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LETTER TO THE EDITOR

Mott g-ratios in $\text{Rb}_x(\text{NH}_3)_{1-x}$ and oxidation state of rubidium compounds from XAS

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Abstract. The x-ray absorption spectra (XAS) of Rb metal, $\text{Rb}_x(\text{NH}_3)_{1-x}$, 2H-$\text{NbSe}_2$ and $\text{RbBr}$ near the Rb K-edge have been used to ascertain that the oxidation state $V$ of rubidium dissolved in ammonia and intercalated in the layer compound is in the range $0 < V < 1$. The observed edge shifts with temperature for semimetals are explained in terms of the population of band states, and the ratio of the density states near the mobility edge over that calculated for a free electron model, i.e. the Mott ratio $g$, is ascertained using a semiempirical relation developed for the x-ray absorbance from $1s$ levels to empty states near the mobility edge.

XAS is traditionally divided into an XAES region where the ejected electron transitions to bound states are observed (the so-called absorption edge) and an EXAFS region ($10^2$ to $10^3$ eV above the latter, the so-called extended x-ray absorption fine structure region) where transitions to free electron states are observed (Kronig 1932, Hartree et al 1934, Stern et al 1975). The XAES region contains information on the oxidation state of the absorber and recent semiempirical relations have shown that the edge position increases linearly with say the valence of Mn, Fe, Mo, Rb and Sr (Cramer et al 1976, J A Kirby unpublished, Acrivos et al 1980). Also transitions to bound states of the absorber can be resolved, e.g.

$$(Z^2) \ (1s)^2 \ldots \ 2^{S^* + 1}L_j \rightarrow (Z^0) \ (1s) \ldots \ nl: 2^{S + 1}(L \pm 1)_{j+1}$$

(1)

where $\ldots$ represents other core electrons not directly involved in the transition and the $nl$ states are members of a Rydberg series for a given angular momentum $j$ including the exciton states. Parratt and others (Parratt 1939, 1959, Cauchois and Mott 1949) have related the spacings between the series of transitions (1) with those reported in the literature for the element with atomic number $Z + 1$ and a closed K shell, i.e.

$$(Z + 1)^2) \ (1s)^2 \ldots \ n't: 2^{S + 1}L_j \rightarrow ((Z + 1)^0) \ (1s)^2 \ldots \ nl: 2^{S + 1}L_j$$

(2)

where $S' = S \pm \frac{1}{2}$ and this valuable approximation is correct if exchange interactions between the $K$ electrons and the other core electrons are negligible. In this work we make use of the XAES data including the edge position and the transitions (1) in order to ascertain the valence of rubidium in the metal–ammonia solutions (MAS) and in intercalated compounds for the purpose of determining the metallic nature of the system.
The XAES data for Rb metal, RbBr, RbN₃, and Rb MAS and for 2H-NbSe₂/Rb₀.₂₈ were reported previously (Acrivos et al 1980, Bourdillon et al 1979). Here figure 1 shows that the edge inflection point $E_1$ moves to higher energy by 4.5 eV as the valence increases from 0 in Rb metal to +1 in RbBr and RbN₃, displaying an intermediate value for Rb MAS. The edge positions for the intercalated compounds were not determined with the same standards (Bourdillon et al 1979); however, the most useful observations are related to transitions (1), i.e.

$$(\text{Rb}^{+1}) (1s)^2 \ldots ^3S_0 \rightarrow (\text{Rb}^{+1}) (1s) \ldots np: ^1P_1$$

where $n \geq 5$. The spacing in the Rydberg series $n = 5, 6, 7, 8$ can be estimated from transitions (2) in the literature (Moore 1952) for Sr⁺⁺⁺⁺, i.e.

$$(\text{Sr}^{+3}) (1s)^2 \ldots 5s: ^3S_{1/2} \rightarrow (\text{Sr}^{+3}) (1s)^2 \ldots np: ^3P_{1/2, 3/2}$$

which are indicated by arrows in figure 1 for RbN₃.

