Volume 48, Number 17 PHYSICAL REVIEW LETTERS 26 April 1982

New Magnetoelectric Effect: Evidence for Spin-Dependent Electrical Polarizabilities from Magnetocapacitance Measurements on *n*-type Silicon

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(Received 25 January 1982)

Magnetocapacitance measurements on a nonpolar paramagnetic system of antiferromagnetically exchange-coupled neutral donors in the temperature range 4.2 to 1.1 K reveal a strongly temperature-dependent coefficient of the H^2 term much larger in magnitude than the usual weak diamagnetic effect. The new effect arises from the Zeeman effect of the excited triplet spin state of donor pairs and is proportional to the difference between the singlet- and triplet-state polarizabilities. The temperature dependence is like that of the Schottky specific-heat anomaly.

PACS numbers: 75.80.+q, 72.20.My

The static magnetoelectric effect in insulators has frequently been the subject of active interest even though classically magnetostatics and electrostatics have been regarded as separate subjects. During the old quantum theory period the incorrect belief that a sufficiently large magnetic field would determine the quantization axis of electric dipoles and thereby produce a significant change in the static dielectric constant led to measurements of the static dielectric constant of polar gases in crossed electric and magnetic fields. Van Vleck[1] discussed this idea and reviewed the early negative experimental results. There have been various efforts to measure the magnetic field dependence of the static dielectric constant of various liquids and solids. The effect (measurement of the E^2H^2 term in the free energy) is large in anisotropic liquid crystals,[2] much smaller in liquids,[3] and extremely small in high-symmetry nonmagnetic insulators. On the other hand, Landau and Lifshitz[4] predicted an effect relating $\vec{E}$ and $\vec{H}$ fields in magnetic insulators of sufficiently low symmetry. Dzyaloshinskii[5] calculated this effect for Cr_2O_3 (yielding an EH term in the free energy) and experimental results were obtained by several workers.[6-8] There are also many instances of dielectric anomalies associated with magnetic phase transitions. In the present work we report the direct observation of the E^2H^2 term in the free energy from magnetocapacitance measurements on phosphorus-doped silicon—a nonpolar paramagnetic system featuring antiferromagnetic exchange between the randomly positioned donors. Susceptibility measurements[9] demonstrate that there is *no* long-range order in this system to temperatures as low as 2 mK. Here we report magnetic-field-induced changes in the dielectric-constant contribution resulting from the donor impurities. The temperature dependence of those changes is similar to that for the Schottky specific-heat anomaly and gives direct evidence for spin-dependent electrical polarizabilities of donor clusters. We believe this to be the first experimental evidence for spin-dependent electrical polarizabilities. The results also show different qualitative behavior than calculated by Van Vleck[1] and Buckingham,[10] on the basis of classical statistical mechanics.

For a nonpolar paramagnet statistical mechanics gives a field-dependent partition function[1] $Z = Z_0(1 + A_{21}E^2 + A_{02}H^2 + A_{22}E^2H^2 + \ldots)$, where Z_0 is the zero-fields partition function. This yields an electric susceptibility $\chi_e = N(\frac{1}{3}\mathrm{Tr}\,\alpha_{ij} + bH^2)$ for *induced* electric dipoles and a magnetic susceptibility $\chi_m = N(\langle \mu^2 \rangle / 3kT + bE^2)$. Thus, both susceptibilities depend on the opposite field in lowest order through the same coefficient b. Although Van Vleck[1] found $b \propto T^{-2}(3\cos^2\Omega - 1) \times$(polarizability-susceptibility anisotropy factors) [Ω is the angle between $\vec{E}$ and $\vec{H}$], a more elaborate analysis by Buckingham[10] of the H-dependent static dielectric constant [$\epsilon(H) = \epsilon_0 + BH^2$] demonstrated that, if we ignore a small magnetostriction term, B would take the form $B(T, \Omega) = q_0 + q_1T^{-1} + q_2T^{-2} + \ldots$ with various dependences of the q_i on Ω and the polarizability-susceptibility anisotropies. Buckingham found explicit results for (1) spherical molecules (H atoms and isolated donors), (2) nonpolar diatomic molecules (H_2 and donor pairs) relevant to the present case, and (3) strongly polar molecules with appreciable diamagnetic anisotropy (e.g., nitrobenzene[3]). The latter yields a result similar to Van Vleck's result. These treatments take no account of spin-dependent electrical polarizabilities. The magnetocapacitance data presented below do not exhibit the calculated dependences, but instead arise primarily from a new effect resulting from the Zeeman effect of excited spin states of donor clusters in n-type Si.

