

Temperature-dependent paramagnetic susceptibilities of Cu^{2+} and Co^{2+} as dilute impurities in ZnO

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The temperature-dependent magnetic susceptibilities of $\text{Cu}^{2+}:\text{ZnO}$ have been measured and successfully analyzed on the basis of crystal field theory including the dynamic Jahn-Teller effect. The susceptibility behavior near 154 K suggests that there are small amounts of Cu in antiferromagnetic clusters in the crystal. The analysis determines electronic and vibronic constants of the perturbed Cu^{2+} ion. The simple crystal field model is not successful for the analysis of the temperature dependence of the susceptibilities of $\text{Co}^{2+}:\text{ZnO}$ at low temperatures. Agreement between calculated and observed susceptibilities is possible if it is assumed that there are a small number of Co ferromagnetic clusters in the crystal. Effective Curie temperatures for the clusters are determined from the analysis.

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In the 1960's, the authors and others in collaboration with Lin¹ measured and analyzed the temperature-dependent paramagnetic susceptibilities of several systems of dilute impurity ions from the first transition series in diamagnetic host crystals. The method proved powerful in determining electronic properties of the impurity ion in a crystal field environment. All of the analyses were considered successful except for two systems: Cu^{2+} (Ref. 2) and Co^{2+} (Ref. 3) in ZnO. In both cases anomalous features were found in the analyses. For Cu^{2+} the angular momentum coupling could not account for the temperature dependence of the susceptibilities even with unreasonably large orbital reduction. For Co^{2+} , the susceptibility analysis, based upon the usual crystal field model, gave a zero-field splitting for the ground 4A_2 state 27% smaller than that from electronic spin resonance (ESR)⁴ and optical measurements.⁵ Although there was confidence in the susceptibility measurements, the results were not published since the anomalies were not understood at the time.

Recently the physical basis for these two systems has been reinvestigated with the intent of providing an understanding of what is influencing the magnetic behavior of the respective systems. In the case of Cu^{2+} system, an ion of $3d^9$ configuration in a trigonal crystalline field, inclusion of the dynamic Jahn-Teller effect⁶ proved to be decisive. Further, the analysis was so good that an additional anomaly was detected near 154 K that suggests some of the Cu ions are in antiferromagnetic clusters, possibly in conjunction with oxygen ions. For the Co^{2+} system, a $3d^7$ electron configuration, the low-temperature data suggests that there are small amounts of Co clusters in a ferromagnetic state. In both cases the clustering effects more than likely had to do with the method for doping the ZnO and would not be detectable by either ESR or optical means.

The question as to the possibility of unwanted impurity ions contaminating the systems comes to mind. Chemical analyses were not made. However, unwanted impurity ions of the order of 1/100 of the doping concentration would have no observable effect on the susceptibilities. Further, it was

expected there would be unwanted contaminant impurities but in concentrations much less than 1/100. The ESR and optical studies of these crystals did not indicate the presence of unwanted impurities. In addition, incorporation of contributions to the susceptibility from likely contaminants for the Co^{2+} system in no way helped the analysis. At the same time, it should be noted that for all of the other systems studied by these techniques, unwanted impurities were never detected. It is unlikely that all of the Cu^{2+} or Co^{2+} would enter the crystal substitutionally; some of it could very well cluster or enter interstitially. In one case the system was found to have pairs and triplets of the paramagnetic ion when concentrations were high, but in small quantities. There is no evidence that interstitials play an important role in the previous studies of the iron transition elements in ZnO as the angular momentum would be quenched and would only result in a Curie type behavior.

This paper is a summary of the authors' results. A detailed discussion of the calculation and analyses, including raw data, matrix elements, and susceptibility equations, is available in manuscript form upon request.

$\text{Cu}^{2+}:\text{ZnO}$

The host ZnO crystal has wurtzite structure that gives the property that the Cu^{2+} substitutional impurity ion is in a crystalline electrostatic field of predominantly tetrahedral symmetry. However, the crystal field has a small trigonal component along the hexagonal c axis due to a small distortion of the ideal hexagonal unit cell. In addition to the electrostatic effects from the crystal field, there is some covalent bonding that leads to orbital reduction of the spin-orbit interaction from the free ion values. These latter properties have been found for all $3d$ -impurity ions in host crystals to varying degrees. As to the question of a possible phase change in ZnO over the range of 4.2 K to 300 K, there is no evidence indicating such a change in any of the X:ZnO crystals studied so far. A paper by Reeber¹² concerning the lattice parameters of ZnO shows no phase change over the temperature range considered.