Now the changes in absorbance against $T$ for MAS have to be explained. A semiempirical analysis shows how the variation in the density of states may be extracted from the temperature dependence of the absorbance as follows. In non-metals (NM) the transitions to a continuum of free states from a 1s level give rise to an infinite sum of Lorentzian curves (Richtmyer et al 1958). The absorbance $A$ is the sum of an infinite series of Lorentzians, depending on the temperature $T$ as follows.

$$A = \sum_{n=1}^{\infty} \frac{1}{\pi} \frac{\alpha_n}{\beta_n} \frac{1}{(\frac{\beta_n}{\Delta E})^2 + (\frac{T}{\Delta E})^2}$$

shown in figure 1 as a function of the temperature $T$. $\alpha_n$, which decreases as a function of $n$, and $\beta_n$, which decreases as a function of $n$, are determined from the transition (1) series plus (3).

In alkali metal compounds the conduction band states and these are occupied up to the Fermi energy in the vicinity of the Fermi level $E_F$.

Figure 1. XAES for different Rb compounds. $A_{i\rho}$ evaluated using equation (4) with $E_F = 1.79$ eV is indicated by dots.
Lorentzian curves which start at the edge $E_0 = h
u_0$ in figure 2, i.e. the absorbance is (Richtmyer et al 1934)

$$A_{nm}(v) = D_s(v/2 + \theta_{nm})$$  \hspace{1cm} (3)

shown in figure 3. Here $-\pi/2 \leq \theta_{nm} = \tan^{-1}[2\pi T_s(v - \nu_0)] \approx \pi/2$ and $D_{s,v} = D_s$ is a function of the transition probability and the joint density of states and $T_s$ is a lifetime depending on the initial and final state widths. Then the XAES for Rb in figure 1 are explained as a series of Rydberg transitions (1) (each described by a single Lorentzian which decreases in intensity by a factor greater than two from the previous one in the series) plus (3).

In alkali metals (or alkaline earth metals) the conduction electrons occupy band states and these affect both transitions (1) and (2) as follows. The band states are occupied up to the Fermi level $E_F = k_F^2/2m = \hbar^2 (v_F - v_i^0)$ where $v_i^0$ is the bottom of the conduction band and $v_F$ is the Fermi level in figure 2(a). However, $v_F$ may be in the vicinity of the final states in transition (1). In this case mixing of localised and extended
states can and does occur (Fano 1961), leading to occupancy of the final states in transition (1) and to the absence of exciton states. The overall absorbance is then written:

$$A(v) = A_1(v) + A_{nm}(v)$$

(4)

where $A_{nm}$ is given by equation (3), and in order to ascertain which of the different models shown in figure 2 describes the MAS correctly we write the absorbance below the edge separately:

$$A_1 = D_v \int_{v_0}^{v_1} \frac{2\pi T_v d\nu' (1-f)}{1 + 4\pi^2 (\nu' - \nu) T_v^3} N(\nu')/N(\nu_0).$$

$f$ is the Fermi distribution function for the occupation of a level in figure 2, and the density of states $N(\nu')$ has been normalised to the value at $\nu_0$ for the metal and $D_v$, has been replaced by $D_\nu$. For a spherical Fermi surface the density of states near the bottom of the conduction band varies as the square root of the kinetic energy, i.e.

$$N(\nu')/N(\nu_0) = [(\nu' - \nu_0)/(\nu_0 - \nu_0)]^{1/2}$$

and as exciton states appear variations in $A_1$ are expected as one goes from a metal to an insulator.

The physical significance of $A_1$ may be ascertained by introducing dimensionless variables $y$ in units of $2E_F$ in equation (4) ($y = y(v) = uh(\nu - \nu_0)/2E_F$) as shown in figure 2, where the uncertainty principle requires that $T_v L_F \gg h/2$ and defines the parameter $u = 2T_v E_F / h > 1$. Then

$$A_1(y) = [D_v (u\alpha)^{1/2}] \int_{y-1}^{y} dx (1-f) \text{Re}[i(y')^{1/2}]$$

Figure 3. Normalised absorbance $A_1$ against $(E - E_1)/2e\nu$ with $u, \alpha = 1$ in equation (4).

where $y' = x - i - i\hbar/2\epsilon_r$.

(a) For semic, using relation 2.2 absorbance, $A_1$, causes the edge to shift as discussed below.

(b) For metals giving rise to the relation $A_2$ have been plotted up to 1.79 eV to show the shift.

