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Thermally induced abrupt collapse of a shallow donor state in a ferromagnetic semiconductor

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We calculate the free energy of a donor interacting with spin waves and atomic displacements of a ferromagnetic semiconductor. With increasing temperature the free-energy minimum associated with a severely localized state is lowered below that of a large-radius donor. Concomitantly, large-radius donors suddenly severely localize.

Some time ago it was discovered that, well below the Curie temperature, the large-radius donor state associated with an oxygen vacancy in the ferromagnetic semiconductor EuO abruptly collapses to a severely localized donor state as the temperature is raised.[1] Subsequently, similar behavior has been observed for donors introduced by substitutional impurities (e.g., Gd) in EuO (Ref. 2) and for donors in other ferromagnetic semiconductors.[3] Here we explain the abruptness of the collapse. Namely, the sudden collapse is caused by the collateral short-range interactions of the donor electron with spin deviations and atomic displacements. This illustrates how the application of dynamic electronic disorder (provided here by the spin fluctuations) acts in tandem with the short-range component of the electron-lattice interaction abruptly to cause severe localization.

A potentially useful outgrowth of the donor-state collapse is that a doped ferromagnetic semiconductor can undergo a transition from metallic conduction to insulating behavior as the temperature is raised. With a sufficient density of donors there can be enough overlap between large-radius donors to generate metallic impurity conduction. With collapse of the donor state this overlap is reduced. Thus, with an appropriate density of donors, the metallic impurity conduction characterizing donors having large-radius states is suppressed when the donors collapse to severely localized states. Since the donor-state collapse occurs as the temperature is raised, this results in a thermally induced metal-to-insulator transition.[1] Despite evidence of an abrupt donor-state collapse,[2] others have offered descriptions of the metal-to-insulator transition which are based on a small continuous shrinking of an isolated donor with increasing temperature.[4–7]

Here, we advance a mechanism for a large and abrupt thermally induced collapse of the donor state. In particular, we calculate the free energy of a system comprising a donor which interacts collaterally with the spin waves and the atomic vibrations of a ferromagnetic semiconductor. The electron-lattice interaction is taken to have a significant short-range component. There are two possible minima of the free energy of this system. One corresponds to the donor being of large radius while the other corresponds to the donor being severly localized. With increasing temperature the severely localized-state minimum is lowered relative to that of the large-radius donor. Meanwhile the large-radius-donor minimum softens. Thus, with rising temperature the large-radius-donor minimum is either energetically destabilized or destroyed. In either case we have an abrupt collapse of the equilibrium donor state with increasing temperature.

Prior attempts to model this transition have ignored the short-range component of the electron-lattice interaction.[4–7] Here the electron-lattice interaction plays a primary role in the thermally induced abrupt donor-state collapse. Indeed, in agreement with others (e.g., Ref. 4), without the short-range component of the electron-lattice interaction, our work yields only a small gradual reduction of the donor-state radius with increasing temperature.

A crucial element of our model is that the (standard linear) electron-lattice interaction contains a short-range component. That is, the energy of an electron at a site depends on the positions of the atoms adjacent to it. For such a situation the ground state of the donor is diochotomous.[8] It is either localized at the site of the donor atom or is of large radius, extending over many sites of the solid. In particular, with the ground state of the donor electron being spherically symmetric, characterized by the reduced (dimensionless) radius R, the electron's energy in the absence of magnetic interactions is[8]

$$E = T_e/R^2 - V_{\rm int}/R^3 - V_c/R \ . \tag{1}$$

Here the first term represents the donor electron's kinetic energy. The second term is the lowering of the donor electron's potential energy due to the polaronic displacements it induces. The third term is the Coulombic energy of the donor electron. The minimum physically meaningful value of R, $R=1$, corresponds to the electron being sufficiently confined at an atomic site that the electron-lattice contribution equals that from single-site confinement in a discrete model of the lattice. This corresponds to a donor-state radius which is much less than the lattice constant in EuO. Thus, values of R which are less than unity are ignored, as they are artifacts of a continuum treatment of the donor state. Inclusion of a long-range component of the electron-lattice interaction, as occurs in ionic solids, does

not alter the form of Eq. (1).[8]