The temperature dependent paramagnetic susceptibilities χ_{\parallel} and χ_{\perp} for $\text{Cu}^{2+}:\text{ZnO}$ have been measured from 31 to 297

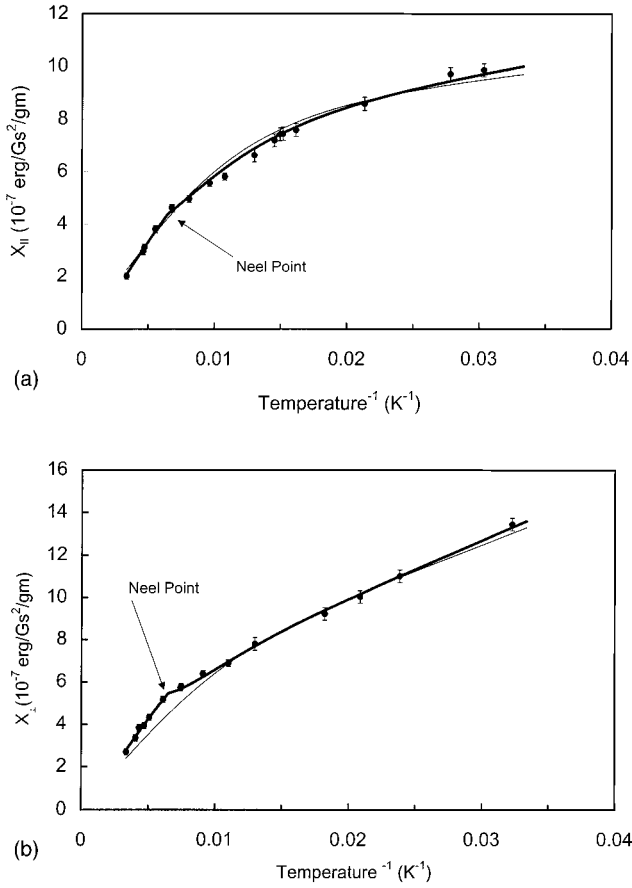


FIG. 1. Components of the magnetic susceptibility for $\text{Cu}^{2+}:\text{ZnO}$. Dots represent the data points, see the text for the physical significance of the curves. The error bars for data between room temperature and nitrogen temperature is the size of the plotted points. Below the nitrogen point the errors are three times the size of the plotted points. (a) X_{\parallel} and (b) X_{\perp} .

K using a Faraday-type balance.¹ This paramagnetism is due to the Cu^{2+} ion that has a 1.1% concentration in the ZnO host crystal. The cubic crystalline field splits the 2D orbital state into $^2T_2 + ^2E$ with further splitting due to the trigonal field and spin-orbit coupling. The energy levels in increasing order are $\Gamma_6(^2T_2)$, $\Gamma'_6(^2T_2)$, $\Gamma_{4,5}(^2T_2)$, $\Gamma_{4,5}(^2E)$, and $\Gamma_6(^2E)$. Energy differences measured by Dietz *et al.*⁷ are $\Gamma_{4,5}(^2E) - \Gamma_6(^2T_2) = 5784 \text{ cm}^{-1}$, $\Gamma_6(^2E) - \Gamma_6(^2T_2) = 5823 \text{ cm}^{-1}$, $\Gamma_6(^2E) - \Gamma'_6(^2T_2) = 5707 \text{ cm}^{-1}$, and $\Gamma'_6(^2T_2) - \Gamma_6(^2T_2) = 123 \text{ cm}^{-1}$. ESR measurements by Dietz *et al.* and more accurately by De Wit *et al.*⁸ give $g_{\parallel} = 0.7383$ and $g_{\perp} = 1.5237$ for $\Gamma_6(^2T_2)$. Optical Zeeman measurements by Dietz *et al.* give $g_{\parallel} = 1.63$ and $g_{\perp} = 0$ for $\Gamma_{4,5}(^2E)$. An orbital reduction model, with the extreme 60% for the 2T_2 manifold, by Dietz *et al.* is necessary to explain the above empirical constants but is completely unsuccessful in the analysis of the temperature dependence of the paramagnetic susceptibilities.² Only the 2T_2 manifold affects the susceptibilities.

