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Electron-Spin Relaxation by Tunneling States in β-Al_2O_3:Na

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(Received 30 March 1979)

Spin relaxation measurements on a color center in the conduction plane of β-Al_2O_3:Na reveal an exceptionally fast rate with an anomalous temperature and microwave frequency dependence. The data are quantitatively described by a mechanism involving the coupling of a color center to the phonon-induced relaxation of a nearby localized two-level tunneling state. The required density of such states is nearly the same as that used to explain the low-temperature properties of β-Al_2O_3:Na.

In addition to being widely studied as a fast ionic conductor, sodium β-alumina is of interest because its low-temperature properties resemble those of a glass.[1-5] These properties of the β-aluminas, like other amorphous materials, have been explained in terms of the phenomenology of localized tunneling states (LTS).[6,7] We have observed an anomalous temperature and microwave frequency dependence in the electron spin relaxation rate of a paramagnetic center produced in the conduction plane of β-Al_2O_3:Na by low-temperature irradiation. These anomalies are satisfactorily explained by a density of tunneling states which also predicts the specific heat, thermal conductivity, and dielectric susceptibility data reported by Anthony and Anderson.[4]

The absorption derivative spectrum of the center is shown in Fig. 1. It has been independently observed and reported by O'Donnell, Barklie, and Henderson.[8] The intensity ratios in the eleven-line hyperfine pattern are characteristic of an electron interacting with two equivalent $I=\frac{5}{2}$ nuclei. From the anisotropy of the principal g factors and the magnitude of the hyperfine splitting, O'Donnell, Barklie, and Henderson argue convincingly that the defect is an F^+ center, i.e., an electron trapped at an oxygen vacancy, at the $O(5)$ site.[9] This site is 0.168 nm from the Al nuclei and 0.323 nm from Na ($I=\frac{3}{2}$) nuclei in the unperturbed lattice.

Our relaxation measurements were made at X and Ku band microwave frequencies using the pulse saturation and recovery technique. Spectrometer details have been published elsewhere.[10,11] None of the recoveries was strictly

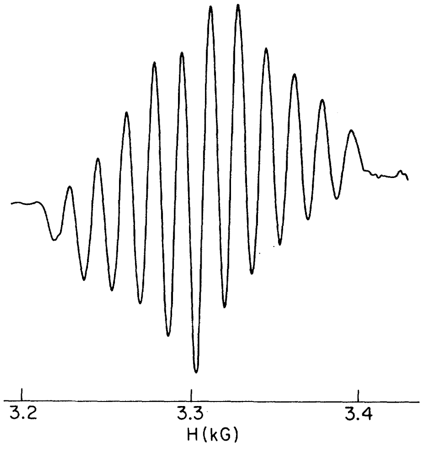

FIG. 1. Derivative of the EPR absorption spectrum from a color center in the conduction plane of β-Al_2O_3:Na as measured at 77 K and 9.3 Ghz, with $\vec{B}$ parallel to the c axis.

exponential. Our relaxation times should be construed as representative of the recovery between times at which the signal is 60% and 90% recovered to its thermal equilibrium value.

Figure 2 shows relaxation data for one sample at two different frequencies. These data cannot be explained in terms of the usual phonon coupling. For an F^+ center one would expect the dominant relaxation mechanism to be a phonon-induced modulation of a hyperfine interaction.[12] At these temperatures T, and microwave frequencies ν, this time-even interaction should also lead to a low-temperature relaxation rate which varies as $\nu^2 T$. At higher temperatures it should lead to a two-phonon Raman process varying initially as T^7, but eventually as T^2 in the high-temperature classical limit. In addition one would expect relaxation rates of the order of 10^{-3} s^{-1} at 2 K. Instead, the data of Fig. 2 indicate a nearly constant rate below 4 K, then a sharp increase faster than T until 15 K, above which the relaxation rate varies linearly with T.

Nuclear spin relaxation rates are known to be much faster in amorphous materials than in crystals.[13,14] This suggests that the relatively rapid relaxation rate we observe is dominated by the interaction of the F^+ centers with the LTS in the disordered conduction plane. Various models for nuclear or electronic spin relaxation in glasses exist.[13-18] It is known that the LTS in β-$\mathrm{Al_2O_3}$:Na relax much faster than the F^+ centers in that material.[4] We therefore assume in our model that the LTS are always in thermal equilibrium with the lattice. The mechanism we propose for the electron spin relaxation of an F^+ center in a glass is similar to the process by which protons relax in the presence of paramagnetic impurities, especially as it applies to dynamic nuclear polarization.[19] There, protons with a Zeeman splitting δ are weakly coupled to electrons with a Zeeman splitting $E \gg \delta$. This is shown schematically in Fig. 3. The weak coupling provides wave-function admixtures which allow "forbidden" relaxation transitions σw, where σ is proportional to the square of the wave-function admixture and w is the "allowed" relaxation transition in which just an electron spin is flipped. In our model the electron spins are replaced by LTS, designated by $|\pm 1\rangle$ in Fig. 3, and the energy splitting E varies from site to site. The F^+ centers, denoted by $|\pm\rangle$ in Fig. 3, have a uniform energy splitting $\delta \approx 2\mu_B H \ll E$.