Intra-atomic exchange provides the magnetic interaction of the donor electron of spin σ with the local magnetic moments of the ferromagnetic semiconductor at position $\mathbf{r}$, $\mathbf{S}(\mathbf{r})$:

$$E_{\text{mag}} = -I\int d\mathbf{r}\sigma\cdot\mathbf{S}(\mathbf{r})|\psi(\mathbf{r})|^2 . \quad (2)$$

Here I is the intra-atomic exchange interaction constant and $\psi(\mathbf{r})$ is the wave function of the donor electron.

Adding this magnetic contribution to the nonmagnetic part of the electron's energy contained in Eq. (1) gives the total electronic energy for a donor state of radius R. We then include the atomic distortional and vibrational energies as well as the spin-wave energies. This yields the total energy of the system comprising a donor electron coupled to the atomic displacements and the spin waves of the ferromagnetic semiconductor. Specifically, we have

$$E_{\text{total}} = T_e/R^2 - V_{\text{int}}/2R^3 - V_c/R + E_{\text{phonon}} + E_{\text{magnon}}(R) . \quad (3)$$

The equilibrium strain energy associated with the polaronic distortion is $V_{\text{int}}/2R^3$ and the vibrational energy is E_{phonon}. For the standard linear electron-lattice interaction, the polaronic effect shifts the equilibrium positions of the atoms of the solid but does not affect the vibrational frequencies. Thus, the vibrational energy, E_{phonon}, is unaltered by the presence of the donor electron. However, the magnetic coupling between the donor electron and the spin deviations of the ferromagnet produces a dependence of the magnon energies on the presence of a donor electron.

We may use the energy of Eq. (3) to calculate the free energy associated with a hydrogenic donor state of radius R. To do this we must ascertain the effect of the donor electron on the magnon spectrum. For simplicity, we take the spin of the donor electron to be aligned in the + direction. Then,

$$E_{\text{mag}} = -IS + \frac{I}{N}\sum_{\mathbf{q}}\sum_{\mathbf{q}'} c_{\mathbf{q}}^* c_{\mathbf{q}'}(1+|\mathbf{q}-\mathbf{q}'|^2R^2/4)^{-2} , \quad (4)$$

where $c_{\mathbf{q}}^*$ and $c_{\mathbf{q}}$ are creation and annihilation operators for spin waves of energy $\hbar\omega_{\mathbf{q}}$ and (dimensionless) wave vector $\mathbf{q}$. Taken together with the magnon energy in the absence of a donor electron, $E^0_{\text{magnon}} = \sum_{\mathbf{q}}\hbar\omega_{\mathbf{q}}(c_{\mathbf{q}}^* c_{\mathbf{q}} + \frac{1}{2})$, Eq. (4) leads to infinitesimal ($\sim 1/N$) shifts of each of the N magnon frequencies. Treating E_{mag} as a perturbation, one readily finds that the first-order shift of the magnon energy of the qth mode I/N is independent of the donor-state radius while the second-order shift is not:

$$\hbar\Delta\omega_{\mathbf{q}} = \frac{I}{N} - \left(\frac{I}{N}\right)^2 \sum_{\mathbf{q}'} \frac{(1+|\mathbf{q}-\mathbf{q}'|^2R^2/4)^{-4}}{\hbar\omega_{\mathbf{q}'} - \hbar\omega_{\mathbf{q}}} . \quad (5)$$

Noting that the shift of each of the N magnon energies is infinitesimal, $\sim 1/N$, we readily show that the change of the free energy of the magnons induced by the presence of the donor electron is

$$\Delta F_{\text{magnon}} = \sum_{\mathbf{q}} \frac{\hbar\Delta\omega_{\mathbf{q}}}{\exp(\hbar\omega_{\mathbf{q}}/k_BT) - 1} , \quad (6)$$

where k_BT is the thermal energy. Taking the unperturbed magnon dispersion relation to be $\hbar\omega_{\mathbf{q}} = Dq^2$, we evaluate the double integral which results from inserting Eq. (5) in Eq. (6). We find that the second-order (R-dependent) change of the free energy of the magnons induced by the presence of the donor electron is

$$-[27(4\pi)^{2/3}/(8\pi)^2]k_BT(I/k_BT_C)^2R^{-2} .$$

Here T_C is the Curie temperature. The R dependence of the electron-induced change of the magnon's free energy arises because the donor electron interacts most effectively with magnons of wavelengths exceeding the donor-state radius, $qR < 1$.

