Letters to the Editor

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X-Ray Spectroscopy of the Solid State*

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MOST work in x-ray spectroscopy of the solid state has been concerned with interpretations of observed spectra in terms of crystal lattice energy bands. These interpretations have in a few outstanding instances been remarkably fruitful, but many have been fraught with frustration. It is suggested that a significant reason for our difficulties is that we have lost sight of an important group of energy levels in the solid.

X-ray spectroscopists are well aware that x-ray energy levels arise in an atom when there exists an inner electronic vacancy, and that these levels are essentially atomic in character even for a solid. On the other hand, solid-state experts are well aware that, when atoms (or ions) come together to form a stable solid, the mutual interactions with neighboring atoms greatly modify the normal atomic levels into a system of energy bands characterized essentially by the solid state. By virtue of the inner vacancy, atomic levels are set up below the occupied and unoccupied mother bands of the solid just as they are set up below the normally occupied inner levels a little deeper in the atom. The atomic levels below the occupied bands are themselves occupied, and radiative transitions can and do occur from them.

Each of the outer atomic levels is split into several discrete levels by the interactions between the vacancy and a few near neighboring atoms. This makes otherwise singlet x-ray emission lines appear as a series of lines. The actual separations and relative intensities of the components in the series are difficult to calculate from theory, but the separations are expected to decrease from perhaps a few electron volts for the strongest lines to zero for the weakest lines at the series limit. This limit may itself be contained within the broad mother band.[1]

Whether or not the radiative transitions from the occupied atomic levels will be observed depends upon the resolving power used (both instrumental and the width of the inner vacancy state) and upon the relative transition probability. In some preliminary work which we are doing in the $K\beta$ region of potassium and of chlorine in KCl, the radiative transition from the lowest atomic level (first in the series) below the occupied $3p$ band is about five times as intense as the transition from the $3p$ band itself, and is markedly less for each succeeding line in the series. In these two cases, the lowest atomic level is about 2.75 ev below the bottom of the $3p$ mother band for potassium and about 3.8 ev for the chlorine case. Emission lines from such atomic levels are very narrow and are not expected to have a shape or width comparable with the shape or width of the mother band.

Studies of the energy positions, shapes, and widths of the band emissions are under way. It appears tentatively that the $3p$ band for potassium, at least, has an intensity maximum near the low energy side, indicating perhaps that the transition probability from the band is not uniform but favors electrons from the low energy region, as though here too the $1s$ vacancy has added an atomic flavor to the band in addition to extracting from it the discrete atomic levels.

The atomic levels below the unoccupied ionization continuum in insulating solids have already been recognized and used in ultraviolet absorption,[2] where the mobile exciton is produced, and also in x-ray absorption.[3] In practically all work showing these unoccupied atomic levels, the effective resolving power has been inadequate to reveal more than the lowest level of the series. However, attention is called to K-edge absorption measurements[4] on potassium and chlorine in KCl, in which it is likely that at least two of these levels appear. Here, one observes an interesting reversal of transition probability to the two lowest atomic levels for potassium as compared with chlorine. The electrostatic field in which the electron finds itself bound in the lowest level in this ionic crystal depends sensitively upon the type of near neighbors. The observed intensity relation indicates that, for potassium, the electron in the lowest bound level must be pushed by the nearest Cl^- neighbors to a position farther removed from the vacancy site than is the case for chlorine.

It is suggested that our case of KCl is not unusual and that many observations in x-ray spectroscopy of solids (both emission and absorption) may be similarly interpreted in terms of discrete atomic levels with consequent improvement in fit with expected energy position and line width, and with better understanding of the forces in the solid state.

* Supported in part by the ONR.
[1] For the unoccupied levels below the ionization continuum band, the series limit must be at the bottom of the band, as shown by G. H. Wannier, Phys. Rev. **52**, 191 (1937).
[2] E.g., see F. Seitz, *The Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940).
[3] Y. Cauchois and N. F. Mott, Phil. Mag. **40**, 1260 (1949).
[4] J. W. Trischka, Phys. Rev. **67**, 318 (1945).

Nuclear Matrix Elements of β-Decay

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THE nuclear matrix elements have been evaluated using a single-particle model, in the Dirac representation, for first-forbidden and l-forbidden ($\Delta J=1$, $\Delta l=2$) β-transitions in all forms of interaction.[1] Using term assignments from the Mayer nuclear shell scheme,[2] values of $\log(|M|^2ft)$ have been calculated (the expression $|M|^2$ is the sum of the squares of the matrix elements appearing in a given interaction, each multiplied by its appropriate spectral correction factor). The study included all nuclei for which there is sufficient information up to neutron number 100, both for odd-A and for those even-A for which Nordheim's empirical rule[3] predicts coupling of the odd nucleons to minimum spin. A full listing of the matrix elements, together with subsidiary calculations and a tabulation of $\log(|M|^2ft)$ values, will be published, but some of the more salient results are enumerated here:

1. The Dirac representation is necessary for the evaluation of the following matrix elements: (a) those involving operators containing $\boldsymbol{\alpha}$ or γ_5 (for instance, among these, the usual neglect of a factor β can introduce very large errors), (b) those involving the small components of the Dirac wave functions (see 3).

2. In agreement with the experimental ft values, the matrix elements, contrary to previous qualitative estimates, do not fall into sharply distinct orders of magnitude. Thus, roughly:

$$|M|^2\approx 1 \text{ for } 1,\ \beta,\ \boldsymbol{\sigma},\ \beta\boldsymbol{\sigma}(\Delta l=0);$$
$$|M|^2\approx 10^{-2} \text{ for } \boldsymbol{\alpha},\ \beta\boldsymbol{\alpha},\ \gamma_5;$$
$$|M|^2\approx 10^{-3} \text{ for } \beta\gamma_5,\ \mathbf{r},\ \beta\mathbf{r},\ \boldsymbol{\sigma}\cdot\mathbf{r},\ \beta\boldsymbol{\sigma}\cdot\mathbf{r},\ \boldsymbol{\sigma}\times\mathbf{r},\ \beta\boldsymbol{\sigma}\times\mathbf{r};$$
$$|M|^2\approx 10^{-4} \text{ for } B_{ij}\text{'s } (\Delta l=1),\ \boldsymbol{\sigma} \text{ and } \beta\boldsymbol{\sigma}(\Delta l=2);$$

for high l, the matrix element of $\boldsymbol{\alpha}$ decreases into the third category.

3. The matrix elements for the l-forbidden transitions are chiefly the result not of the second-forbidden operators ($\boldsymbol{\alpha}\times\mathbf{r}$, etc.) but of the small-component contribution of $\boldsymbol{\sigma}$ or $\beta\boldsymbol{\sigma}$; this is