and also for a calculation carried out for a number of initial conditions, and to N. A. Irisova for discussing the problems associated with the performance of experiments.

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Nuclear relaxation in silicon in weak magnetic fields

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Nuclear spin lattice relaxation in silicon in weak magnetic fields was investigated with the aid of optical polarization of ^{29}Si nuclei. It was shown that a reduction in the magnetic field was accompanied by a reduction in the nuclear relaxation time due to an increased contribution of flip-flop and flip-flip transitions during the dipole–dipole interaction between the ^{29}Si nuclei and electrons localized on deep impurity levels, and also as a result of the influence of the local magnetic field due to the ^{29}Si nuclei in the silicon crystal.

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The degree of dynamic polarization of nuclear angular momenta in silicon doped with both deep and shallow donor impurities depends on the strength of the external longitudinal magnetic field in which the optical pumping process takes place, on the ratio of concentrations of the impurities introduced into the crystal, and on the nuclear spin-lattice relaxation time.[1,2] It has been shown[1] that silicon doped with gold and phosphorus, and optically pumped in weak magnetic fields, exhibits an inversion of nuclear magnetization when the magnetic field is varied. This phenomenon is connected with the different type of interaction between ^{29}Si nuclei and the oriented photoexcited electrons trapped in deep (gold) and shallow (phosphorus) donor levels, respectively. When a photoexcited conduction-band electron is trapped in a shallow donor level, its contact interaction with the ^{29}Si nucleus is found to predominate,[3] whereas, if the electron is trapped in a deep level, the dipole-dipole interaction is found to predominate. The dipole-dipole interaction between an electron localized in a deep donor center of the ^{29}Si nucleus then leads to the dynamic polarization of the nuclear angular momenta only in weak fields. This is connected with a particular ratio of the probabilities of flip-flop transitions, i.e., transitions with a mutual reorientation of electron and nuclear spins, and also transitions with a reorientation of only the nuclear spin, which are responsible for the nuclear spin-lattice relaxation, and the flip-flop transitions, i.e., transitions with simultaneous reorientation of both nuclear and electron spins.

By varying the longitudinal magnetic field, it may be possible to separate the contact and dipole-dipole interaction between the ^{29}Si nuclei and electrons localized in deep and shallow donor centers. In order to elucidate the phenomenon of inversion of nuclear magnetization, we must consider nuclear relaxation processes in weak magnetic fields. However the nuclear relaxation time is exceptionally difficult to measure under equilibrium conditions in the absence of illumination because the NMR signals characterizing the magnetization in the field are too weak. On the other hand, when silicon is illuminated with circularly polarized light, the degree of polarization of the ^{29}Si nuclei increases by several orders of magnitude, so that the nuclear relaxation processes can be investigated even in very weak magnetic fields.

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We have investigated nuclear relaxation in silicon doped with phosphorus and gold, and pumped optically in weak magnetic fields. We have examined nuclear spin diffusion under dipole-dipole interaction between the ^{29}Si nuclei and electrons localized on gold donor centers. We have also determined the nuclear relaxation time in fields of the order of the local field H_L due to the nuclei.

1. RELAXATION OF ^{29}Si NUCLEI IN SILICON UNDER DIPOLE-DIPOLE INTERACTION WITH ORIENTED ELECTRONS TRAPPED IN DEEP CENTERS

Consider the nuclear spin-lattice relaxation due to the interaction between the spin of the ^{29}Si nucleus at a distance r from a deep center and the spin of an electron trapped by the same center.

Abragam has shown[4] that, in solids containing fixed paramagnetic impurities, the predominant interaction is the dipole-dipole interaction between the lattice nuclei and these impurities. If the relaxation of the nuclear spin occurs in a magnetic field for which $\omega_S \tau_S \gg 1$ ($\omega_S = \gamma_S H_0$, where γ_S is the gyromagnetic ratio and τ_S is the time of spin-lattice relaxation of the electron localized in a deep donor center), only the terms I_+S_Z and I_-S_Z, which are responsible for the nuclear relaxation, will be present in the dipole-dipole interaction. This is the most commonly encountered case in nuclear magnetism and is examined in detail by Abragam.[4] The rate of nuclear relaxation can be written in the form

$$1/T_1(r) = Cr^{-6},$$

where

$$C = \frac{2}{5}\gamma_s^2\gamma_I^2\hbar^2 S(S+1)\frac{\tau_s}{1+\omega_I^2\tau_s^2}, \tag{1}$$

γ_S, γ_I are the gyromagnetic ratios of the electron and nucleus, repsectively, $\omega_I = \gamma_I H_0$, and $\hbar = h/2\pi$ is Planck's constant.

