AN INVESTIGATION OF ELECTRON-NUCLEAR INTERACTIONS IN RUBY BY MEANS OF DOUBLE ACOUSTIC-MAGNETIC RESONANCE

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Experiments on double acoustic-magnetic electron-nuclear resonance are described. The electron spin system of Cr^{3+} ions ($c \sim 0.05$ at.%) is used to detect acoustic NMR of Al^{27} nuclei at 4.2°K in ruby. The experimental results show that the sensitivity of acoustic NMR measurements can be enhanced by double acoustic resonance. From a comparison of the experimental data and theoretical calculations it is concluded that the system of Cr^{3+} impurity ions greatly influences the interaction between acoustic phonons and the nuclear spin system. The change in nuclear level populations due to sonic saturation is calculated.

ELECTRON-NUCLEAR double resonance (ENDOR) is being applied to investigate the mechanisms of spin-lattice relaxation, cross-relaxation, and interactions between electronic and nuclear spin systems. ENDOR permits both direct and indirect measurements of various structural constants.

By utilizing the effects of acoustic vibrations on spin systems the ENDOR techniques enable us to investigate directly the mechanisms of spin-phonon interactions and relaxation processes in both dielectrics and metals. On the one hand, double acoustic-magnetic resonance techniques are considerably more sensitive than single acoustic NMR and EPR techniques, and, on the other hand, they enable us to utilize the advantages of quantum acoustic methods.

In the present work we study both theoretically and experimentally electron-nuclear double magnetic-acoustic resonance in an Al_2O_3 crystal containing 0.05 at.% Cr^{3+} ions. The sample was subjected to a constant magnetic field and to two periodic fields—an ultrasonic field at the frequencies of nuclear transitions in Al^{27} and an electro-magnetic field at the frequencies of electron spin transitions in Cr^{3+} ions. To observe the acoustic NMR of Al^{27} nuclei we used the electron spin system of Cr^{3+}.

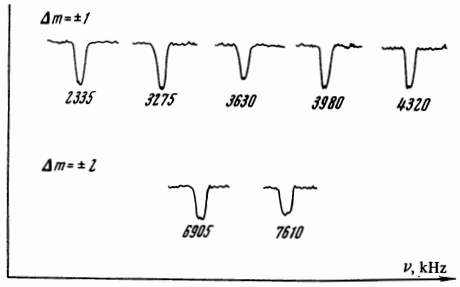
Although ruby has been investigated by means of ENDOR for some time,[1-3] many aspects of the dynamic interactions that are involved have continued to be discussed.

EXPERIMENTAL TECHNIQUES AND RESULTS

A electron-nuclear double acoustic resonance spectrometer was constructed for the aforementioned purposes.[4] The EPR system was of the conventional design with a reflection-type working resonator. The sample was a ruby laser single crystal 47 mm long and 5 mm thick with its trigonal c axis perpendicular to the longitudinal axis of the rod. The upper end of the sample was inserted into the working resonator, consisting of a standard-waveguide section; the optic axis of the crystal was perpendicular to the magnetic vector of the microwave field. The acoustic head, mounted on the lower end of the ruby, consisted of a cylindrical brass can with a chuck that clamped the sample. For the purpose of shielding, and also for grounding the quartz transducers, the lower part of the sample was silver-coated with the thickness of the skin layer taken into account. A quartz transducer in the form of a disk with silvered faces was covered with vacuum grease and then clamped against the flat end of the sample by means of an elastic bronze electrode. An NMR "autodyne" spectrometer was fastened around the middle of the sample. The working resonator together with the sample and the acoustic head was placed in a helium cryostat made of metal. The portion of the waveguide that was placed inside the cryostat and also three coaxial connections, one of which went to the acoustic head, were made of stainless steel. Acoustic vibrations in the investigated sample were induced by quartz transducers excited by high-frequency generators permitting a smooth variation within the range $10-10^4$ Hz/sec.