(c) For semin the finite temperatur absorbance is

$$A_3$$

which can be interpreted as a finite temperatur absorbance.

$$A_4$$

For a semiconductor, equation (6) is drawn

$$A_1''(E)$$

where $r = (A_1'' - A_1)$. The relation of states being $r$ evaluated from

$$A_1''(E)$$

and the magnitude of equation (7)

$$A_1''(E)$$

causing the shifts in figure 4 the slope is unrealistic.

This is unrealistic which apply to MAS near

(d) Mott has disordered mater qualitatively by $A_1 = \text{Re}[i(y')^{1/2}]$. It is careful to say $E_c$ a correction for the

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L560 Letter to the Editor

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Absorbance is then written:

$$A_s = A_m^0 + \int_0^{\mu/2} (1 - f) \, dA^0 \exp(-\beta E_g)$$

which can be integrated by parts to obtain the semiconductor edge absorbance $A_s$, at finite temperature ($\beta = 1/k_B T$):

$$A_s = A_m^0 - \left[ A_m^0 - A_m^0 + 2\beta E_F \int_0^{\mu/2} A_0^0(1 - f) \, dy' \right] \exp(-\beta E_g).$$

For a semiconductor $f(1 - f)$ is negligible and in a first approximation the last term in equation (6) is dropped, i.e.

$$A_s^{0}(y, T) = A_m^0[1 - r \exp(-\beta E_g)]$$

where $r = (A_m^0 - A_m^0)/A_m^0$ is the fractional reduction of the absorbance due to the population of states between the bottom of the conduction band and $\mu_0$ and the magnitude of $r$ evaluated from equation (4) is $\sim 0.2$ near $\nu_F$. The edge absorbance changes with $\beta$ as

$$\left(\partial \ln A_s^{0}/\partial \beta\right)_v = E_g(A_0^0 - A_0^0)/A_s^{0}(0)$$

and the magnitude of $y$ near the edge inflection point increases with $T$, because in equation (7)

$$A_s^{0}(y, T)/A_s^{0}(y, 0 K) = 1 - r \exp(-\beta E_g) < 1$$

causing the shifts observed in figure 4. When $T = -56^\circ C$ to $-10^\circ C$ for Rb-NH$_3$ (5 MPM) in figure 4 the slope $\partial \ln A_s^{0}/\partial \beta$ is $4 \times 10^{-3}$ to $2 \times 10^{-2}$ eV gives an energy $E_g \approx 0.26$ eV. This is unrealistically high, indicating that the simple band model in figure 2(a) does not apply to MAS near the metal-insulator transition. Other band models must be considered.

(d) Mott has described various cases for the calculation of the density of states in disordered materials as shown in figure 2. The conductivity in MAS has been described qualitatively by $N(E_c)$ forming two overlapping bands where localised states are occupied up to say $E_c$ in figure 2(b) (Mott 1974). Then the absorbance must be written with a correction for the density of states, i.e.

$$A_g(y) = A_{eg}(y) + A_{sm}(y)$$

where

$$A_{eg}(y) = \int_{\nu_F}^{\mu_0} g(\nu') \, dA^0$$

and

$$A_{sm}(y) = \int_{\nu_F}^{\mu_0} g(\nu') \, dA^0$$
where \( y_c = E_c / 2E_F \) and \( g(v') = N(v') / N(v')_{\text{freeelectron}} \) is the ratio of the density of states relative to that for a free electron gas, i.e. \( g_c < 1 \) near \( v = v_c \) is the Mott ratio and \( g \to 1 \) as \( v \to v_0 \). Integration by parts then gives

\[
A_g(y) = A_i^0 - g_c(A_i^0 - A_i^n) - \int_{y_c}^{y} A^0 \, dg
\]

and the absorbance correct to first order, neglecting the last term in equation (9'), is

\[
A_g(y) = A_i^0 (1 - g_c)
\]

written in a form similar to equation (7), i.e.

\[
A_g(y') = A_i^0 (1 - g_c)
\]

where \( E_g \) in equation (7) has been replaced in equation (10) by \(-\beta g_c \beta \) which is not constant with \( \beta \) (i.e. \( g \to 0 \) as \( \beta \to \infty \)). We apply equation (10) to the data in figure 4 (5 MPM Rb-NH$_3$ with \( r = 0.2 \)). Then, \( g_c(-31^\circ \text{C}) - g_c(-56^\circ \text{C}) = 0.3 \) and \( g_c(-10^\circ \text{C}) - g_c(-56^\circ \text{C}) = 0.9 \) support a density of states shape given by figure 2(b). Here \( g_c(-56^\circ \text{C}) \approx 0.2 \) was evaluated from conductivity data (Sharp et al. 1971).