If the magnetic field in which the relaxation of the lattice nuclei takes place is so small that $\omega_S \tau_S \gg 1$ is not satisfied, the analysis of nuclear relaxation resulting from dipole-dipole interaction with electrons trapped in deep centers must take into account[2] the terms I_+S_-, I_-S_+, I_+S_+, and I_-S_- which are responsible for the flip-flop and flip-flip transitions of the nuclear angular momentum. These processes together provide a contribution to the nuclear relaxation which, by analogy with Refs. 2 and 4, can be represented by the quantity

$$C' = C + \gamma_s^2\gamma_I^2\hbar^2 S(S+1)\left[\frac{2}{15}\frac{\tau_s}{1+(\omega_s-\omega_I)^2\tau_s^2} + \frac{4}{5}\frac{\tau_s}{1+(\omega_s+\omega_I)^2\tau_s^2}\right]. \tag{2}$$

Hence, the nuclear relaxation time under the dipole-dipole interaction can be written in the form

$$\frac{1}{T_1(r)} = \frac{\gamma_s^2\gamma_I^2\hbar^2 S(S+1)}{r^6}\left[\frac{2}{15}\frac{\tau_s}{1+(\omega_s-\omega_I)^2\tau_s^2} + \frac{4}{5}\frac{\tau_s}{1+(\omega_s+\omega_I)^2\tau_s^2} + \frac{2}{5}\frac{\tau_s}{1+\omega_I^2\tau_s^2}\right]. \tag{3}$$

To calculate the total relaxation time of all the nuclei in the crystal, we must take into account the nuclear spin diffusion which occurs when nuclear magnetization can be transferred from the polarization centers (for example, donor centers in semiconductors) to lattice nuclei.

In the case of the dipole-dipole interaction between lattice nuclei and electrons localized on donor centers, the total nuclear relaxation time, including the contribution of nuclear spin diffusion, can be obtained from the result obtained by de Gennes[5]:

$$T_1 = 1/4\pi N_D D\delta, \tag{4}$$

where N_D is the concentration of donor centers, D is the nuclear spin diffusion coefficient ($D = 2.4\times10^{-14}$ cm^2/sec for ^{29}Si in silicon), and δ is the diffusion length defining the distance over which the spin-flip probability for ^{29}Si in the presence of the relaxation interaction with electrons localized on the donor centers, $1/T_1(\delta)$, is equal to the spin-flip probability for ^{29}Si (D/a^2) due to the interaction of lattice nuclei with one another (nuclear spin diffusion). For $r = \delta$, we thus have

$$1/T_1(\delta) = D/a^2 \quad (a = 6.5\ \text{Å}). \tag{5}$$

Relaxation processes are faster than spin diffusion with a sphere of radius δ. Outside this sphere, the rate of spin diffusion is greater. In the case of the dipole-dipole interaction between the ^{29}Si nucleus and spin of an electron trapped by a donor center, we have[6] $\delta = 0.68(C'/D)^{1/4}$, and, if we substitute this in (4), we obtain

$$T_1 = 1/2.72\pi N_D D(C'/D)^{1/4}. \tag{6}$$

It is clear from (3) and (6) that the nuclear relaxation time is a function of the external magnetic field. In weak magnetic fields, when $\omega_S \tau_S \ll 1$, the influence of the external magnetic field would appear to be negligible. However, in magnetic fields comparable with the local magnetic field due to the lattice nuclei, the nuclear spin-lattice relaxation time is reduced.[7] To describe the spin systems in weak magnetic fields, we have to introduce the idea of spin temperature.[4,7]

The nuclear spin-lattice relaxation time, including the contribution, due to the local field H_L of the lattice nuclei, can be written in the form[7]:

$$\frac{1}{T_1} = \frac{1}{T_{1Z}}\frac{H_0^2 + (T_{1Z}/T_{1D})H_L^2}{H_0^2 + H_L^2}, \tag{7}$$

where $1/T_{1Z}$ is the rate of relaxation of the Zeeman subsystem of spins and $1/T_{1D}$ is the rate of relaxation of the dipole spin subsystem.[7]

In the case of the interaction between lattice nuclei and the spin of electrons localized on donor centers in semiconductors, we have $T_{1Z}/T_{1D} = 3$.[7] The final expression for the nuclear spin-lattice relaxation time, including the contributions due to nuclear-spin diffusion and the local field of the lattice nuclei, can be written in the form

$$T_1 = \frac{1}{2.72\pi N_D D(C'/D)^{1/4}}\frac{H_0^2 + H_L^2}{H_0^2 + 3H_L^2}. \tag{8}$$

Figures 1 and 2 show the results of calculations of the nuclear relaxation time for silicon containing a deep donor impurity (gold). The local field due to the nuclei begins to contribute only in magnetic fields less than 1

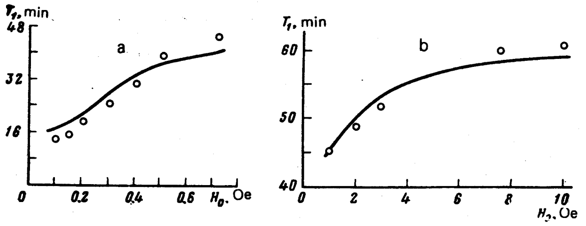

FIG. 1. Spin-lattice relaxation time of ^{29}Si nuclei as a function of magnetic field H_0. Solid curve—calculated.