Magnetocapacitance measurements were made with a precision capacitance bridge (GR1616) and lock-in amplifier (PAR 129A) on n-type Si samples ($5\times10^{16} < N_D < 3\times10^{18}/\mathrm{cm}^3$) in the temperature range 4.2 to 1.1 K. Measurements were made both at the University of Rochester with a superconducting solenoid (0–11.5 T) and an electromagnet (0–1 T) and at the Massachusetts Institute of Technology Magnet Laboratory (0–18 T). Since the low-frequency dielectric response $\epsilon'(N_D, \omega, T, H)$ depends on temperature and more weakly on ω (for $N_D < 0.3N_c$, N_c the metal-insulator transition concentration) it was crucial to maintain careful temperature control of both sample and bridge. Measurements were made at an optimum frequency ($\nu \cong 10$ kHz) for maximum sensitivity. Sensitivity considerations permitted measurements of $\Delta C/C \approx 3\times10^{-6}$. The uncompensated n-type Si samples were prepared as described previously.[11]

Using the Clausius-Mossotti relation to define an effective magnetic-field–dependent donor polarizability $\alpha_{\mathrm{eff}}(N, T, H)$ given by

$$\alpha_{\mathrm{eff}}(N, T, H) = \frac{3}{4\pi N}\left[\frac{\epsilon(N, T, H) - \epsilon_h(T, H)}{\epsilon(N, T, H)/\epsilon_h(T, H) + 2}\right] \quad (1)$$

we obtain $\alpha_{\mathrm{eff}}(N, T, H)$ from the measured dielectric constant $\epsilon(N, T, H)$, the host (pure Si) value $\epsilon_h(T, H)$, and the neutral donor concentration ($N = N_D$) from RT resistivity measurements. For the more heavily doped samples ($N_D > 2\times10^{17}/\mathrm{cm}^3$) discussed below the small changes in $\epsilon_h(H)$ have a negligible effect on the determination of $\alpha_{\mathrm{eff}}(N, T, H)$. For comparison with the reduction in the size of the donor wave function resulting from the magnetic field as recently calculated by Dexter[12] [$\alpha_{\mathrm{H\ atom}}(H)$] and Lipari and Dexter[13] [$\alpha_D(H)$] it is useful to define the ratio

$$\mathcal{R}(N, T, H) = \frac{\alpha_{\mathrm{eff}}(N, T, H=0)}{\alpha_{\mathrm{eff}}(N, T, H)}, \quad (2)$$

which is independent of N except for the implicit N dependence of $\alpha_{\mathrm{eff}}(N, T, H)$.

In Fig. 1 $\ln\mathcal{R}(B)$ vs B is shown for a Si:P ($N_D \approx 1.0\times10^{18}/\mathrm{cm}^3$) sample in the pumped-^{4}He temperature range. The magnetic field dependence is virtually quadratic as expected by theory[12,13] [$\alpha_{\mathrm{eff}}(H) = \alpha_{\mathrm{eff}}(0)(1-\eta H^2)$] in the low-field region ($B < 5$ T). For $B > 5$ T there is a trend toward a weaker field dependence and less temperature dependence characteristic of the onset of the intermediate-field range. Here we limit our discussion to the low-field, temperature-dependent behavior. The temperature dependence in Fig. 1 at $B = 1.0$ T is of the form $T^{-n(T)}$ with $n(T) < 1$ at higher temperatures and $n(T) > 1$ in the lower-T region (see Fig. 2). There is less than 1% anisotropy (Ω dependence) in $\ln\mathcal{R}$ for this sample contrary to the above theoretical

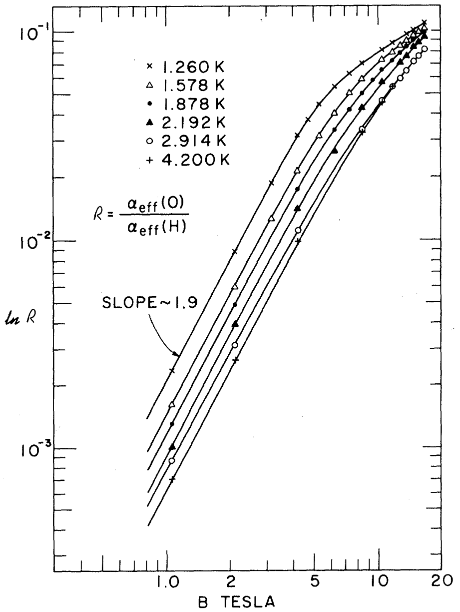

FIG. 1. $\ln\mathcal{R}$ vs B obtained from Eqs. (1) and (2) for an uncompensated Si:P sample ($N_D \sim 1.0\times10^{18}/\mathrm{cm}^3$) for a series of temperatures between 4.2 and 1.26 K.