Inclusion of the dynamic Jahn-Teller effect⁶ accounts for the magnetic susceptibilities and the empirical constants of Dietz *et al.* without the excessive orbital reduction. Our

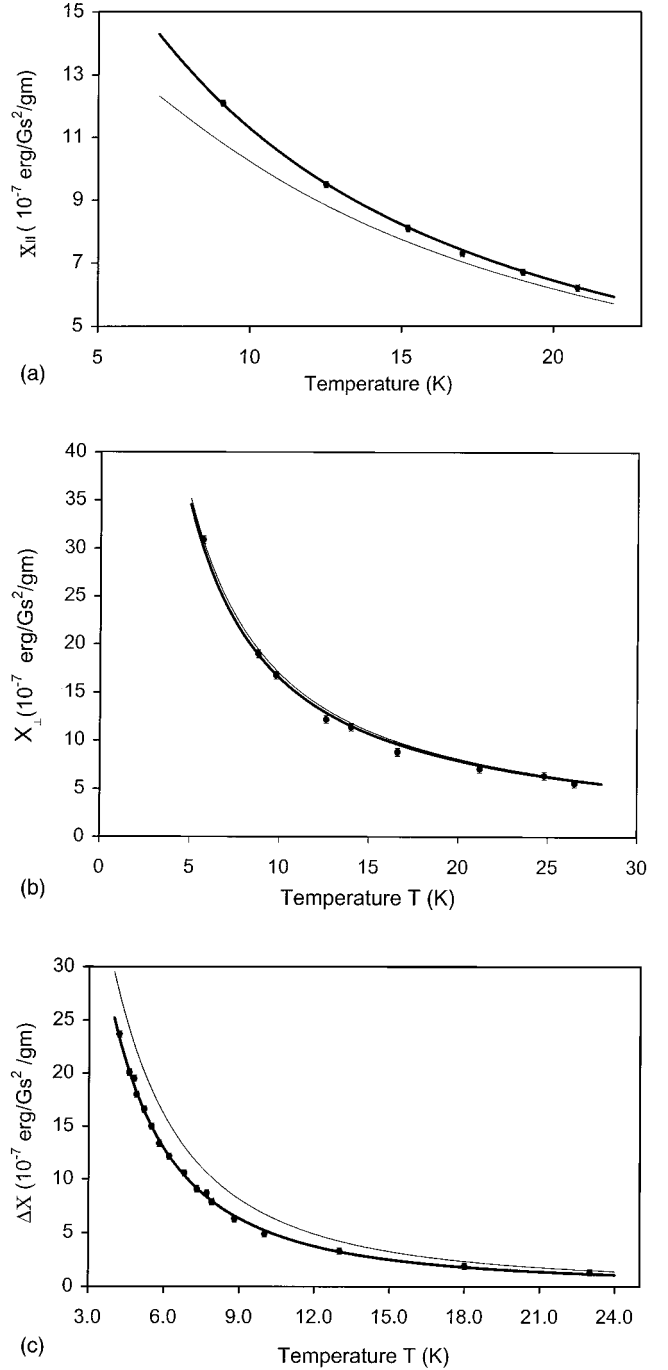


FIG. 2. Components of the magnetic and anisotropic susceptibilities for $\text{Co}^{2+}:\text{ZnO}$. Dots represent the data points, see the text for the physical significance of the curves. The error bars for the experimental data is the size of the plotted points. (a) X_{\parallel} , (b) X_{\perp} , and (c) $\Delta X = X_{\perp} - X_{\parallel}$.

model parallels that developed by Macfarlane⁹ to explain the optical and magnetic properties of $\text{Ti}^{3+}:\text{Al}_2\text{O}_3$, a $3d^1$ system related to the $\text{Cu}^{2+} 3d^9$ system. Our approach uses the theory of Ham⁶ that takes into account second-order perturbations from the lattice vibrations. Our extension of the model to include third-order contributions had little effect on the angular momentum coupling nor on the energy levels.

