

Local configurational instability of the lattice near an impurity in a cubic crystal

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A spontaneous local change in the lattice structure of a cubic crystal near an impurity in a narrow temperature interval has been observed for the first time. The effect is interpreted as the onset of an instability with respect to a quasilocal vibration of symmetry A_2 associated with a manganese impurity in a BaF_2 crystal.

In this letter we report the observation by an ESR method of a spontaneous distortion of the lattice near an impurity, which arises in a narrow temperature interval. The effect is observed in the cubic crystal BaF_2 activated with manganese and corresponds to a local configurational instability of the lattice near the impurity at a certain temperature with respect to a quasilocal vibration of symmetry A_2 . Below the temperature of the instability, a nonzero distortion of symmetry A_2 arises in the nearest neighborhood of the impurity (the impurity itself is not displaced from the lattice site). For the first time in the case of a local center we are seeing an analog of a ferroelastic phase transition in a matrix. This might be called a "local phase transition," but we will use the more precise term "local configurational instability."

We studied the ESR spectra of Mn^{2+} ions replacing Ba^{2+} ions. The Mn^{2+} ion has the electronic configuration $3d^5$ (${}^6S_{5/2}$ state), and its ESR spectrum consists of six hyperfine transitions (the nuclear spin of manganese is $I = 5/2$), in each of which we observe a superhyperfine structure.

At temperatures above 50 K, the Mn^{2+} ions are at the center of a cube formed by eight F^- ions, and the superhyperfine structure results from an interaction of unpaired Mn^{2+} electrons with these ions. The ESR spectra of Mn^{2+} ions in a BaF_2 crystal were studied at $T = 300$ K in Ref. 1.

As the temperature is lowered, there is an abrupt transformation of the superhyperfine structure in the ESR spectrum, furnishing evidence of a substantial change in the superhyperfine interaction with the nearest F^- ions. A fine structure does not appear in the ESR spectrum, so that the symmetry of the center remains no worse than cubic. Figures 1 and 2 show the transformations of the superhyperfine structure for one hyperfine transition with $M = 1/2$ (the same effects are observed for the other hyperfine transitions) for the $B \parallel \langle 100 \rangle$ and $B \parallel \langle 111^+ \rangle$ orientations, respectively. A further lowering of the temperature to 4 K results in no new changes in the ESR spectrum. The changes in the superhyperfine structure are unambiguous evidence of a change in the lattice structure near the impurity.

Analysis of the superhyperfine structure at $T < 50$ K shows that for the orientation $B \parallel \langle 100 \rangle$ this structure consists of five groups, each containing five lines (in each of the six hyperfine transitions). This result means that we are observing a superhyper-

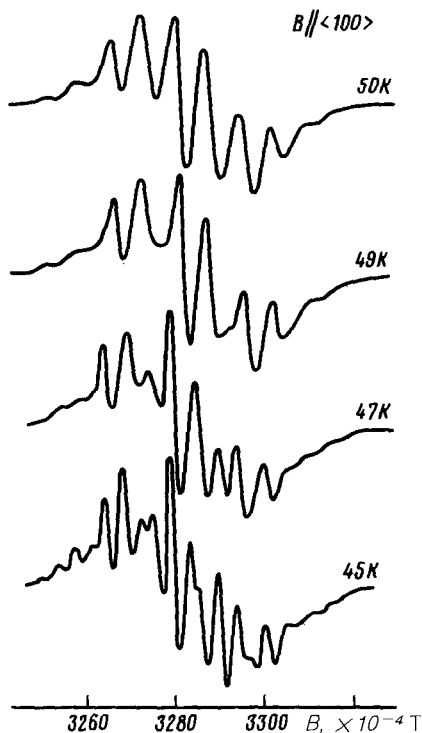


FIG. 1. Change in the superhyperfine structure of a hyperfine transition with $m = 1/2$ for Mn^{2+} in a BaF_2 crystal in the region of a local configurational instability ($B \parallel \langle 100 \rangle$, $\nu = 9.1$ GHz).

fine interaction with two groups, each consisting of four equivalent F^- ions. The cubic surroundings of Mn^{2+} , consisting of eight F^- ions, can be thought of as two tetrahedra which are equivalent at $T > 50$ K. At $T < 50$ K, the dimensions of one of the tetrahedra decrease, while those of the other increase; the impurity Mn^{2+} remains at the center of both tetrahedra. There is a condensation (“freezing”) of the quasilocal vibration of symmetry A_2 . As a result, the superhyperfine interaction with the four F^- ions (the small tetrahedron) increases, while that with the other four F^- ions (the large tetrahedron) decreases.