Other models which predict a density of states which changes with temperature near the mobility edge, such as the Mott–Hubbard model in figure 2(c), would also explain the absorbance near \( v_T \) or \( v_c \). Here, if the density of states decreases for \( E_c \) above \( E_c \) as in figure 2(c), the absorbance should show additional structure above the onset of the continuum of states. Also, when \( v_0 \gg v_b \) in figure 2(c) and the edge is identified near \( v_c \), the decrease in the density of states as \( E_c > E_c \) would affect the EXAFS relation. Here

\[
\frac{E_c}{2E_F} \gg \frac{h}{2}
\]

is an initial state.

In summary, it follows:

(i) The value of \( A_{01}(y) \) in figure 1 in the region to note that the energy \( T_E \approx h/2 \), which is initial state.

(ii) \( E_c \) for Rb$_x$ (Sharp et al. 1971) is sharper than the others.

(iii) The Rb edge is similar to A of M and metallic. The ratio \( g_c \) has been separated in figure 4(b) charge transfer to an accurate edge position in two possibilities is two.

In conclusion, the 5 of metal–insulator transition materials where the importance in order of M-NH$_3$ where the other measurements show collisions occurring proportional to the values above \( E_0 \) from equation (1) and how thermal disorder.

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References


Cramer S P, Eccles T P, and

J Reynolds and J C.
the ratio of the density of states $\nu = \nu_c$ is the Mott ratio and the last term in equation (9'), is

$$V_c = \text{the Mott ratio and }$$

$$\text{last term in equation (9'), is}$$

$$\text{by } -(\alpha g_{\beta})_1 = -(\alpha g_{\beta})_2 = -(\alpha g_{\beta})_3 = \text{the averages and } -10^\circ \text{C respectively}.$$
Appendix: glossary of terms used

**MAS** metal-ammonia solutions

**XAS** x-ray absorption spectroscopy

**XAES** x-ray edge absorption spectroscopy

**V** valence of absorber

**Z** atomic number of absorber

**A** absorbance of x-rays by a given material:
- $A_{\text{non}}$ for non-metals
- $A_s$ for semimetals
- $A_m$ for metals
- $A_g$ for materials with overlapping bands
- $A_N$ for material near 0 K
- $A^{(1)}$ first-order approximation (neglecting $(1-f)f \ll 1$ and/or $dE \approx 0$)

$A_1 = A - A_{\text{non}}$ absorbance below the edge $E_0$.

**$\nu$** frequency of x-ray photons measured from the 1s level of absorber:
- $\nu^b_0$ to the bottom of the conduction band
- $\nu_F$ to the Fermi level
- $\nu_L$ to the edge of the continuum of free states in non-metals ($E_0 = h\nu_L$)

$y = y(\nu) = (\nu - \nu^b_0)/2E_F u^{-1}$: dimensionless parameter which measures the photon energy from the bottom of the conduction band in units of a resonance line half-width at half height ($h/T_s = 2E_F/\nu$).

**$N(\nu)$** density of states near $E = h\nu$ above the 1s level of the absorber

**$D_\nu$** relative intensity of resonance line near $E = h\nu$

**$2E_F$** activation energy in simple semimetal

**$g_c$** Mott ratio $g$ measured near the mobility edge.

### 1. Introduction

It is now well established that the distribution functions of liquid points are almost identical to those of the atomic forces. Frisch et al. (1976) in the study of a high-density liquid and solid state, that the calculated distribution functions for various perturbations near an atoms in a liquid, such as liquid metal, and solid, are not far removed from each other. What role do these forces play in determining the structure and properties of these systems?

1. What then is the role of these forces in determining the structure and properties of these systems?

2. Is it possible to directly attribute some of the properties of these systems to the forces in determining the structure and properties of these systems?

3. If so, which forces are the most significant in determining the structure and properties of these systems?