Our experimental procedure was as follows. The optic c axis of the ruby crystal is set parallel to the static magnetic field H_0, which is determined from the maximum splitting of Al^{27} nuclear levels. The EPR signal from Cr^{3+} impurity ions is then observed. The power of the microwave field is increased to achieve relative saturation of the EPR line at ~15%. The external magnetic field H_0 is given a fixed strength corresponding to the peak of the first derivative of the signal indicating absorption by the chromium ions. We then switch on the frequency sweep of acoustic saturation, covering the transition frequencies of Al^{27} nuclear spins; variation of the EPR signal is registered as a function of the ultrasonic frequency with constant H_0. The relative change of EPR intensity for a known relative deformation enables us to evaluate the constants of the spin-phonon interactions. The amplitudes of the alternating deformations induced by the acoustic waves were measured in advance with a capacitive detector,[5] but an impedance technique was used during the observation of double acoustic resonance. The frequency dependence of acoustic vibration intensity was taken into account in determining the constants of the spin-phonon interaction.

Measurements were performed at fixed values of



the static magnetic field (H_0 = 3390 gauss) and of the microwave field frequency (Ω_S = 9506 MHz), at 4.2°K. Double resonance was indicated by an intensity change in the EPR line of the Cr^{3+} ions [$(\frac{1}{2}) \longleftrightarrow (-\frac{1}{2})$]. Intensity changes of the EPR signal were observed when acoustic saturation was reached at frequencies corresponding to nuclear spin transitions with $\Delta m = \pm 2$, $\Delta m = \pm 1$. The relative intensity changes of EPR signals at the centers of double resonance lines were of the order (10–15)% for $\sim 3 \times 10^{-7}$ relative deformation. These resonance lines are of approximately Gaussian shape with $\sim 2 \times 10^4$ Hz width at half-maximum.[6]

The accompanying figure shows double acoustic electron-nuclear resonance lines and the frequencies for signals corresponding to Al^{27} nuclear spin transitions between levels with $\Delta m = \pm 2$ and ± 1.

Our results can be divided into two groups. In the first case, acoustic excitation of nuclear transitions with $\Delta m = \pm 2$ $\{\frac{5}{2} \longleftrightarrow \frac{1}{2}, \frac{3}{2} \longleftrightarrow -\frac{1}{2}\}$, we observed an identical intensity change of the EPR line. In the cause of ultrasonic excitation of $(\pm\frac{5}{2} \longleftrightarrow \pm\frac{3}{2})$ and $(\pm\frac{3}{2} \longleftrightarrow \pm\frac{1}{2})$ nuclear transitions the EPR intensity change was greater than with ultrasonic excitation of the central transition $(\frac{1}{2} \longleftrightarrow -\frac{1}{2})$.

DISCUSSION OF RESULTS

1. Coherent acoustic phonons generated in a crystal lattice by an external source can interact with the nuclear spin system in nonmagnetic crystals containing paramagnetic impurities, mainly in two ways.

In the first case the acoustic vibrations modulate the gradients of the crystal field. The induced variable electric gradients interact with the nuclear quadrupole moments. The other possible coupling mechanism consists in the modulation of magnetic interactions by the acoustic vibrations.

On the basis of the quadrupole selection rules it becomes evident that the effect of the acoustic vibrations on $\Delta m = \pm 2$ transitions between nuclear levels is completely determined by quadrupole mechanisms. Acoustic saturation of the central $(\frac{1}{2} \longleftrightarrow -\frac{1}{2})$ transition of the Al^{27} nuclear spin system can be achieved only by magnetic dipole mechanisms, but saturation of the side transitions with $\Delta m = \pm 1$ can result from both quadrupole and magnetic interactions. An analysis of the matrix elements of spin-phonon interaction tensors for dipole selection rules[7] showed that direct dipole-dipole interactions of aluminum nuclei, and also the direct interaction of nuclei with paramagnetic impurities, cannot account for a contribution to changes of level populations. In the same article two indirect mechanisms were suggested, which are based on a strong interaction between the Al^{27} nuclear system and the system of $Cr^{3+} \longleftrightarrow Cr^{3+}$ dipole-dipole interactions. Through modulation of the $Cr^{3+} \longleftrightarrow Cr^{3+}$ dipole-dipole or exchange interactions acoustic energy is transferred to the nuclear spin system of aluminum. The participation of the paramagnetic spin system in the transfer of acoustic vibrational energy to nuclei is of virtual nature and induces no population changes in the electron spin system of the ions.

