PARAMAGNETIC RESONANCE AS A PROBE FOR CRITICAL PHENOMENA

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I. INTRODUCTION

Critical phenomena have been greatly in evidence in recent years, especially last year in view of the Nobel Prize being awarded to K. G. Wilson for his Renormalization-Group (R.G.) theory (1). With this theory, one can quantitatively calculate the response of cooperative systems undergoing phase transitions, be they of the continuous, second-order, or discontinuous, first-order, variety. Especially for the former, experimentalists had observed appreciable deviations from so-called mean-field theory. The properties observed in early experiments were, for example, specific heat c_p, compressibility κ, and the so-called order parameter η. The latter quantity measures the degree of order below a transition T_c in a ferromagnetic system, the magnetization m, in an antiferromagnet, the staggered magnetization m_s, etc. For the above-mentioned quantities, $c_p(T)$, $\kappa(T)$ or $\eta(T)$ power-law dependences were observed as

$$\eta = \eta_0\left[\frac{(T_c - T)}{T_c}\right]^{\beta}, \qquad (1)$$

in the range $t = (T_c - T)/T_c$ of 10^{-2} to 10^{-5}. In three dimensions, $\beta \simeq 0.32$ as compared to the mean-field value $\beta = 1/2$. These power laws result from the divergent correlation length $\xi = \xi_0 t^{-\nu}$ towards T_c, where ξ measures the correlation between like spins, for example. They posed tremendous nonlinear problems which Wilson, Kadanoff, Fisher and others showed how to treat (1).

It is obvious that in systems where one of the above-mentioned properties has local character, which magnetic resonance measures, it can contribute to the field of critical phenomena, since the resonance frequencies and magnetic fields are easily determined to the accuracies of 10^{-5} required, but this is also necessary for the relative temperature. Thus, if T_c is at 100 K, an accuracy of 1 millikelvin, or if T_c is at 800 K, 8 millikelvin stability is required. In the case of paramagnetic resonance, cavity systems were developed earlier in our laboratory applicable to T_c's below room temperature, and most recently also above T_c going up to 1000 K (2), i.e. in a range where no other experiments of *any* kind have ever been performed.

In the present paper, examples of such investigations in the field of structural phase transitions will be given (3). A phase transition in a solid is called structural when a regular lattice is distorted by a small displacement or ordering in lattice positions of single atoms or molecules. In section II, early determinations of β will be summarized. These were of importance because previously, due to imprecision of the β measured by techniques other than magnetic resonance, $\beta = 1/2$ had been inferred. For the displacive variety of SPT's, an optical or acoustic mode ω_s vanishes if $\beta = 1/2$. It could subsequently be shown quantitatively by EPR that, if a system is critical and $\beta \approx 1/3$, a crossing over of displacive to order-disorder behavior will occur upon approaching T_c in quantitative agreement with nonvanishing ω_s. This we shall address in section III. The critical exponents are *universal*. They depend only on the lattice dimensionality d, the symmetry of the system and the order-parameter components n. One can break the symmetry by external fields; magnetic ones in case of magnetic order or electric fields in ferroelectrics. In the case of SPT's, uniaxial stresses can be applied. Several

second or first-order phase boundaries meet at such a multicritical point. EPR in SPT demonstrated such bi- and tetracritical points as predicted by R.G. (4) and was first to show the existence of so-called Lifshitz (5) and Potts transitions (6) not observed before in other cooperative systems. Selected examples are discussed in section III.

II. CRITICAL BEHAVIOR IN $SrTiO_3$ AND $LaAlO_3$

Both crystals listed in the heading are cubic in their high-temperature phase, and crystallize in the perovskite lattice ABO_3. In such a lattice, BO_6 octahedra are linked at the corners. The A ion is dodecahedrally coordinated. In each of the crystals upon cooling, one SPT occurs where TiO_6 or AlO_6 octahedra start to rotate, respectively. Adjacent octahedra rotate by $+\varphi(T)$ or $-\varphi(T)$ due to their common oxygen corner linkage. $\varphi(T)$ is the order parameter of the transition. It had been demonstrated previously by EPR that in $SrTiO_3$ this rotation occurs around $\langle 100 \rangle$, and in $LaAlO_3$ around $\langle 111 \rangle$ pseudocubic axes, i.e. $SrTiO_3$ becomes tetragonal with space group I4/mcm, and $LaAlO_3$ trigonal with group R$\bar{3}$c. The transition temperatures are 105 K and 796 K, respectively.

