

Confirmation of the EPR identification of $\text{Cr}^{4+} 3d^2$ in *p*-type Cr-doped GaAs by means of applied uniaxial stress

J. J. Krebs and G. H. Stauss

Naval Research Laboratory, Washington, D.C. 20375

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Uniaxial stress has been used to study the isotropic Cr-related EPR center in *p*-type GaAs:Cr. Stress linearly splits the EPR line into two components, showing that the center is due to substitutional $\text{Cr}^{4+} 3d^2$ rather than interstitial $\text{Cr}^{1+} 3d^5$. The stress coefficients are $C_{11} = -8$ and $C_{44} = 168$ [in units of $10^{-13} \text{ cm}^{-1}/(\text{dyn}/\text{cm}^2)$], with only relative signs known.

Three distinctive charge states of the isolated Cr ion have been identified by EPR in semi-insulating Cr-doped GaAs. One of these states, which gives rise to a single isotropic resonance signal with no clearly characteristic feature, was first tentatively identified as $\text{Cr}^{1+} 3d^5$. However, its existence in strongly *p*-type Cr-doped GaAs showed^{1,2} that it is most probably due to $\text{Cr}_s^{4+} 3d^2$ substituted for Ga. Since this is the only Cr-related EPR signal found in strongly *p*-type samples, and since a significant fraction of the Cr^{3+} population can be converted to this center by optical means in semi-insulating GaAs, a strong circumstantial case can be built for this assignment. Nevertheless, there exists some speculative support^{3,4} for assigning this EPR signal to $\text{Cr}_i^{1+} 3d^5$ at an interstitial site. These two possible candidates both leave the Cr ion in T_d symmetry with an orbital-singlet ground state.

Following a suggestion of Watkins,⁵ we have per-

formed uniaxial stress experiments which unambiguously show that the center in question is $\text{Cr}_s^{4+} 3d^2$. This is based on the fact that uniaxial stress causes the isotropic signal to split into two equal-intensity components as shown in Fig. 1. This is just what one expects for Cr_s^{4+} with spin $S = 1$. On the other hand, $\text{Cr}_i^{1+} S = \frac{5}{2}$ should yield five components.

The stress apparatus has been described previously.⁶ Stress up to $1800 \text{ kg}/\text{cm}^2$ was applied to a *p*-type Cr-doped sample of dimensions $1.5 \times 1.5 \times 15 \text{ mm}^3$ with the long (stress) axis along [112]. The sample was cut adjacent to the sample numbered 2A earlier² and contains stable (dark) concentrations of both Cr^{3+} and Cr^{4+} near 10^{17} cm^{-3} . Spectra were obtained with the magnetic field applied throughout the (112) plane, all at 4.2 K.

As derived by Feher,⁷ the first-order magnetic field shift of the $M - 1 \rightarrow M$ EPR line due to applied stress in a cubic crystal is given by

$$\delta H(M - 1 \rightarrow M) = -(2M - 1) \left\{ \frac{3}{4} C_{11} \sum_i X_{ii} (3\alpha_i^2 - 1) + 3C_{44} \sum_{i < j} X_{ij} \alpha_i \alpha_j \right\}, \quad (1)$$

where the magnetic quantum number M can take on $2S + 1$ values, C_{11} and C_{44} are constants which describe the stress response of the center, and the α_i are the direction cosines of the magnetic field \vec{H} in the cubic coordinate system of the crystal. The stress components X_{ij} are related to the uniaxial stress P applied along the $(\beta_1, \beta_2, \beta_3)$ direction by $X_{ij} = P\beta_i\beta_j$. Thus, for the sample used here $X_{11} = X_{22} = X_{12} = P/6$, $X_{33} = 2P/3$, and $X_{13} = X_{23} = P/3$. If \vec{H} is restricted to the (112) plane and η is the angle between \vec{H} and [110], then Eq. (1) simplifies to

$$\delta H(M - 1 \rightarrow M) = -(2M - 1)P \left[-\frac{1}{2} C_{44} - \frac{1}{8} (3C_{11} - 2C_{44}) \cos^2 \eta \right]. \quad (2)$$

The distinction between the $S = 1$ and the $S = \frac{5}{2}$ cases noted earlier follows immediately from Eq. (2).

From the angular dependence of the splitting between the two lines under stress it is possible to determine both C_{11} and C_{44} using Eq. (2). Absolute signs are not known but relative to each other we obtain $C_{44} = 168$ and $C_{11} = -8$ with an error of ± 8 [in units of $10^{-13} \text{ cm}^{-1}/(\text{dyn}/\text{cm}^2)$]. These values give a

good fit to the angular variation of δH . To facilitate comparison with existing data on transition metal ions⁷⁻⁹ in MgO we convert to the corresponding strain coefficients⁷ G_{ii} with the result $G_{11} = -0.5 \text{ cm}^{-1}/\text{unit strain}$ and $G_{44} = 10.1 \text{ cm}^{-1}/\text{unit strain}$. These G_{ii} values fall in the range of values found for the various orbital-singlet ground-state ions studied in MgO (Cr^{3+} , Mn^{2+} , Fe^{3+} , and Ni^{2+}). It is of in-

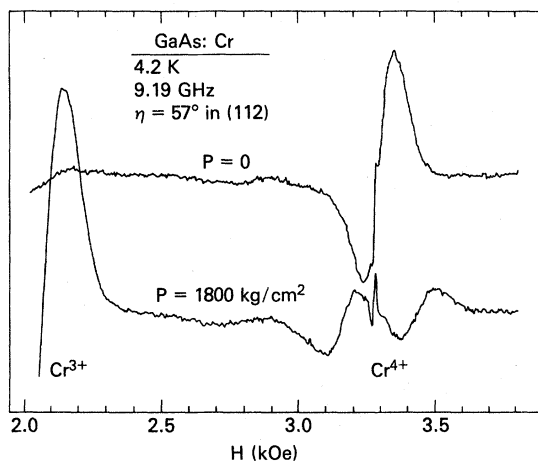


FIG. 1. Changes in Cr derivative EPR signals with [112] uniaxial stress. The field direction η is measured from $[1\bar{1}0]$. The very narrow line is unidentified. Background signals digitally subtracted.

terest that only Cr^{3+} with $G_{11} = 0.6$ and $G_{44} = 4.4$ (in the same units) has $|G_{44}| \gg |G_{11}|$.

A number of other observations concerning the stress data can be made. First, the center of the Cr_s^{4+} EPR spectrum (Fig. 1) is essentially unshifted by stress. Second, the splitting is linear in the applied

stress. Third, the shapes and the peak amplitudes of the separated lines are affected by stress. While the peak-to-peak linewidths remain almost constant, the individual line shapes seem to lose the Gaussian form of the zero-stress signal. This shape change may be due to a nonuniformity of the applied stress or, alternatively, to stress-induced changes in the ligand hyperfine interactions which are the source of the zero-stress linewidth. Finally, the sharp EPR line contained in both spectra of Fig. 1 occurs with essentially the free-electron g value. Its identity is unknown.

As noted earlier, the sample contains both Cr_s^{3+} and Cr_s^{4+} centers. We thus expect to observe the Cr^{3+} signals when stress is applied.¹⁰ The great improvement in the observability of this signal with stress is evident in the figure. Only one of the six possible Jahn-Teller distortions is energetically favored by the large [112] stress¹⁰ and we find that the field position of its EPR signal shows the expected angular dependence.

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