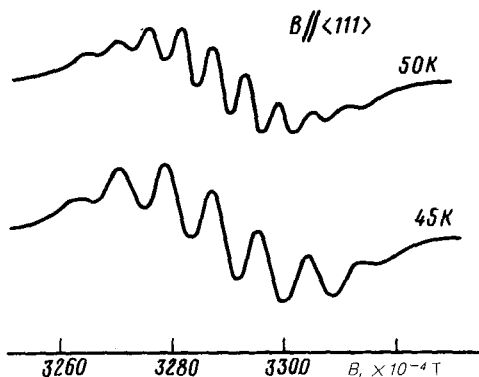


FIG. 2. Superhyperfine structure at temperatures above and below that of the local configurational instability for a hyperfine transition with $m = 1/2$ ($B \parallel \langle 111 \rangle$).

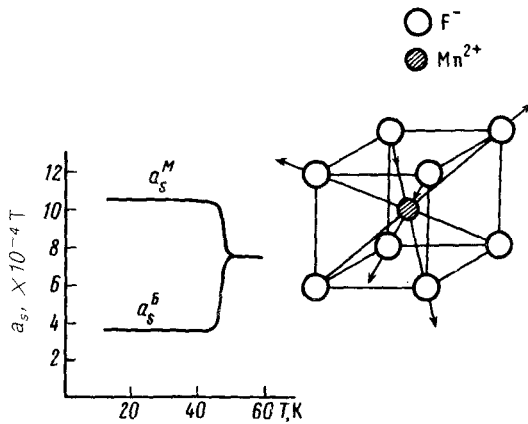


FIG. 3. Temperature dependence of a_s ; displacement of F^- ions near a Mn^{2+} ion in a $BaF_2:Mn$ crystal.

The constants of the superhyperfine interaction change sharply in the temperature range 50–45 K. For a parallel orientation of the magnetic field, along the $Mn^{2+}-F^-$ axis, at 55 K we find $a_{||} = 11.9 \times 10^{-4}$ T, while for the perpendicular orientation we find $a_{\perp} = 5.4 \times 10^{-4}$ T. The corresponding values at 45 K are $a_{||} = 16.3 \times 10^{-4}$ T and $a_{\perp} = 7.4 \times 10^{-4}$ T for the small tetrahedron and $a_{||} = 5.8 \times 10^{-4}$ T and $a_{\perp} = 2.7 \times 10^{-4}$ T for the large one.

The most direct information on the distances between ions comes from the constants of the isotropic superhyperfine interaction, a_s , so we show in Fig. 3 the temperature dependence of a_s , where a_s^l and a_s^M are the constants of the isotropic superhyperfine interaction for the small and large tetrahedra, respectively. In the region of the local configurational instability, we see a sharp change in the constants a_s . Figure 3 also shows the directions of the displacements of the F^- ions in the course of the local configurational instability. Our estimates show that the displacements of the F^- ions in this instability are on the order of 0.3 Å for the large tetrahedron and 0.14 Å for the small one. We carried out experiments with samples with various concentrations of manganese, ranging from 0.5 mole % to minimal residual concentrations in nominally pure crystals. In all cases, we observed a local configurational instability, and in the same temperature interval.