We may now write the free energy of the system comprising an occupied donor of radius R interacting with both the atomic displacements and the magnons of a ferromagnetic semiconductor:

$$F = T_e/R^2 - V_{\text{int}}/2R^3 - V_c/R - [27(4\pi)^{2/3}/(8\pi)^2]k_BT(I/k_BT_C)^2/R^2 + (I/N)\sum_{\mathbf{q}}\langle c_{\mathbf{q}}^* c_{\mathbf{q}}\rangle + F^0_{\text{phonon}} + F^0_{\text{magnon}} . \quad (7)$$

Since the atomic vibrational frequencies are unaffected by the donor electron (with a linear electron-lattice interaction), the free-energy contribution arising from the atomic vibrations is just that of the system devoid of the donor electron, F^0_{phonon}. F^0_{magnon} is the free energy of the spin-wave system in the absence of a donor electron. The fifth term is the first-order contribution to the free energy arising from the electron-magnon interaction. It is proportional to the sum of the thermal average of the number of magnons of wave vector $\mathbf{q}$. The final three terms are, of course, independent of the donor electron's radius, R.

The interaction of the donor electron with the spin waves, contained in the fourth term of Eq. (7), causes the free-energy of a severely localized state to be lowered with respect to a more extended state as the temperature is raised. The physical origin of this effect is clear. A donor electron interacts most effectively with spin waves whose wavelengths exceed the radius of the donor state. Thus, donor states of progressively smaller radii interact effectively with an increasing fraction of the available spin waves. Hence, the interaction term increases in magnitude as the donor-state radius is reduced. Furthermore, since the number of available spin waves increases with temperature, this term increases in magnitude as the temperature is raised. These general features are model independent.

The radius assumed by the donor electron is that which minimizes the free energy of the system. The electron-magnon interaction provides a term, the fourth term of Eq. (7), which drives the donor electron toward localization (attaining a small-R free-energy minimum). This term becomes increasingly important as the temperature is raised. In Fig. 1 plots of the R-dependent portion of the free energy against R at three temperatures illustrate the abrupt donor-state collapse for values of the parameters which are representative of EuO.[9] There are two minima of the free energy. The minimum at $R \gg 1$ corresponds to the donor assuming the large-radius state. The minimum at $R = 1$ denotes the severely localized donor state. At $T = 0$ K the absolute minimum of the free energy is at $R > 10$. As the temperature is raised to 25 K, the minimum at $R = 1$ is