2. For a theoretical analysis of electron-nuclear interactions in the Al_2O_3:0.05 at.% Cr^{3+} crystal we distinguish three subsystems: the nuclear (Al^{27}) subsystem, the electronic subsystem (electron spins of Cr^{3+} impurity ions), and the dipole-dipole reservoir of Cr^{3+} electron spins. In each subsystem a definite temperature is established (differing, in general, from the temperatures of the other subsystems), which is changed by external influences. The equations describing changes of the reciprocal temperatures of the nuclear subsystem (β_I), electronic subsystem (β_S), and dipole-dipole reservoir (β_d) that are induced by variable magnetic and acoustic fields and relaxation processes have the following form in common[8]:

$$\frac{d}{dt}\beta_s = -\frac{\beta_s - \beta_L}{T_{sL}} - 2W_s^m\left(\beta_s - \frac{\omega_s - \Omega_s}{\omega_s}\beta_d\right),$$

$$\frac{d}{dt}\beta_d = -\frac{\beta_d - \beta_L}{T_d} + \frac{\beta_I - \beta_L}{T_{dL}} - 2W_s^m\frac{\omega_s(\Omega_s - \omega_s)}{\omega_d^2}\left(\beta_s - \frac{\omega_s - \Omega_s}{\omega_s}\beta_d\right),$$

$$\frac{d}{dt}\beta_I = \frac{\beta_d - \beta_L}{T_d} + \frac{\beta_d - \beta_L}{T_{dL}} - 2W_I^u\beta_I. \qquad (1)$$

Here W_S^m is the probability of ordinary EPR, W_I^u is the probability of acoustic NMR, ω_S and ω_I are the frequencies of EPR and acoustic NMR, Ω_S and Ω_I are the frequencies of the external variable magnetic and acoustic fields, β_L is the reciprocal temperature of the lattice;

$$\frac{1}{T_d} = \frac{1}{T_{dL}} + \frac{1}{T_{dI}}, \quad \frac{1}{T_I} = \frac{1}{T_{IL}} + \frac{1}{T_{Id}}, \qquad (2)$$

T_{IL}, T_{SL}, and T_{dL} are the spin-lattice relaxation times of the nuclear and electronic subsystems and the dipole-dipole reservoir; T_{Id} and T_{dI} are the relaxation times of the nuclear system to the dipole-dipole reservoir and vice versa; ω_d is the "quantum" of energy of the dipole-dipole reservoir.[8]

In the general case, under saturating action of the electromagnetic field on the electron spin system ($W_S^m \gg 1/T_{SL}$) and simultaneous acoustic saturation of the nuclei ($W_I^u \gg 1/T_{IL}$), and also

$$T_{Id} \ll T_{IL}, \quad T_{dI} \ll T_{dL}, \quad \frac{\omega_s|\omega_s - \Omega_s|}{\omega_d^2} \gg 1, \quad \frac{c_I T_{dL}}{c_d T_{IL}} \ll 1, \qquad (3)$$

we obtain for the reciprocal temperatures

$$\beta_s = \beta_L\frac{(\omega_s - \Omega_s)^2}{Z}, \qquad (3a)$$

$$\beta_d = \beta_L\frac{(\omega_s - \Omega_s)\omega_s}{Z}, \qquad (3b)$$

$$\beta_I = \beta_L\frac{\omega_s(\omega_s - \Omega_s)}{(1 + 2W_I^u T_{Id})Z}, \qquad (3c)$$

$$Z=\left[(\omega_s-\Omega_s)^2+2\omega_d^2\left(\frac{1}{T_{1d}}+2W_I^u\frac{T_{dL}}{T_{dI}}\right)\left(\frac{1}{T_{1d}}+2W_I^u\right)^{-1}\right]$$

where c_I and c_d are the specific heats of the nuclear and dipole-dipole reservoirs.[3]

