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# Zeeman Splitting of Anomalous Shallow Bound States in ZnO

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Apparent 1*s*-to-2*p* transitions, observed with far-infrared spectrometers at 5.9 and 7.2 meV, exhibit linear Zeeman splitting but are not otherwise consistent with the effective-mass hydrogenic model because the activation energy is an order of magnitude too small and the quadratic Zeeman shift is absent. Cyclotron resonance was observed at 5 K but not at 1.3 K, which confirms the existence of shallow bound states.

We have observed evidence of shallow bound states in ZnO at 1.3 K, which cannot be described theoretically by a simple hydrogenic model of a substitutional donor. This appears to be the first observation of optical absorption by a state of this type. Two absorption lines which appear to behave like 1*s*-to-2*p* transitions of bound states have been observed at frequencies of 48 and 58 $\text{cm}^{-1}$ which represent transition energies of 5.9 and 7.2 meV, respectively. The hydrogen model for ZnO predicts an activation energy of about 60 meV, however, for a substitutional donor, and this has been confirmed for the conventional donor in our ZnO specimens by measuring an activition energy of 54 meV from the low-temperature dependence of the Hall constant.[1] Therefore, the transitions reported here appear not to be a part of the spectrum associated with the conventional deep donor because they are an order of magnitude too small in energy. They cannot be higher excited states of a deep donor because the temperature of 1.3 K is too low to populate higher states. Both the 5.9- and 7.2-meV transitions exhibit linear Zeeman splitting as shown in Fig. 1. Both transitions display identical Zeeman splitting. If we assume that the Zeeman splitting is that characteristic of a *p* state, we can calculate an effective mass using the relation $e\mu_0 H/m^*c = \Delta\mathcal{E}_z$, where $H$ is the magnetic field intensity, $m^*$ is the effective mass, and $\Delta\mathcal{E}_z$ is the energy separation of the upper and lower Zeeman lines. We find that $m^* = 0.3m_0$ for $H \parallel c$ and $0.34m_0$ for $H \perp c$. These values are comparable to cyclotron-resonance effective masses but there are discrepancies. We discuss these in a subsequent paragraph. The absence of an observable

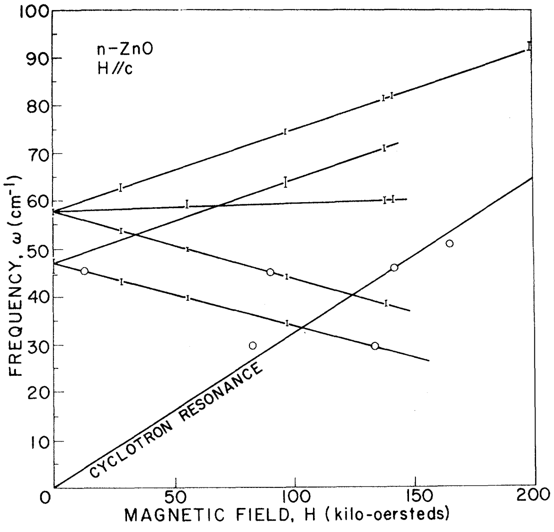

FIG. 1. Positions of absorption lines observed at far-infrared frequencies at 5 K with a laser spectrometer (circles) and at 1.3 K with a Fourier-transform spectrometer (bars). Linear Zeeman splitting of bound states is observed, but quadratic Zeeman splitting is absent.

quadratic Zeeman shift in Fig. 1, even at magnetic field intensities as high as 200 kOe, is not consistent with the predictions of the effective-mass hydrogenic model. The quadratic Zeeman shift expected would be

$$\Delta\mathcal{E} \approx \kappa^2(\hbar\omega_c)^2 m^* c^2 e^2/\hbar c \approx 0.9 \text{ meV}$$

at 200 kOe for an activation energy of 60 meV. This should be easily observable on the scale of Fig. 1. Its absence is even more puzzling if we assume that the binding energy of the shallow bound state is of the order of the observed transition energies, i.e., about 10 meV. In the expression above, $\kappa = 8$ is the dielectric constant, $\omega_c$ is the cyclotron frequency for a magnetic field of 200 kOe, and the other symbols have their usual significance.

Figure 2 shows the transmission of monochromatic laser radiation through a typical doped ZnO specimen at a wavelength of 220 $\mu$m. At high fields the transmission decreases as a result of the onset of electron cyclotron resonance. The two minima observed at a temperature of 6 K near 20 and 90 kOe are associated with the Zeeman-split bound state. These points appear on Fig. 1 as circles at a frequency of 45.5 $\text{cm}^{-1}$. As the temperature is increased, the two Zeeman lines become weaker and the cyclotron-resonance absorption becomes stronger as indicated in Fig. 2. A very crude estimate of a few meV for the activation energy of the shallow bound state was made from the temperature dependence of the intensity of these lines. This can be taken as another piece of evidence for the existence of very shallow bound states.