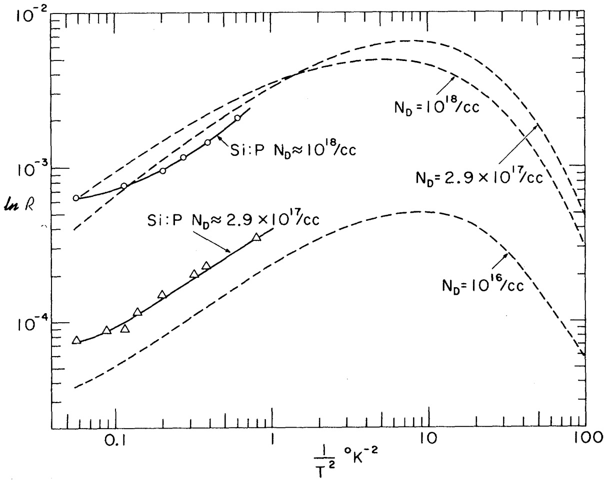

FIG. 2. $\ln\mathcal{R}$ vs $1/T^2$ for two Si:P samples ($N_D \sim 1.0\times10^{18}$ and $2.9\times10^{17}/\mathrm{cm}^3$) for $B = 1.0$ T. The dashed curves show calculated curves of $\ln\mathcal{R}$ vs $1/T^2$ based on isolated donors and pairs only, assuming a Poisson distribution of donors, for three different donor concentrations.

predictions. More dilute samples show a smaller magnitude of $\ln\mathcal{R}$ at 1 T, but have a similar temperature dependence that steepens as the temperature is lowered. Figure 2 shows the temperature dependence of a Si:P sample with $N_D = 2.9\times10^{17}/\mathrm{cm}^3$. There is a flattening temperature dependence at higher temperatures. This sample has more isolated donors than donor pairs and larger clusters (based on Poisson statistics) suggesting that it might have had a smaller temperature dependence and larger anisotropy. Except for a negligible relativistic correction[14] the isolated donors contribute an anisotropic temperature-independent contribution to $\ln\mathcal{R}(H, T)$. The strong temperature dependence, which definitely does not result from a frequency-dependent hopping-conductivity contribution to $\epsilon(N, \omega, T, H)$, most probably results from pairs and larger donor clusters.

Considering isolated donors and pairs [the pairs having spin-triplet (t) and spin-singlet (s) states] only, we show that $\alpha_{\mathrm{eff}}(N, T, H)$ is given, in the quadratic field range, by

$$\alpha_{\mathrm{eff}}(N, T, H) = \frac{N_i}{N}\,\alpha_i(0)(1-\eta_i\gamma^2) + \frac{N_p}{N}\left\{\frac{\alpha_s(0)(1-\eta_s\gamma^2)+\alpha_t(0)(1-\eta_t\gamma^2)e^{-J/T}(e^{h/T}+1+e^{-h/T})}{1+e^{-J/T}(e^{h/T}+1+e^{-h/T})}\right\}, \tag{3}$$

where $J = J(R)/k$ with $J(R)$ the exchange splitting of a pair of spacing R of the triplet and singlet states, $\alpha_s(0) = \alpha_s(0, R)$ and $\alpha_t(0) = \alpha_t(0, R)$ are, respectively, the zero-field singlet and triplet polarizabilities, $h = g\mu_B H/k$ is the usual Zeeman splitting divided by k, the η_j are the various diamagnetic polarizability reduction factors (tensor components), and γ^2 is the usual ratio of the diamagnetic energy to the donor binding energy ($\gamma^2 = \epsilon_h a^{*3}H^2/m^*c^2$, with a^* the isotropic donor Bohr radius and m^* an isotropic effective mass). N_i/N is the fraction of isolated (i) donors while N_p/N is the fraction of pairs. The factor $e^{h/T}+1+e^{-h/T}$ comes from the Zeeman effect of the triplet state. Performing a low-field expansion to order γ^2 we obtain, neglecting small field-dependent changes in $J(R)$,

$$\alpha_{\mathrm{eff}}(N, T, H) = \alpha_{\mathrm{eff}}(N, T, 0) - \gamma^2\left\{\frac{N_i}{N}\,\alpha_i(0)\eta_i + \frac{N_p}{N}\left[\frac{\alpha_s(0)\eta_s + 3\alpha_t(0)\eta_t e^{-J/T}}{1+3e^{-J/T}}\right]\right.$$
$$\left. + \frac{N_p}{N}\,\frac{\Delta\alpha e^{-J/T}}{(1+3e^{-J/T})^2}\left(\frac{T_0}{T}\right)^2\right\} + O(\gamma^4), \tag{4}$$