In the analysis, the $^2E - ^2T_2$ interaction parameters deter-

mined by Dietz *et al.* (these do not show the large orbital reduction) were used: spin orbit, $\zeta' = 720 \text{ cm}^{-1}$; trigonal coefficient, $K' = -77 \text{ cm}^{-1}$; and orbital reduction, $k' = 0.87$. The parameters from the Jahn-Teller calculation for the 2T_2 manifold are; the Jahn-Teller parameter, $x = 2.975$; the second trigonal field parameter, $K = -71 \text{ cm}^{-1}$; and the phonon energy, $\hbar\omega = 1059 \text{ cm}^{-1}$. These then give the calculated values: $\Gamma_{4,5}({}^2T_2) - \Gamma_6({}^2T_2) = 176 \text{ cm}^{-1}$, $g_{\parallel}(\Gamma'_6) = 0.1368$, $g_{\perp}(\Gamma'_6) = 1.526$, $g_{\parallel}(\Gamma_{4,5}) = 2.229$, and $g_{\perp}(\Gamma_{4,5}) = 0.278$. The orbital reduction factor was taken to be $k = 0.87$, the same as k' . There are in addition off-diagonal matrix elements in the magnetic field that determine the Van Vleck susceptibility.

The agreement between calculated and observed susceptibilities was extremely good for both χ_{\parallel} and χ_{\perp} except near $T = 154 \text{ K}$. The residual $\chi(\text{obs}) - \chi(\text{cal})$ were analyzed by a very simple antiferromagnetism model with excellent results. The makeup of the clusters in $\text{Cu}^{2+}:\text{ZnO}$ remains subject to speculation. The Neel temperature T_N of monoclinic CuO is 230 K , which is 50% higher than our value 154 K for Cu^{2+} clusters in tetrahedral ZnO . It could be that the difference in the Neel temperatures is due to the different crystalline structure for the two systems.

The agreement between observed and calculated susceptibilities, including all terms, is illustrated in Fig. 1. The light curve shows the calculated results neglecting the antiferromagnetic terms from the presumed clusters. The error bars for data between room temperature and nitrogen temperature are the size of the plotted points except for points near 90 K where it was difficult to maintain the temperature long enough to insure that the sample temperature was the same as the housing tube. Below the nitrogen point the errors are larger and are three times the size of the plotted points.

More recently Volz *et al.*¹⁰ studied the nearly cubic crystal $\text{Cu}^{2+}:\text{ZnTe}$ using infrared techniques to observe the phonon spectrum. These authors measured the spin-orbit splitting in the 2T_2 ground state, $E_{so} = 68 \text{ cm}^{-1}$, and found it to be much reduced from that expected for a free Cu^{2+} ion value, 1244 cm^{-1} . They attribute this reduction to a dynamic Jahn-Teller coupling in the 2T_2 ground state. On the other hand $\text{Cu}^{2+}:\text{ZnO}$ has a large trigonal field associated with it and that complicates the calculation. In addition there are large terms connecting the ground state with the excited states.

$\text{Co}^{2+}:\text{ZnO}$

The temperature dependence of the magnetic susceptibilities χ_{\parallel} and χ_{\perp} of $\text{Co}^{2+}:\text{ZnO}$ were measured from 5.7 to 295 K with a Faraday Balance¹ and the anisotropy $\Delta\chi = \chi_{\perp} - \chi_{\parallel}$ from 4.2 to 23 K with a Torsion Balance.¹ The Co^{2+} ion, concentration 0.049% , has electron configuration $3d^7$ with

4F being the ground state. The predominant tetrahedral crystalline field splits 4F into ${}^4A_2 + {}^4T_2 + {}^4T_1$ and 4P into 4T_1 . The smaller trigonal distortion and spin-orbit interaction split the ground 4A_2 state into $E_{1/2} + E_{3/2}$.

Optical measurements by Weakliem⁵ give the cubic field parameter $10Dq = 3900 \text{ cm}^{-1}$. ESR measurements by Estle *et al.*⁴ on the $E_{1/2}$ ground state give $g_{\parallel} = 2.2404$ and $g_{\perp} = 2.2790$ along with the zero-field splitting $E_{3/2} - E_{1/2} = 2D = 5.5 \text{ cm}^{-1}$. Subsequent measurements of the optical Zeeman effect by Weakliem⁵ gave a slightly larger value for $2D$ and g values consistent with the ESR results. Anderson¹¹ revisited the optical spectra of $\text{Co}^{2+}:\text{ZnO}$ with results suggesting $2D$ slightly larger than 5.5 cm^{-1} and the existence of a small number of Co^{2+} pairs in the samples with concentrated doping.