The relaxation rate $1/\tau$ of a LTS with an energy splitting $E = (\epsilon^2 + \Delta^2)^{1/2}$ is given by

$$\frac{1}{\tau}(E,\Delta) \approx \frac{3}{2\pi\rho v^5 \hbar^4}\left(\frac{\gamma\Delta}{E}\right)^2 E^3 \coth\left(\frac{E}{2kT}\right), \qquad (1)$$

where ϵ is the asymmetry energy of the double well, Δ is the overlap energy, $\gamma = 0.5\, \partial\epsilon/\partial e$ is the coupling parameter due to the modulation of

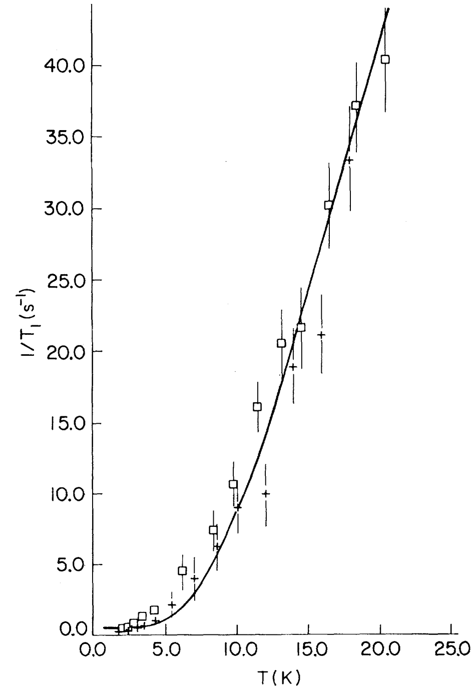

FIG. 2. Spin relaxation rate of the color center of Fig. 1 as measured at microwave frequencies of 9.5 GHz (squares) and 16.5 GHz (crosses).

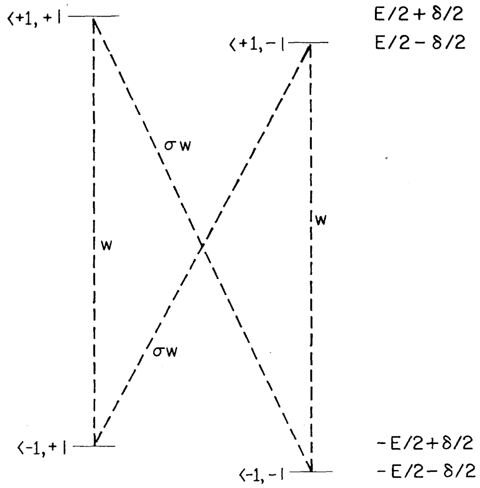

FIG. 3. Schematic diagram of the energy levels and product wave functions for a coupled system.

ϵ by the phonon-induced strain e, ρ is the crystalline mass density, and v is a suitably averaged acoustic phonon velocity. The minimum value of τ occurs when Δ equals E and $\tau_{\text{min}}/\tau = (\Delta/E)^2$. There is a density of tunneling states according to E and Δ values[20]:

$$P(E,\Delta) = \frac{1}{\Delta}\,\frac{1+\Delta^2/E^2}{(1-\Delta^2/E^2)^{1/2}}\,P(E). \tag{2}$$

The coupling of the F^+ center to the LTS is assumed to be a Fermi contact hyperfine (hf) interaction with a sodium nucleus which can tunnel a distance d through the barrier of the asymmetric double-well potential. It is further assumed that the value of $|\psi|^2$ at the sodium nucleus[21] falls off roughly as R_0^{-3}. This allows us to write the interaction between the LTS containing a Na ion and the F^+ center as

$$H_1 = \frac{A\vec{I}\cdot\vec{S}}{E}\left(\frac{3d}{2R_0}\right)\begin{pmatrix}-\epsilon & \Delta\\ \Delta & \epsilon\end{pmatrix} \tag{3}$$

in the basis where the LTS is diagonal. Scaling the measured aluminum hf interaction by the known crystal structure, we estimate $A/h \approx 6.4$ MHz for sodium. In computing the relevant wavefunction admixtures we require elements of Eq. (4) which are diagonal in the LTS, but off-diagonal in S. This leads to an F^+-center relaxation rate

$$\frac{1}{T_{1F}} = \frac{5}{2\tau}\left\{\frac{3A\epsilon d}{2R_0E\delta}\right\}^2 \operatorname{sech}^2\left(\frac{E}{2kT}\right), \tag{4}$$

where averaging over the nuclear spin operators yields the factor of $\frac{5}{2}$. Combining Eqs. (1) and (4) we obtain the relaxation rate of an F^+ center in contact with an LTS of energy E and overlap energy Δ:

$$\frac{1}{T_{1F}}(E,\Delta,T) = \frac{135}{8\pi\rho v^5\hbar^4}\left\{\frac{A\gamma d}{\delta R_0}\right\}^2 \times\left\{1-\frac{\Delta^2}{E^2}\right\}\frac{\Delta^2 E}{\sinh(E/kT)}. \tag{5}$$