Oe (the solid curve in Fig. 1a is the calculated result), whereas the maximum rate of variation in the nuclear relaxation time due to the increasing contribution of flip-flop and flip-flip transitions is observed in magnetic fields below 10 Oe [the solid curve in Fig. 1b is calculated from (2) and (9)].

The nuclear relaxation time for the ^{29}Si nuclei was measured in silicon pumped optically in magnetic fields between 0.1 and 10 Oe. The method employed was similar to that described in our previous paper.[1] The silicon specimen, doped with phosphorus and gold, was illuminated by circularly polarized light in a weak magnetic field parallel to the direction of the beam of light. The Earth's magnetic field was compensated by three mutually perpendicular pairs of Helmholtz coils. Even the smallest nuclear relaxation time (13 min for $H_0 = 0.1$ Oe) was sufficient to ensure that the specimen could be illuminated in a given position at $T = 77°$ K and could then be transported into the magnet of the rf spectrometer in which the resulting magnetization was recorded at $T = 300°$ K by examining the increase in the NMR signal.

Figures 1a and b show the experimental results. The nuclear relaxation time varied from 60 min at 10 Oe to 13 min at $H_0 = 0.1$ Oe. It is clear from Figs. 1a and b that there is good agreement between the experimental results and the calculated curves. This behavior of the nuclear relaxation time in weak magnetic fields can be used to examine in detail the mechanisms responsible for the interaction between the spins of the lattice nuclei, on the one hand, and oriented electrons trapped in deep donor centers, on the other.

It is important to note that optical polarization of lattice nuclei can be used to investigate nuclear spin-lattice, relaxation in weak magnetic fields even in materials with low concentrations of the magnetic isotope (for example, the concentration of the ^{29}Si nuclei in silicon was about 4.7%).

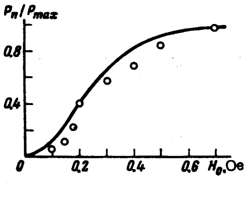

FIG. 2. Relative degree of optical polarization of nuclei, $P_n/P_{n\,\max}$, as a function of the magnetic field H_0.

2. DYNAMIC POLARIZATION OF ^{29}Si NUCLEI IN SILICON IN MAGNETIC FIELDS OF THE ORDER OF H_L

Having examined the influence of the local magnetic field on the nuclear spin-lattice relaxation time, we can now consider in greater detail the influence of the local magnetic field on the degree of dynamic polarization of nuclei in weak magnetic fields under the dipole-dipole interaction between the spin of the ^{29}Si nucleus and the spin of an electron localized on a deep donor center.

It was shown previously[2] that, in this case, the degree of dynamic polarization P_n of the ^{29}Si nuclei depended on the external longitudinal magnetic field as follows:

$$P_n \sim \left(\frac{T_{1\mathrm{Au}}}{T_{1\mathrm{P}}} - \xi_{\mathrm{Au}}\right)\frac{H_0^2}{H_0^2+3H_L^2}, \tag{9}$$

where

$$\xi_{\mathrm{Au}} = 5/(13+\alpha H_0^2)\ [^2], \qquad \alpha = 6\gamma_S^2\tau_S^2.$$

In the case of silicon containing the paramagnetic gold atoms with sufficient concentration [in our experiments, we used specimens with $N(\mathrm{Au}) \approx 10^{16}$ cm^{-3}], the relaxation of the ^{29}Si nuclei is completely determined by their interaction with electrons trapped by gold donor centers. Therefore, $T_{1\mathrm{Au}} \approx T_1$ and depends on the magnetic field in the same way as T_1 (see Figs. 1a and b). The relaxation time of the ^{29}Si nuclei, determined from their contact interaction with electrons localized on shallow phosphorus levels, is large because the concentration of the phosphorus centers in the gold-compensated silicon, filled with electrons, is small. In silicon doped only with phosphorus to a concentration $N(\mathrm{P}) \approx 2\times10^{13}$ cm^{-3}, the nuclear relaxation time was 18 h at $H_0 = 10$ Oe and 8.5 h at $H_0 = 0.2$ Oe. In silicon doped with both gold and phosphorus, the nuclear relaxation time was again found to vary by a factor of two when the magnetic field was varied from 10 to 0.2 Oe.