The temperature dependence of the octahedral rotation angle $\varphi(T)$ was monitored by EPR of Fe^{3+} replacing Al^{3+} and Ti^{4+} ions in $LaAlO_3$ and $SrTiO_3$. The spin Hamiltonians are axial in both crystals below T_c with a cubic component

$$\mathcal{H} = g\beta\vec{S}\vec{H} + D\left[S_\zeta^2 - \frac{S}{3}(S+1)\right] + a\left[S_x^4 + S_y^4 + S_z^4 - \text{const.}\right]. \qquad (2)$$

For symmetry reasons, $D = c\varphi^2(T)$, which was monitored in $LaAlO_3$ with c known and $\zeta \parallel \langle 111 \rangle$. In eq. (2), the x, y and z axes in the Hamiltonian point towards the corners of the octahedra and rotate proportional to $\pm\varphi(T)$. The resulting magnetic resonance splitting ΔH, proportional to $2\varphi(T)$, was measured in $SrTiO_3$. The two experiments thus exemplify that one can use magnetic resonance to study properties proportional to φ or φ^2.

In fig. 1, the measured order-parameter behavior is shown by plotting $\varphi(T)^2$ versus reduced temperature t for both crystals considered. This plot shows clearly a deviation of $\varphi(T)^2$ from mean-field behavior which, with $\beta = 1/2$, would yield a straight line, whereas a clear bending down is observed upon approaching T_c from below. In both cases, $\beta = 0.33 \pm 0.02$ was obtained. The crossing over from the straight mean-field line to critical behavior is closely the same in both $LaAlO_3$ and $SrTiO_3$ in reduced units despite the T_c's differing by a factor eight.

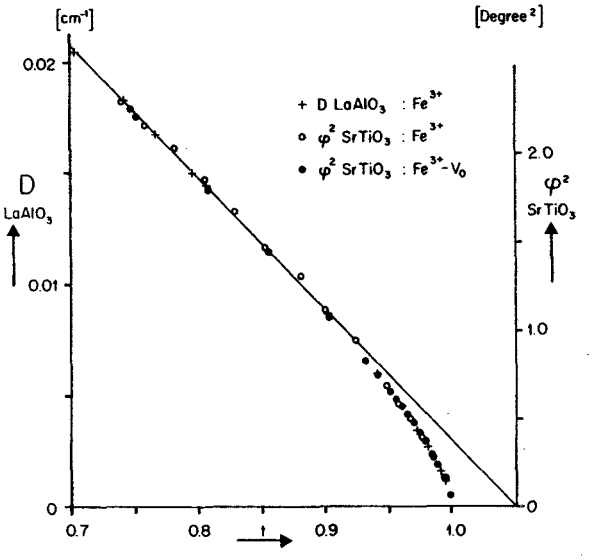

Fig. 1

φ^2 of $SrTiO_3$ and D of $LaAlO_3$ versus t between 0.7 and 1, showing the changeover from Landau to critical behavior. After K.A. Müller and W. Berlinger, Phys. Rev. Lett. 26, 13, 1971. © 1971 APS

III. DISPLACIVE TO ORDER-DISORDER CROSSOVER IN $SrTiO_3$

In dynamic lattice theory, it is in general assumed the atoms or molecular units move in a harmonic potential $V(r) = \alpha r^2 + \text{h.o.}$ In this theory, the probability distribution around the equilibrium position is a Gaussian $P(r) = P_0 \exp -(\alpha r)^2$. In displacive transitions, a soft mode freezes out at T_c, $\omega_s \to 0$.

