Determination of the width of the central peak near structural phase transitions using the EPR method

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A rigorous quantitative method is proposed for determining the width of the defect-induced central peak in the fluctuation spectrum of the order parameter. The method is based on the theory of defect broadening of EPR lines near structural phase transitions.

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Various methods, including neutron scattering and Raman and Mandel'shtam–Brillouin spectroscopy have been used recently to establish that the fluctuation spectrum of the order parameter near the temperature of a structural phase transition T_c contains an unusual and anomolously narrow peak at zero frequency, whose width exceeds the resolution of the experiment (see, for example, Ref. 1). The extreme interest in the problem of the central peak is related to the explicit breakdown of the generally accepted concept of a soft mode, which approaches zero as $T \to T_c$. In the presence of the central peak, the frequency of the soft mode remains finite at the phase transition point, while only the width of the central peak decreases critically. For this reason, it is very important to study the central peak in order to understand the nature of phase transitions correctly. As a result of numerous investigations, it has become clear[2] that only defects capable of reorientation can be responsible for such a narrow central peak. In addition, the critical narrowing of the central peak is related to the interaction of defects, which near T_c retards their reorientation.

The possibility of determining the width of the central peak using the EPR method was proposed in Ref. 3. This possibility is based on the fact that low-frequency fluctuations in the order parameter must lead near T_c to critical broadening of the EPR lines. However, due to the absence of a rigorous quantitative theory, it turned out that the interpretation of the experimental results was not unique (for example, the spread in the values presented for the width of the central peak in $SrTiO_3$ was 70–0.6 MHz).

In this paper, we develop a rigorous quantitative theory for determining the width of the defect-induced central peak using the EPR method.

In typical situations, the shift in the EPR frequency $\Delta\omega$ is linearly related to the order parameter η at the location of the paramagnetic probe $\Delta\omega = a\eta$. The defect-induced distribution $\eta(r)$ can be represented in the form[2]

$$\eta(\mathbf{r}_i,t) = \Sigma_j K_{ij}(\mathbf{r}_{ij}) h_j(t). \tag{1}$$

For simplicity and without loss of generality, we examine the case of a single-component order parameter with the correlation function $K(r)$. In the absence of long-range forces, $K(r) \propto r^{-1} e^{-r/r_c}$, r_c is the correlation radius of a pure crystal, and h_i depends on

the orientation of the defect (which, in particular, can be an electric or elastic dipole) and characterizes the intensity of its interaction with the order parameter. The time dependence of h_i takes into account the possible thermal reorientation of the defects.

We shall calculate the shape of the EPR lines for two of the most important limiting cases: in the static case and in the motional-narrowing limit. In the static limit, the shape of the line follows the distribution function of the local values of the order parameter, which near T_c for $nr_c^3 \gtrsim 1$ (n is the concentration of defects), due to the central limit theorem, must be nearly Gaussian.[4] For this reason, the line width is described by the second moment M_2:

$$M_2 = a^2\langle\eta^2\rangle = a^2\int d\mathbf{q}K_{\mathbf{q}}K_{-\mathbf{q}}S_{\mathbf{q}}, \tag{2}$$

where $K_{\mathbf{q}}$ are the Fourier coefficients of the function $K(r)$, and $S_{\mathbf{q}}$ is the static structure factor, which describes the correlation between the orientations of defects ($S_{\mathbf{q}} = n\langle h_i^2\rangle + n^2\langle h_i h_j\rangle_{\mathbf{q}}$) and is related to the dynamic structure factor $S_{q\omega}$ by the relation $S_{\mathbf{q}} = \int d\omega S_{\mathbf{q},\omega}/2\pi$.

We note that the correlations between the orientations of different defects and the problem of EPR line broadening are taken into account for the first time in the present paper. Usually, only the first term in S_q is taken into account[5]; however, this is not valid near T_c.