We turn now to a possible model for the substantial and extremely sharp temperature dependence of the displacements of the ligands which is observed. This dependence may be interpreted as the onset of a local configurational instability with respect to a quasilocal vibration of an impurity of symmetry A_2 . When a Ba^{2+} ion (ionic radius of 1.34 Å) is replaced by an Mn^{2+} ion (ionic radius of 0.80 Å), the potential of the $Mn^{2+}F_8^-$ defect does not have a minimum as a function of the dynamic variable of the A_2 mode, Q_{A_2} , when the ligands are in lattice sites ($Q_{A_2} = 0$), because of the sharp decrease in the contribution of repulsive Born-Mayer forces and also because of the Coulomb forces, which account for an instability of the static system of charges. The square of the corresponding effective frequency at $Q_{A_2} = 0$ satisfies $(\omega_{A_2}^{(0)})^2$. In contrast with the case in which a negative value of the square of the seed frequency of a quasilocal mode is of a pseudo-Jahn-Teller nature,² the nature of the instability in

the present case is determined exclusively by ion-ion interactions.

In the case we have $Q_{A_2} \neq 0$ in the equilibrium state (we are taking the stabilizing and harmonic interactions into account). We now consider the anharmonic interactions of fourth order of the A_2 mode with other quasilocal modes, which serve as a "fast" subsystem with respect to the A_2 mode, of the type $H' = \sum_{\Gamma_\nu} V_4(\Gamma_\nu) Q^2(\Gamma_\nu) Q_{A_2}^2$. Here $Q(\Gamma_\nu)$ is the dynamic variable of the quasilocal mode of the fast subsystem, which transforms under a Γ_ν -irreducible representation. For the frequency ω_{Γ_ν} and the natural width of the corresponding quasilocal mode, Γ_{Γ_ν} , of the fast subsystem, we have $\omega_{\Gamma_\nu} \gg \tilde{\omega}_{A_2}$, $\Gamma_{\Gamma_\nu} \gg \tilde{\omega}_{A_2}$, where $\tilde{\omega}_{A_2}$ is a characteristic value of the splitting in the spectrum of the vibrations of the A_2 mode, where anharmonic effects are taken into account. In examining the A_2 vibrations, we can thus introduce an effective potential

$$\mathcal{H}_{\text{eff}} = \frac{1}{2} \mu_{A_2} (\omega_{A_2}^{(0)})^2 \cdot Q_{A_2}^2 + \sum_{\Gamma_\nu} V_4(\Gamma_\nu) \langle Q^2(\Gamma_\nu) \rangle_T Q_{A_2}^2, \quad (1)$$

where $\langle Q^2(\Gamma_\nu) \rangle_T$ is the mean value, over the temperature, of the square of the displacement corresponding to the fast Γ_ν vibrations. In the limit $\omega_{\Gamma_\nu} \gg \Gamma_{\Gamma_\nu}$, we then find the resultant frequency of the A_2 vibrations to be

$$\omega_{A_2} = \left\{ (\omega_{A_2}^{(0)})^2 + \sum_{\Gamma_\nu} \frac{\hbar V_4(\Gamma_\nu) \coth[\hbar\omega(\Gamma_\nu)/2kT]}{\mu_{A_2} \mu(\Gamma_\nu) \omega(\Gamma_\nu)} \right\}^{1/2} \quad (2)$$

In the case $V_4(\Gamma_\nu) > 0$, there may be a transition from $\omega_{A_2}^2 < 0$ to $\omega_{A_2}^2 > 0$ with increasing temperature, accompanied by transition from a distorted configuration of ligands with symmetry A_2 to an undistorted configuration. The temperature T_c , corresponding to the condition $\omega_{A_2}(T_c) = 0$, is the temperature of a local configurational instability of the center. The local configurational instability is induced by a soft quasilocal mode, (2). At $T < T_c$, we have $Q_{A_2}(T) \neq 0$, corresponding to a nonzero local order parameter.

The local configurational instability observed here near an impurity is quite general in nature and can be observed in crystals with other impurity ions of small radius (e.g., Ca^{2+} and Mg^{2+}). It should be noted that the local configurational instability can have a strong effect on the strength of single crystals, especially at transitions through a temperature corresponding to a change in structure.

¹R. J. Richardson, S. Lee, and T. J. Menne, Phys. Rev. B **6**, 1065 (1972).

²A. G. Badalyan, P. G. Baranov, V. S. Vikhain, M. M. Petrosyan, and V. A. Khramtsov, Zh. Eksp. Teor. Fiz. **88**, 1359 (1985) [Sov. Phys. JETP **61**, 808 (1985)].

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