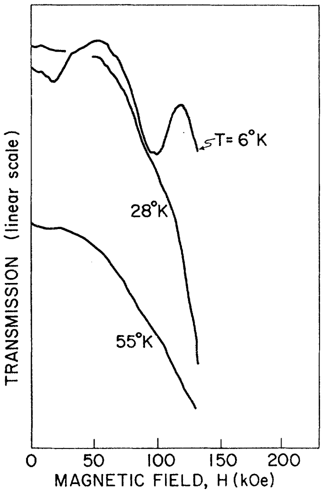

FIG. 2. Transmission of 220-$\mu$m radiation through $n$-ZnO as a function of magnetic field intensity with $H \parallel c$. The two absorptions lines representing bound-state transitions at 6 K disappear at higher temperature as the shallow bound state becomes thermally ionized.

Our spectroscopic measurements were restricted to the frequency range 20 to 120 $\text{cm}^{-1}$ which corresponds to an energy of 2.5 to 15 meV. We have observed no transitions in this range other than those reported here. Spectroscopic data are not available in the 54-meV range where transitions belonging to the conventional hydrogen-like donor may appear.

Measurements were made on two specimens of ZnO grown in Erlangen by the vapor-phase reaction method.[2] The data shown here were taken from a specimen doped with $10^{17}$ donors. This specimen was 9 mm long in the $c$ direction and 7 mm thick perpendicular to the $c$ direction. The second crystal had 7- and 4-mm dimensions, respectively, and provided essentially the same spectroscopic results. Both specimens were clear, untinged with color, free of flaws, and had perfect hexagonal facets. The transmission measurements that provided the points shown as circles in Fig. 1 were taken at a specimen temperature of about 6 K and the cw radiation was provided by HCN, DCN, and $H_2O$ lasers as described previously.[3] The points shown as vertical bars in Fig. 1 were taken at 1.3 K by using a Michelsen-type Fourier-transform spectrometer. The cyclotron-resonance absorption was not seen at 1.3 K because the free electrons were frozen out to the shallow bound states in the temperature range between 1.3 and 5 K. As mentioned above, the activation energy of the shallow bound states, which when partially ionized provide the free electrons for cyclotron resonance, is of the order of magnitude of a few meV, not 54 meV.

The Faraday-rotation measurements of Baer[4] at visible optical wavelengths yield a calculated value of $0.24m_0$ for the effective mass of the electron. He calculated the polaron mass of $0.29m_0$ which agrees favorably with the value of $0.3m_0$ that we have calculated from the linear Zeeman splitting. The effective mass has been determined from the plasma frequency and the absorption of free carriers. The values were $0.265m_0$[5] and $0.27m_0$.[6] Our submillimeter cyclotron-resonance measurements at 30, 45.5, and 51.2 $\text{cm}^{-1}$ using HCN, $H_2O$, and DCN lasers yield a mass of about $0.28m_0$ for $H \parallel c$. These three points, shown in Fig. 1, do not scale properly with frequency. However, additional points will be required before the scaling rule can be seriously challenged. Lower-frequency lasers are being developed for this purpose. The Fourier-transform spectrometer will also be modified as to place the low-temperature detector and the sample in separate cryostats. The temperature of the specimen can then be raised to excite free electrons for cyclotron resonance.

The cyclotron-resonance mass has also been found to change as the temperature is increased to 55 K. This will be investigated by repeating the measurements on specimens of different carrier concentration and different size.

Finally, a cyclotron-resonance mass of $0.24m_0$ for $H \perp c$ has been measured. This cyclotron-resonance anisotropy is inverse to the anisotropy measured from the Zeeman splitting where 0.34 $m_0$ was obtained for $H \perp c$. It will be necessary to develop a theoretical model for the shallow bound states before the splitting can be interpreted quantitatively.

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# Electronic Structure and Kinetics of the Oxidation of Ba and Sr†

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Photoemission spectra are used to identify unusually narrow chemisorbed levels of $O^{2-}$ on Ba and Sr at 4.6 and 4.8 eV below the Fermi level $E_F$, respectively. Nitrogen on Ba forms narrow states 1.3 and 5.3 eV below $E_F$. Measurements of sticking probability and of electron emission in the dark show that the oxygen-metal chemical activity is initially small, increases to a maximum, and then abruptly decreases as the mass of oxide increases.

Detailed knowledge of the interaction of a gas and a solid surface is important to both science and technology. Reported in this communication are the first direct and detailed observations of a gas-solid interaction with ultraviolet photoemission spectroscopy (UPS) combined with measurements for the mass of sorbed gas and "chememission" (electron emission in the dark during gas exposure). In addition to obtaining the electronic structure at various states of reaction, we obtained information about the reaction kinetics. The systems observed were Ba and Sr exposed to $O_2$ as well as the exposure of Ba to $N_2$ and $H_2$. The oxide systems were studied from submonolayer oxide coverages to oxides thick enough to obtain bulk-oxide UPS data. The chemisorbed oxygen and nitrogen from very narrow atomiclike states on Ba and Sr, in contrast to the broad states formed by oxygen on Ni, Ti, Tl, and Pb.[1,2] It is also found that the chemisorbed oxygen on Ba and Sr enhances the photoemission from the metal. The observations indicate that the thin oxide forms a crevicelike structure rather than a uniform film.

An *in situ* two-step evaporation technique was used for sample preparation making possible maximum pressures *during* sample deposition of $(2-8)\times 10^{-10}$ Torr. The second step used a Mo ribbon evaporator which was well "outgassed" prior to receiving a charge from the primary