experiment.

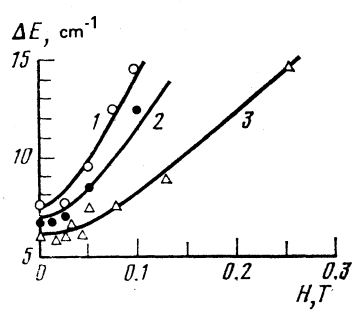

FIG. 3. Comparison of the theory with the experimental data of Fig. 2 of Ref. 9: ○, ●, △-results of Ref. 9 obtained at 2.5, 2.2, and 4.2 K, respectively. Curves 1, 2, and 3-calculated shift of the Stokes components at the indicated temperatures, using $\Theta=1.8$ K and $\Delta=-70\ \mathrm{cm}^{-1}$ at $\bar{N}$ equal respectively to 650, 700, and 800.

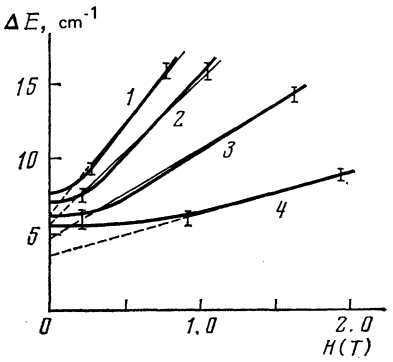

FIG. 4. Comparison of the theory with the experimental data of Fig. 3 of Ref. 10. Solid line—regions of experimental values of Ref. 10 with their accuracy limits, obtained at various temperatures; dashed lines—linear extrapolation of the experimental data to weak fields, carried out in Ref. 10. Curves 1–4 show the calculated shifts of the Stokes component, using $\Delta=-12\ \mathrm{cm}^{-1}$, $\Theta=0$, and $\bar{N}$ and T equal respectively to 26 and 3.32 K, 27 and 41.6 K, 28 and 6.91 K, and 30 and 14.7 K.

The proposed model describes thus all the principal result of the experiments not only qualitatively but also quantitatively.

We note in conclusion that the "plane bounded wave function" model used in this paper may apparently not be quite exact for the description of the behavior of the magnetic-field dependence in weak fields (outside the accuracy limits of the experiments of Refs. 9 and 10) and for the description of the SFRS line shape, details that should be sensitive to the inhomogeneity of the LSM magnetization distribution in the carrier localization region. On the other hand, an advantage of the model is the possibility of consistently describing the entire picture of the spin correlation of the carrier and the LSM, and the possibility of obtaining analytic solutions.

The authors are grateful to S. I. Gubarev, M. A. Krivoglaz, and B. V. Egorov for helpful discussions of the questions touched upon in the article.

[1]M. A. Krivoglaz, Usp. Fiz. Nauk **111**, 617 (1973) [Sov. Phys. Usp. **16**, 856 (1974)].
[2]E. L. Nagaev, Magnitnye poluprovodniki (Magnetic Semiconductors), Nauka, 1979.
[3]T. Kasuya and A. Yanase, Rev. Mod. Phys. **40**, 684 (1968).
[4]T. Kasuya and A. Yanase, Phys. Soc. Jpn. **25**, 1025 (1968).
[5]A. V. Komarov, S. M. Ryabchenko, O. V. Terletskiĭ, I. I. Zheru, and R. D. Ivanchuk, Zh. Eksp. Teor. Fiz. **73**, 608 (1977) [Sov. Phys. JETP **46**,

318 (1977)].
[6]G. Bastard, C. Figaux,and A. M. Mycielski, Phys. Stat. Sol. (b) **79**, 585 (1977).
[7]S. M. Ryabchenko, Izv. AN SSSR, ser. fiz. **46**, 440 (1982).
[8]J.A. Gaj, J. Phys. Soc. Jpn. Suppl. **A49**, 797 (1980).
[9]M. Nawrocki, R. Planel, G. Fishman, and R. R. Galazka, Phys. Rev. Lett. **46**, 735 (1981).
[10]D. L. Alov, S. I. Gubarev, V. B. Timofeev, and B.N. Shepel', Pis'ma Zh. Eksp. Teor. Fiz. **34**, 76 (1981) [JETP Lett. **34**, 71 (1981)].
[11]A. Golnik, J. A. Gaj, M.Nawrocki, R. Planel, and C. Benoit à la Guillaume, J. Phys. Soc. Jpn. Suppl. **A49**, 814 (1980).
[12]E. L. Nagaev, Zh. Eksp. Teor. Fiz. **74**, 1375 (1978) [Sov. Phys. JETP **47**, 719 (1978)].
[13]M. F. Deĭgen and A. B. Roĭtsin, Zh. Eksp. Teor. Fiz. **36**, 176 (1959) [Sov. Phys. JETP **9**, 120 (1960)].
[14]Y. Yafet, Phys. Rev. **152**, 858 (1966).
[15]K. Douglas, S. Nakashima, and J. F. Scott, Bull. Am. Phys. Soc. **27**, 13 (1981).

Translated by J. G. Adashko