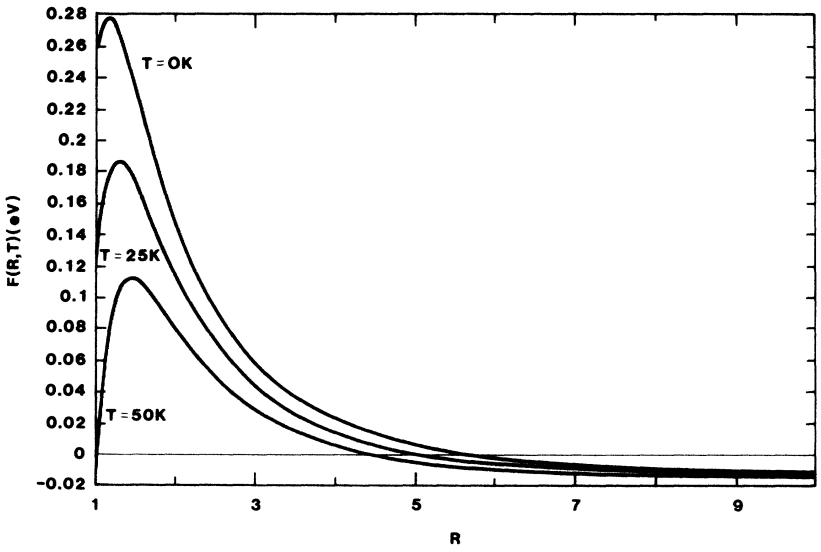

FIG. 1. The free energy of a donor electron interacting with atomic displacements and spin waves, Eq. (7), is plotted vs donor-state radius, R, at three temperatures. Because of the discreteness of the lattice, these curves only have meaning for values of R exceeding unity. The minimum at $R=1$ corresponds to the collapsed state while that at $R>1$ is the large-radius state. The parameters correspond to the large-radius donor in EuO: $T_e=1.73$ eV, $V_{\rm int}=2.42$ eV, $V_c=0.27$ eV, $I=0.1$ eV, and $T_c=70$ K. Since the values of T_e, V_c, and $V_{\rm int}$ are sensitive to the small-radius cutoff they should be taken as only illustrative.

lowered more than the large-R minimum. Nonetheless, the absolute minimum of the free energy remains that of the large-radius donor. However, upon raising the temperature to 50 K, the minimum at $R=1$, corresponding to the severely localized donor state, is lowered sufficiently to become the absolute minimum. This lowering of the $R=1$ minimum below the minimum of larger R corresponds to the donor-state collapse.

Thus, we see a general mechanism for the thermally stimulated abrupt collapse of shallow donors in ferromagnetic semiconductors to severely localized states. This donor-state collapse is a synergistic effect. It involves the collateral effects of the electron-magnon interaction and the short-range interaction of the donor electron with the atomic displacements. The presence of a short-range component of the electron-lattice interaction ensures that the donor states are dichotomous. Thus, corresponding to a large-radius donor state there is also a potential small-radius solution. The interaction of the donor state with the spin waves generates a driving force for localization. With increasing temperature the spin deviations and this driving force for localization increase. Ultimately the absolute free-energy minimum becomes that of the severely localized state (at $R=1$). This corresponds to the donor-state collapse. A further experimental test of our model would be measurement of the latent heat associated with the change of the absolute free-energy minimum. For the parameters of Fig. 1, the latent heat is $\sim 10^{-20}$ cal/donor (1 cal/cm^3 for 10^{20} donors/cm^3).

We emphasize that the thermally induced abrupt collapse of a shallow donor in a ferromagnetic semiconductor is an example of disorder-induced small-polaron formation rather than Anderson localization.[10] The largest energies in the problem are the electronic bandwidth parameter and the small-polaron binding energy. The Coulomb attraction additionally contributes to the electronic localization. Because of the relative sensitivity of the $R=1$ minimum of the free energy, Eq. (7), to changes of the parameters, with reasonable parameters a modest amount of spin-induced electronic disorder can *trigger* the abrupt collapse of the donor state. In particular, at the transition temperature in EuO, 50 K, the magnetization is only 20% below saturation.[11] Thus, the associated disorder energy is only $\sim 0.2IS=0.07$ eV.

We note that the small (20%) deviation of the magnetization from saturation at the transition temperature (50 K)[11] justifies our perturbation treatment of the electron-magnon interaction. In addition, the temperature of the donor-state collapse (50 K) is sufficiently below the Curie temperature (70 K) to justify the spin-wave treatment of the spin deviations. In particular, the magnetization predicted from simple spin-wave theory only deviates from the observed magnetization at 50 K by $\sim 5\%$.[11] Finally, we point out (consistent with other findings, e.g., Ref. 4), that with neglect of the electron-lattice interaction, the R^{-3} term of Eq. (7), there would only be a small continuous shrinking of the donor with rising temperature. Thus, it is the electron-lattice interaction which plays a pivotal role in producing an *abrupt collapse* of an isolated donor state. Indeed, the present work provides an analytic example, in which the disorder is both well characterized and controlled, where modest disorder induces the formation of a small-polaronic state. This notion is consistent with previously advanced arguments for small-polaron formation in wide-band amorphous semiconductors.[12-14]

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