However, for a transition to occur an anharmonicity in V(r) has to be present. V(r) is flatter than a parabola at least. Upon approaching T_c from above or below, computer simulations indicated this anharmonicity increases due to the correlated clusters of octahedral rotations. The soft mode ω_s did not freeze out at T_c but remained finite. Inelastic neutron and Raman scattering experiments gave $\omega_s(T_c) = 0.14$ THz. Because $\omega_s(T) = 0.69\varphi(T)$ below T_c, one could estimate $\varphi_{sr} = \pm 0.20°$ where φ_{sr} is the nonvanishing short-range order parameter at T_c. The probability distribution would then be a superposition of two Gaussians $P(\varphi)$ separated by $\pm$ 0.20° of the octahedral units. X-ray and elastic neutron scattering had yielded 2.1° for the harmonic amplitude width of the Gaussian distribution. These scattering experiments were unable to resolve φ_{sr} of 0.20° because their intensities are measured in wave-vector space and need Fourier transformation, with much too low a precision due to background problems. EPR was able to resolve this problem because it acts as a low pass filter: The high-frequency ω_s amplitudes of 2.1° at 0.14 THz are so much faster than the inverse EPR linewidth and are thus motionally averaged out. On the other hand, the correlated clusters are pinned by impurities and move much slower than the inverse EPR linewidth. Thus, the anharmonic probability distribution can be probed by EPR.

The experiments were conducted with the Fe^{3+}-V_0 center in $SrTiO_3$, an Fe^{3+} ion with a next-neighbor oxygen vacancy. Due to its large axiality, $D >> h\nu$, this center is more sensitive to $\varphi(T)$ than the non-charge-compensated Fe^{3+} but exhibits the same linear dependence on φ as can be seen in fig. 1. In fig. 2, the EPR line shapes recorded at T_c are shown, both in the usual derivative as well as in the integrated form. The latter represents the probability distribution of $P(\varphi)$ without the harmonic component. It is seen to be much better fitted by a superposition of two Gaussians separated by $0.44° = 2\varphi_{sr} = 2\sigma$ than a single Gaussian.

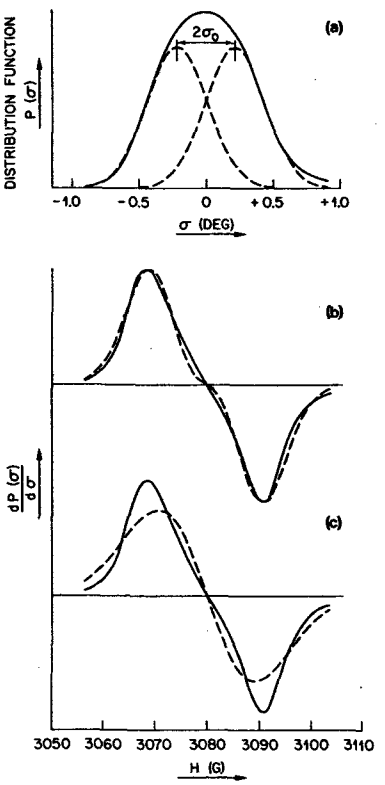

Fig. 2

(a) The experimental distribution function $P(\sigma) = P(\varphi)$ at T = 105.5 K (solid line) together with two displaced Gaussians with whose superposition (not shown) we model the spectrum. (b) The derivative of the experimental $P(\sigma)$, solid line, and of its double-Gaussian representation defined in (a). (c) The derivative of the experimental $P(\sigma)$ and its single-Gaussian representation. After A.D. Bruce, K.A. Müller and W. Berlinger, Phys. Rev. Lett. 42, 185 (1979). © 1979 APS

This has been regarded as an important success of EPR in recent anharmonic investigations of SPT. The residual linewidth is caused by the strains in the crystal.