From the dielectric susceptibility data[4] it can be estimated that 25% of the F^+ centers should be in hf contact with a tunneling, nearest-neighbor sodium. Spin diffusion should allow the remaining 75% of the F^+ centers to reach thermal equilibrium rapidly. We can then expect an F^+ center to return to thermal equilibrium after saturation, at a rate $\langle 1/T_{1F}\rangle$ given by the average of Eq. (5) over the distribution of LTS given by Eq. (2). From the data of Anthony and Anderson[4] we estimate $\gamma = 0.3$ eV, $d = 0.03$ nm, $\Delta_{\text{min}}/E = 10^{-3}$, $\rho = 3.22$ g cm^{-3}, and $v = 4.1\times10^5$ cm s^{-1}. Their data can be fitted with a LTS density such that

$$\int_{\Delta_{\text{min}}}^{E} P(E,\Delta)\,d\Delta = 2.4\times10^{33}(E/kT_N)^{0.2} + 4.5\times10^{29}(E/kT_N)^3 \text{ erg}^{-1}\text{ cm}^{-3} \tag{6}$$

with $T_N = 1$ K and a cutoff at $E_{\text{max}}/k = 65$ K. With use of this set of self-consistent parameters our model predicts a relaxation rate of approximately 130 s^{-1} at 15 K and 9.5 GHz. The temperature dependence of the solid line in Fig. 2 is described by a constant rate plus the temperature dependence of $\langle 1/T_{1F}\rangle$ obtained by changing the factor of 4.5 in Eq. (6) to 2.2, and lowering the cutoff from 65 to 40 K.

We believe that the temperature-independent relaxation below 4 K is associated with those fast-relaxing F^+ centers which are in hf contact with a LTS having the same energy splitting as the F^+ center. These centers are few in number, but the remaining F^+ centers can relax through these sites by spin diffusion. Our model predicts a δ^{-2} dependence which is absent from the data, but there is evidence of a slightly lower rate of the higher-frequency data. The inclusion of spin diffusion would probably correct this shortcoming. We believe that these measurements have clearly established the relaxation of paramagnetic centers by tunneling states in β-Al_2O_3:Na, and that our model correctly describes this relaxation mechanism.

We wish to acknowledge assistance and advice from M. M. Abraham, J. B. Bates, and Y. Chen during the initial stages of these experiments while one of us (H.J.S.) was on leave at the Oak Ridge National Laboratory. We have also benefitted from useful discussions with A. C. Anderson, P. J. Anthony, and M. W. Klein. This research was supported by the U. S. Department of Energy under Contract No. EY-76-C-02-1198.

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Analysis of the Anomalous Temperature-Dependent Resistivity on Potassium below 1.6 K

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(Received 9 March 1979)

Recent precision measurements of the resistivity of potassium between 0.38 and 1.6 K revealed a surprising $T^{1.5}$ temperature dependence. We show that scattering of electrons by phasons—the collective excitations of an incommensurate charge-density wave—can provide an explanation.

Recent measurements by Rowlands, Duvvury, and Woods,[1] indicate the presence of an anomalous contribution to the resistivity of potassium, which, if fitted to a pure power law, varies as $T^{1.5}$. Previously proposed mechanisms that contribute to the resistivity at low temperatures, including electron-phonon and electron-electron scattering, yield curves of resistivity versus temperature that are the wrong shape to explain this high-precision data. As a resolution of this difficulty, we propose a new mechanism—scattering of electrons with phasons,[2] the collective excitations associated with phase modulation of a charge-density wave. We will see that this assumption leads to the prediction of a temperature-dependent resistivity that is in good agreement with the data.

Conventional studies of the resistivity of a metal at low temperatures yield the following contributions[3]:

$$\rho(T)=\rho_0+AT^5+BT^p\exp(-\hbar\omega_0/k_BT)+CT^2, \quad (1)$$

where ρ_0 is the residual resistivity. The term AT^5 results from normal electron-phonon scattering in the low-temperature limit. It may be greatly reduced in magnitude from the value predicted by the Bloch-Grüneisen formula if phonon-drag effects are important. Electron-phonon umklapp scattering, which is essentially unaffected by phonon drag, contributes a term at low temperatures of the form $BT^p\exp(-\hbar\omega_0/k_BT)$, where ω_0 is the frequency of the phonon with the minimum wave vector that allows participation in an umklapp process. Electron-electron scattering produces the term CT^2 at all temperatures.

The relative importance of each of these mechanisms is revealed by examining the low-temperature resistivity data in potassium. Highly accurate measurements[4,5] exhibit an exponentially decaying resistivity with decreasing temperature below about 4 K, supporting the electron-phonon umklapp scattering mechanism and lending credence to the concept of phonon drag. Below 2 K, however, significant deviations from exponential behavior have been observed, suggesting the presence of an additional scattering mechanism. In order to discover the characteristic behavior of this additional mechanism, one must first subtract the known electron-phonon umklapp contribution from the data. Unfortunately, the form of this umklapp term below 2 K is not well determined. While van Kempen *et al.*[4] have fitted