On the basis of the derived expressions we obtain the following estimated values of the parameters in (3a)–(3c):

$$\omega_s=9486\ \text{Hz},\ \omega_I=4\cdot10^6\text{Hz},\omega_s-\Omega_s=3\cdot10^7\ eq,$$
$$W_I^u=1\,\text{sec}^{-1},\ (\varepsilon=3\cdot10^{-7})[9],\ T_{1L}=4\text{sec},$$
$$T_{dL}=T_{sL}/2\approx60\cdot10^{-3}\text{sec},\ T_{dI}=3\cdot10^{-5}\text{sec},$$
$$T_{1d}=3\cdot10^{-4}\text{sec}$$

A qualitative calculation taking into account the coupling of the dipole-dipole reservoir to the nuclear Zeeman reservoir shows that electromagnetic saturation of the EPR line increases nuclear polarization by two orders of magnitude over the static nuclear polarization; this agrees well with the results for nuclear polarization in[10,11]. The change of nuclear polarization accompanying ultrasonic saturation of the nuclei (simultaneously with the microwave saturation of the EPR line) can be evaluated by means of the expression

$$K=\left(\frac{1}{T_{1d}}+2W_I^u\frac{T_{dL}}{T_{dI}}\right)^{1/2}\left(\frac{1}{T_{1d}}+2W_I^u\right)^{-1/2},\qquad(4)$$

where K is the ratio of nuclear polarization in the absence of sound to nuclear polarization in the case of acoustic saturation. The ratio of the microwave powers absorbed by electron spins with acoustic saturation (P_S) and without acoustic saturation ($P_S^{(0)}$)[8] is obtained as follows:

$$\frac{P_s}{P_s^0}=\frac{(\omega_s-\Omega_s)^2+2\omega_d^2}{Z}\approx0.8,\qquad(5)$$

in agreement with the experimentally studied change of EPR signal intensity under acoustic pumping.

CONCLUSION

1. The double acoustic resonance technique enabled us to observe acoustic nuclear resonance in Al^{27}; this had not previously been observed by a direct method. Theoretical calculations show that acoustic ENDOR enables us to enhance the sensitivity of acoustic resonance absorption measurements by more than one order of magnitude over "single" acoustic resonance. An additional advantage of acoustic double resonance consists in the observation of acoustic NMR for $\Delta m=\pm2$ transitions.

2. Experiments on double acoustic resonance show that acoustic energy can be transferred to the nuclear spin system in ruby by means of (a) the interaction of the gradients of crystal fields with nuclear quadrupole moments, and (b) the coupling of magnetic dipole-dipole interactions of Cr^{3+} ions with nuclear magnetic moments of Al^{27}.

3. A comparison of our experimental results with theoretical calculations for the mechanisms of relaxation and dynamic nuclear polarization corroborates the existence of strong coupling between the dipole-dipole system of Cr^{3+} ions and the Al^{27} nuclear spin system.[10,11] This coupling leads to the magnetic spin-lattice relaxation of Al^{27} nuclei. In the process of double acoustic-magnetic resonance the following occurs: with microwave saturation of the EPR line the temperature of the Cr^{3+} – Cr^{3+} dipole-dipole reservoir changes as compared with nonsaturating conditions; this in turn reduces the temperature $|T_N|$ of the nuclear spin system via the channel (Cr^{3+} – Cr^{3+}) ⟷ Al^{27}.

Sonic excitation of nuclear quadrupole transitions reduces the population differences of the spin levels (polarization reduction) and thus leads to heating of the dipole-dipole system. As a final result, the coupling between the Zeeman electron system of Cr^{3+} ions and the system of dipole-dipole interactions of the same ions enhances the temperature of the electron spin system; this is observed as reduced intensity of the EPR signal.

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