IV. MULTICRITICAL BEHAVIOR IN $SrTiO_3$, $LaAlO_3$ AND $RbCaF_3$

In well-annealed crystals of $SrTiO_3$ or $LaAlO_3$, three {100} or four {111}-type domains are equally possible. Applying uniaxial stress alters this. Pulling along a particular [100] direction in

$SrTiO_3$ favors a {100} domain above the other two {010} or {001} because the c/a ratio is larger than one. Pushing along a [111] direction in trigonal $LaAlO_3$ favors this domain above the other three. T_c as a function of such Σ stress is increased. Mean field predicts a linear shift in T_c, R.G. theory $(T_c(\Sigma) - T_c(0))/T_c(0) \propto \Sigma^{\psi}$ with the shift exponent $\psi = 1.25$ for the particular boundary. Upon extrapolating EPR D(T) parameters of Cr^{3+}, S = 3/2, substitutional in $LaAlO_3$ for given stresses Σ, to zero, $T_c(\Sigma)$ was determined (4). The resulting phase boundary is shown in fig. 3. It is the first boundary at such a high temperature of 800 K determined. $\psi = 1.31 \pm 0.7$ was measured, in agreement with R.G. predictions. The inset illustrates the phase diagram predicted for pushing and pulling. In the latter case, a second-order phase boundary separating the pseudocubic from the phase with three equivalent $\{11\bar{1}\}$-type domains occurs. For $\Sigma = 0$, both second-order boundaries meet therefore the name bicritical point. Applying [100] stress, four second-order boundaries separating four different phases meet a so-called tetracritical point. This has also been verified by EPR of Fe^{3+} for $\Sigma > 0$ (4).

The existence of more sophisticated multicritical points was also realized in structural phase transitions, again with EPR: a tricritical Lifshitz point in $RbCaF_3$ under near [100] stress (5). Tricritical means here that the transition point changes from second to first-order character, and Lifshitz means highly anisotropic near two-dimensional correlations. For the order-parameter exponent, $\beta = 0.18$ was found intermediate between three-dimensional $\beta = 0.32$ and two-dimensional $\beta = 0.13$ (5). The existence of a so-called three-state Potts transition was first shown to occur in [111]-stressed $SrTiO_3$ (6). The first-order character, i.e. the jump $\delta\varphi$ of the order parameter, is strongly renormalized due to fluctuations. The jump is $\delta\varphi \propto \varphi^{\delta^*}$. The measured exponent is $\delta^* = 0.62 \pm 0.07$ as compared to $\delta^* = 0.56$ of R.G. and $\delta^* = 1$ from mean-field theory, respectively.

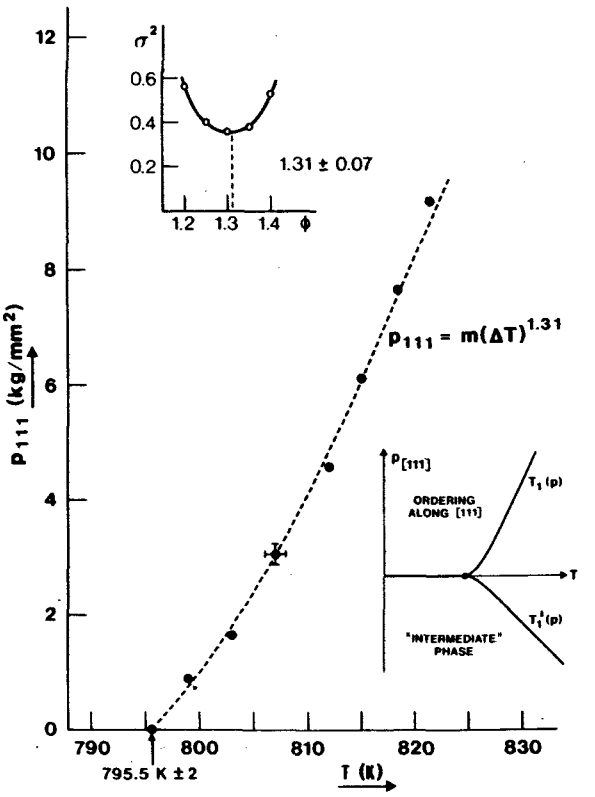

Fig. 3

Bicritical phase boundary T_1 of $LaAlO_3$ under [111] stress. After ref. (4).

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