where $\Delta\alpha = \Delta\alpha(R) = \alpha_s(0) - \alpha_t(0)$ and $T_0 = h/\gamma = g\mu_B H/k\gamma$. For Si $T_0 = 217$ K and the last term in Eq. (4) readily dominates the pair contribution to the γ^2 term for $T < 4.2$ K and $\Delta\alpha \sim 0.05\alpha_s(0)$. All terms in the γ^2 term but the last term yield a very weak temperature dependence while the last term's temperature dependence is identical to the Schottky specific-heat anomaly. The last term is isotropic when the Zeeman interaction is isotropic. The new term results from changing populations of the pair states produced by the Zeeman effect of the triplet while the first two terms result from the anisotropic diamagnetic effect.[10] In addition, the new term is proportional to $\alpha_s(0, R) - \alpha_t(0, R)$. Equation (4) with the new term can qualitatively explain the temperature dependence of the data in Fig. 2. However, $\ln\mathcal{R}$ must first be averaged over a Poisson distribution of pair distances employing suitable expressions for $\alpha_s(0, R)$, $\alpha_t(0, R)$, $\Delta\alpha(R)$, and $J(R)$.[15] This has been done and calculated values of $\langle\ln\mathcal{R}\rangle$ are shown in Fig. 2 for several concentrations. The values of $\alpha_s(0, R)$, $\alpha_t(0, R)$, and $\Delta\alpha(R)$ utilized came from scaled H_2-molecule calculated results.[16-18] The temperature dependence of the calculated curves is similar to the experimental data, but the magnitudes of the calculated $\langle\ln R\rangle$ values are too large, presumably mostly because of the neglect of the central-cell potential, which greatly reduced all the $\alpha(R)$. The calculated results also omit the contribution of larger clusters with their larger $J_{\mathrm{eff}}(R)$ values and various spin multiplet states. The calculated curves reveal that one must obtain $T < 0.1$ K to freeze out the Zeeman-effect contribution of the high spin states to $\alpha_{\mathrm{eff}}(N, T, H)$. The calculated $\ln\mathcal{R}$ curves increase rapidly with N as the number of pairs increases. The results still show a significant temperature dependence in the dilute limit ($N = 10^{16}/\mathrm{cm}^3$, $N_i/N \sim 0.975$) indicating the dominance of the Zeeman-effect contribution of a small number of pairs to the γ^2 term of $\alpha_{\mathrm{eff}}(N, T, H)$ over the diamagnetic effect from all the donors.

Calculated H_2-molecule values of $\alpha_s(0, R < 4)$ by Kolos and Wolniewicz[16] indicate that $\alpha_s(0, R)$ increases above $2\alpha_{\mathrm{H\ atom}}$ (as R decreases) reaching a peak for $R/a_B \sim 3.5$, then rapidly decreases toward $\alpha_{\mathrm{He}}((1s)^2)$ as $R \to 0$. The results of DuPré and McTague[17] and Clarke-Hunt Buckingham[18] show $\alpha_t(0,R)$ initially decreasing below $2\alpha_{\text{H atom}}$ as R decreases, passing through a minimum near the maximum in $\alpha_s(0,R)$, then increasing steeply toward $\alpha_{\text{He}}(1s,2s)$ as $R \to 0$. These results suggest that $\Delta\alpha(R)$ is positive for $R/a_{\text{B}} \gtrsim 3$. The large $J(R)$ values $[J(R) \gg kT]$ for $R/a_{\text{B}} < 3$ suppress the occupancy of the triplet state for close pairs, thus leading to an effective $\langle\Delta\alpha(R)\rangle \sim 0.1\alpha_{\text{H}}$ [the data require $\langle\Delta\alpha(R)\rangle$ positive]. This is sufficient to have the coefficient of the γ^2 term in Eq. (4) dominated by the last term. Without this spin-dependent polarizability difference term the results would be much closer to the behavior calculated by Buckingham.[10]

It has not yet been possible to accurately obtain the η_i ($\eta_{i\parallel}$ for $\Omega = 0$ and $\eta_{i\perp}$ for $\Omega = \pi/2$) for isolated donors. Estimates from the high-temperature extrapolation for the 2.9×10^{17} Si:P sample are not inconsistent with the Si:P calculated value.[13] Measurements on more dilute samples at higher temperatures or well below 0.1 K may permit determination of the η_i tensor components.

In summary the present magnetocapacitance data on n-type Si exhibit a much larger effect than expected from the diamagnetic effect for isolated donors and pairs. The strongly temperature-dependent enhancement of the magnetocapacitance effect arises from the Zeeman effect of excited spin states of exchange-coupled clusters and depends directly on the difference of the polarizability of the different spin states of the cluster. This enhanced temperature dependence is analogous to the Schottky specific-heat anomaly and provides concrete evidence for spin-dependent electrical polarizabilities.

We gratefully acknowledge the opportunity to use the facilities of the Massachusetts Institute of Technology National Magnet Laboratory and the valuable assistance of L. Rubin. We thank K. Klebofski for computational assistance. This work was supported by grants from the National Science Foundation. One of us (D.N.) is the recipient of a Xerox Corporation Research Fellowship.

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