Analysis of the magnetic susceptibility data on the model used by Estle *et al.* resulted in an excellent fit with $2D = 4.0 \text{ cm}^{-1}$, 27% smaller than the ESR value. The consistency of $2D = 5.5 \text{ cm}^{-1}$ from the ESR and optical measurements indicates that the susceptibility measurements are "seeing" something to which the ESR and the optical measurements are not sensitive. Analyses including possible ferro- and antiferromagnetic pairs were unsuccessful. However, ferromagnetic pairs gave a trend of improvement in the data analysis while antiferromagnetic pairs made things worse. Estle and De Wit⁴ did detect very low concentrations of Co^{2+} pair coupling in the crystal which they attributed to ferromagnetic or weakly antiferromagnetic interaction in the crystal. Further, inclusion of a small fraction of ferromagnetic clusters gives an excellent fit to the data when $2D = 5.5 \text{ cm}^{-1}$ along with $T_{\parallel}^c = 2.0 \text{ K}$ and $T_{\perp}^c = 2.8 \text{ K}$, the effective Curie temperatures.

The fit of the analyses to the data is illustrated in Fig. 2. The curve through the data points is essentially the same for $2D = 4.0 \text{ cm}^{-1}$ without cluster effects and $2D = 5.5 \text{ cm}^{-1}$, including the cluster effects. The light curve is for $2D = 5.5 \text{ cm}^{-1}$ without the cluster effects. The error bars for the experimental data are the size of the plotted points.

From the results of the theoretical analysis with the empirical values of $2D$, g_{\parallel} , and g_{\perp} , the reduced spin-orbit coupling constant is determined to be $\lambda = -140 \text{ cm}^{-1}$, a slight reduction from the free-ion value of -176 cm^{-1} . However, the modeling could not determine consistent values for the trigonal coefficients B_2^0 and B_4^0 .

The $\text{Cu}^{2+}:\text{ZnO}$ crystals were supplied by Dr. Thomas Estle and the $\text{Co}^{2+}:\text{ZnO}$ crystals were supplied by Estle and Dr. Herbert Weakliem. It should be noted that the measurements were made in the lab of Professor Chun C. Lin while he was at the University of Oklahoma.

¹W. H. Brumage, C. R. Quade, and C. C. Lin, Phys. Rev. **131**, 949 (1963); W. Brumage, C. C. Lin, Phys. Rev. A **134**, A950 (1964); J. P. Mahoney, C. C. Lin, W. H. Brumage, and F. Dorman, J. Chem. Phys. **53**, 4286 (1970).

²C. F. Dorman, Ph.D. Thesis, University of Oklahoma, 1967.

³W. H. Brumage, Ph.D. Thesis, University of Oklahoma, 1964.

⁴T. Estle and M. De Wit, Bull. Am. Phys. Soc. **6**, 445 (1961).

⁵(a) H. Weakliem, *Zeeman Centennial Conference*, (Netherlands

- Phys. Soc., Amsterdam, 1965); H. A. Weakliem, *J. Chem. Phys.* **36**, 2117 (1962).
- ⁶F. S. Ham, *Phys. Rev.* **138**, A1727 (1965).
- ⁷R. E. Dietz, H. Kamimura, M. D. Sturge, and A. Yariv, *Phys. Rev.* **132**, 1559 (1963).
- ⁸M. De Wit and T. L. Estle, *Bull. Am. Phys. Soc.* **8**, 24 (1963).
- ⁹R. M. Macfarlane, J. Y. Wong, and M. D. Sturge, *Phys. Rev.* **166**, 250 (1968).
- ¹⁰M. P. Volz, C. H. Su, S. L. Lehoczky, and F. R. Szofran, *Phys. Rev. B* **46**, 76 (1992).
- ¹¹R. Anderson, *Phys. Rev.* **164**, 398 (1962).
- ¹²R. R. Reeber, *J. Appl. Phys.* **41**, 5063 (1970).