In the opposite case involving rapid reorientation of defects, motional narrowing of the static contour occurs. As a result, we have a Lorentz line shape with a width

$$\lambda = \int_0^\infty dt\,\langle\Delta\omega(t)\Delta\omega\rangle = a^2\int d\mathbf{q}K_{\mathbf{q}}K_{-\mathbf{q}}S_{\mathbf{q},\omega=0}. \tag{3}$$

It is convenient to calculate $S_{q\omega}$ using the fluctuation dissipation theorem $S_{q\omega} = (2k_BT/\omega)\chi''_{q\omega}$. Since the interaction energy of defects V, according to (1), is equal to $V = \sum_{ij} K_{ij}h_ih_j$, the susceptibility $\chi_{q\omega}$ in the mean-field approximation can be determined in analogy to the dynamic Ising model.[6] This procedure for $T > T_c$ gives

$$\chi_{q\omega} = n\langle h^2\rangle/[(1 - i\omega\tau - n\langle h^2\rangle K_q/k_BT)k_BT] \tag{4}$$

where τ is the reorientation time for isolated defects. Performing the necessary calculations, we finally obtain

$$M_2 = 2A(T - T_0)^{-1/2}\left(1 + \sqrt{(T - T_c)(T + T_c - T_0)/T(T - T_0)}\right)^{-1}, \tag{5}$$

$$\lambda = A\tau[(T - T_c)(T + T_c - T_0)/T]^{-1/2}, \tag{6}$$

where $A \propto n\langle h^2\rangle a^2$, while the omitted coefficients depend on the specific form of the phase transition. The temperature dependences of M_2 and λ presented above are valid for any structural transitions. T_c is the temperature of the phase transition in a crystal with reorienting defects,[2-7] which is higher than the transition temperature of a pure crystal T_0.

From (4), we obtain the width of the central peak Γ, taking into account the relationship between T_c and T_0:

$$\Gamma = \tau^{-1}(T - T_c)(T + T_c - T_0)/T(T - T_0). \tag{7}$$

Using (5)–(7), it is easy to relate Γ to the measured parameters M_2 and λ and, thus, to determine the width of the central peak from EPR data.

According to (5) and (6), the motional-narrowing regime is realized not too close to T_c, since the condition $\lambda \ll \sqrt{M_2}$ must be satisfied. This limits the experimental possibility of determining Γ in the direct vicinity of the phase transition. However, the criterion $\lambda \ll \sqrt{M_2}$ is satisfied closer to T_c, the smaller the constant A, i.e., the smaller the width of the resonance lines. For typical, (for EPR) line widths ~ 1 Oe, we have $\Gamma \sim 1$ MHz, which greatly exceeds the resolution of traditional methods. The use of radio-frequency resonances, such as NMR and NQR, whose lines are several orders of magnitude narrower, so that the motional-narrowing regime will remain significantly closer to T_c, is even more promising.

Using the experimental data in Ref. 8, in which a critical increase in the width of the EPR line of $Fe^{3+} - V_0$ centers in $SrTiO_3$ was observed[1)] ($T_c \approx T_0 \approx 105$ K), we estimated the width of the central peak (observed in neutron experiments[9]). Our estimate is $\Gamma \approx 10$ MHz at $T \approx 140$ K. Since in the $SrTiO_3$ specimens used in Ref. 8, $T_c - T_0 < 0{,}5$ K, according to (7), the critical decrease in Γ should be essentially unobservable at $T - T_c > 1$ K. For this reason, the value $\Gamma \lesssim 0.6$ MHz, presented in Ref. 8, at $T \approx 115$ K is much too low.

Thus, the EPR method allows determining an important parameter of the fluctuation spectrum of the order parameter, namely, the width of the central peak, which at present cannot be determined as accurately by using other methods. It is definitely interesting to perform such experiments with controlled impurity concentrations, which could give a quantitatiave measure of the role of defects in the formation of the central peak.

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[1)] We note that in the presence of the central peak only the contribution to the line width related to it exhibits a critical temperature dependence.[8]

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