The ratio $T_{1\mathrm{Au}}/T_{1\mathrm{P}}$ is thus a slowly-varying function of the magnetic field H_0. This is confirmed by measurements of the spin-lattice relaxation time for ^{29}Si nuclei in silicon doped with both gold and phosphorus, and in silicon doped with phosphorus only.

The electron population of donor centers in our specimens of phosphorus and gold doped silicon, illuminated by light, was small ($10^{-3} - 10^{-4}$). When the phosphorus concentration was 10^{15} cm^{-3}, the amount of paramagnetic impurity responsible for the nuclear relaxation was $10^{11} - 10^{12}$ cm^{-3}, which leads to[3] $T_{1\mathrm{P}} \approx 30$ h. For $T_1 \approx T_{1\mathrm{Au}} \approx 1$ h, we then have $T_{1\mathrm{Au}}/T_{1\mathrm{P}} \approx 0.03$.

Figure 2 shows the result calculated from (9) together with the experimental data. The calculation was performed for[2,8] $\tau_S = 0.74\cdot10^{-7}$ sec, $H_L = 0.176$ Oe, and $T_{1\mathrm{Au}}/T_{1\mathrm{P}} = 0.03$.

We have thus determined the spin-lattice relaxation time for ^{29}Si nuclei in silicon in weak magnetic fields. We have shown that, even in fields of the order of H_L, the nuclear spin-lattice relaxation time is quite high. We have examined the relaxation of ^{29}Si nuclei in the presence of spin diffusion under dipole-dipole interaction with electrons localized on deep donor centers, and have demonstrated experimentally the influence of the local field due to the nuclei on the degree of dynamic polarization of the lattice nuclei.

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Valence-changing metal–insulator phase transitions

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The example of samarium chalcogenides at $T = 0$ is used to consider the metal–insulator phase transition which alters the valence in rare-earth compounds. It is shown that the s–f Coulomb interaction v and a strong single-site correlation of the degenerate f electrons are accompanied by fairly substantial hybridization of the s–f electrons g. In the semiconductor phase the hybridization produces a new hybrid s band near the f-electron level. Consequently, the valence of the semiconductor phase becomes fractional right down to the lowest temperatures. Depending on the energy parameters, the metal–insulator transition can be of the first order (SmS) or continuous (SmSe, SmTe). In the case of SmS a comparison of the phase diagram with the experimental values of the gap and of the number of the f electrons in the semiconductor phase is used to find the values of g and v.

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1. Extensive studies are being made of rare-earth compounds undergoing —as a result of changes in pressure and temperature— isostructural semiconductor–metal phase transitions accompanied by a change in the valence.[1,2] Typical representatives of such compounds are samarium and ytterbium chalcogenides. For example, in the case of SmS there is a first-order transition accompanied by a considerable change in the volume and valence, whereas in the case of SmSe and SmTe this transition is continuous. The existence of these transitions is attributed to the presence, near the bottom of the conduction band, of a level of localized f electrons which may be transferred to the conduction band on increase in pressure or temperature. The experimental data (for example, measurements of the magnetic susceptibility) indicate that fractional valence is retained right down to the lowest temperatures in the insulator (semiconductor) and metal phases.[2]

A theoretical description of this transition has been developed[3-6] on the basis of the Anderson model[7] supplemented by allowing for the Coulomb repulsion v between the s and f electrons, introduced by Falicov.[8] However, in this description either the wide s band is replaced with a level[3] or no allowance is made for the strong Coulomb repulsion of the f electrons at a single site U, the treatment being restricted[4-6] to the spinless model of the s and f electrons. Moreover, the number of the f electrons n_f is calculated[4-6] using the Green functions of the f electrons obtained on the assumption of the existence of a single impurity with the f level.

In contrast to these earlier treatments,[3-6] we shall make a consistent allowance for the repulsion of the f electrons at a single site. This will result, for example, in a strong dependence of the decay of the f level on the degree of its occupancy. Moreover, we shall assume that the distribution of the rare-earth ions in the crystal lattice is regular. This approach alters the physical picture of the semiconductor state of these compounds, compared with that adopted in the single-impurity approach: the fractional valence is found to be associated with the occupancy of the narrow s band, which appears as a result of hybridization under the f level. In the Appendix we shall use the example of the spinless model to show that our approach differs from the single-impurity treatment also in the quantitative sense: the results obtained in the two cases are identical for the insulator phase only in the limit $g/\Delta \ll 1$ (g is the hybridization constant and Δ is the insulator gap). It is then found that the insulator gap itself can

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