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EXPERIMENTAL OBSERVATION OF WANNIER–MOTT IMPURITY GROUND STATES IN AN AMORPHOUS MEDIUM

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The experimental observation of Wannier–Mott impurity ground states in an amorphous material is reported.

1. Introduction

In a recent communication Moreira and Parada [1] have shown that Wannier functions constructed from Bloch functions in a crystal are localized in that they are exponentially decreasing functions. The basis of this approach to the problem of localized Wannier functions has been the (assumed) invariance of the electron potential under a crystal lattice translation, that is, an intrinsic crystallinity in the system.

However, Rice and Jortner [2] had earlier conjectured that localized Wannier-type excitonic impurity states should be amenable to experimental observation in a structurally disordered medium, provided that the conduction band of the medium is free-electron like. The experimental observation of Wannier–Mott excitonic states [3,4] in doped liquid rare gases provided a striking confirmation of the Rice–Jortner picture. To date, the closest approach to true Wannier–Mott impurity ground states has been in the doped Group IV semiconductors [5], silicon [6] and germanium [7]. However, even in these high dielectric systems [$\kappa = 12$(Si); $\kappa = 16$(Ge)] impurity ground states still retain some (albeit small) parentage in the states of the isolated donor atom, as reflected in the donor-dependent optical and magnetic properties [5–7]. As such, these states should be rigorously classified either in terms of a modified Wannier scheme [3,9,10] or a perturbed tight-binding formalism [11]. Thus, so far, the direct observation of true Wannier–Mott impurity states has been confined to *excited* impurity states, and these in non-polar amorphous materials [3,4]. In this note we report the experimental observation of true Wannier–Mott impurity *ground* states in frozen solutions of potassium, rubidium and caesium in the polar medium hexamethylphosphoramide (HMPA).

Typical electron spin resonance (ESR) spectra of frozen potassium– and rubidium–HMPA solutions are shown in fig. 1. The absorptions labelled $^{39}M_G$, $^{85}M_G$ and $^{87}M_G$ arise from spin transitions of intermediate impurity ground states [12,13]. A discussion of the nature of these states has been given in a previous paper [14] (hereafter referred to as I).

A second type of ESR absorption, a singlet resonance with no evidence of resolved hyperfine structure (fig. 1), had linewidths (ΔH_{ms}), and to a lesser extent g_e factors, dependent upon the magnetic moment of the particular alkali metal nucleus. Magnetic parameters for the singlet absorption in frozen potassium–, rubidium–, and caesium–HMPA solutions are given in table 1. An intense colloidal metal resonance [15] in the ESR spectrum of frozen sodium–HMPA solutions effectively masked all other signals in the free spin region ($g_e \approx 2, H \approx 3200$ G).

In potassium, rubidium and caesium spectra, the singlet resonance showed rf power saturation behavior characteristic of an inhomogeneously broadened line

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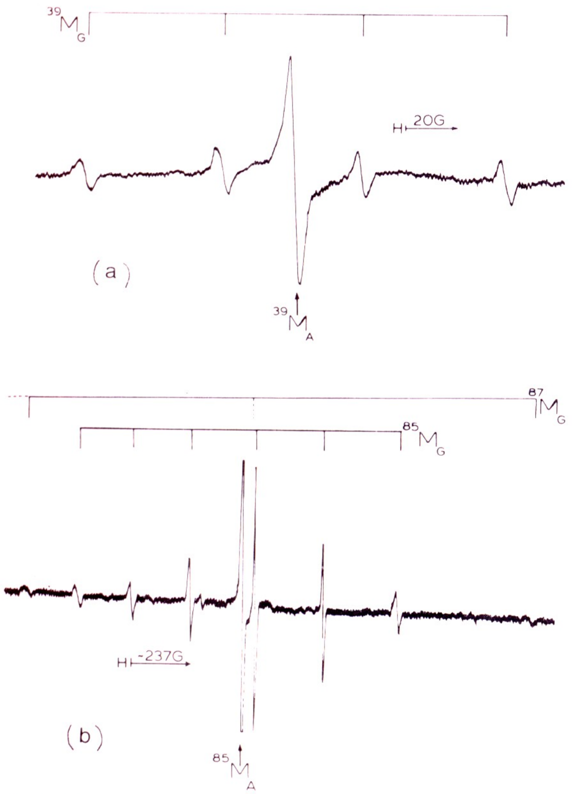

Fig. 1. Electron spin resonance spectra (77 K) of frozen solutions of (a) potassium and (b) rubidium in HMPA. The resonances labelled $^{85}M_G$, $^{87}M_G$ and $^{39}M_G$ arise from electron spin transitions of intermediate (alkali) impurity states, and are discussed in detail in the previous communication (I). The resonances $^{85}M_A$ and $^{39}M_A$ arise from electron spin transitions of Wannier–Mott impurity states. Spectra were recorded at low incident microwave power ($\lesssim$ 2 mW).

[16]. The observed singlet resonance is therefore a superposition of $(2I_M + 1)$ overlapping lines, each of which is broadened by unresolved hyperfine interactions of the electron with the magnetic nuclei of the surrounding medium. Computer simulation of ESR lineshapes under these conditions gave values of the metal hyperfine coupling constant (table 1). On a system of nomenclature outlined in I, we label this localized, low atomic character state in potassium, rubidium and caesium solutions as $^{X}M_A$, where X is the mass number of the particular isotope.

2. The nature of Wannier–Mott impurity states in an amorphous medium

For a material in which the conduction band is free-electron like, an excess electron in the band may be represented by a plane wave state,

$$\phi_{\boldsymbol{k}}(r) = (1/V^{1/2}) \exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}), \tag{1}$$

where V is the volume of the sample. From the Kohn–Luttinger [5,17,18] effective mass approximation (EMA) we know that the wavefunction of a shallow (loose-binding) impurity state is composed predominantly of states split off from the host conduction band and an approximate wave packet for the state may be constructed as follows,

$$\psi(\boldsymbol{r}) \approx \sum_{\boldsymbol{k}} C(\boldsymbol{k})\phi_{\boldsymbol{k}}(\boldsymbol{r}). \tag{2}$$

For a dielectrically screened impurity potential, $V(\boldsymbol{r})$,

Table 1
Experimental magnetic parameters for the $^{X}M_A$ (X = 39, 85, 133) state in low temperature alkali metal–HMPA glasses

Isotope (μ_I) a)	I_M	Temperature (K)	g_e	ΔH_{ms} (G)	A_{iso} (G)
^{39}K	3/2	77 (P) b)	2.0018 ± 0.0004	4.90 ± 0.3 c)	0.80 ± 0.1
(0.39094)		106	2.0017 ± 0.0004	5.19 ± 0.4	
^{85}Rb	5/2	77 (P)	2.0009 ± 0.0004	9.4 ± 0.5 d)	0.41 ± 0.03
(1.3483)					
^{133}Cs	7/2	77 (P)	1.9994 ± 0.0004	14.9 ± 0.8 e)	0.23 ± 0.02
(2.5642)		120 (Q)	1.9994 ± 0.0006	14.1 ± 0.8	

a) Magnetic moment of the isolated alkali atom, in units of the nuclear magneton ($eh/4\pi Mc$).
b) Sample prepared in (P) pyrex; (Q) quartz cell.
c) Average of 5 samples investigated.
d) Average of 2 samples investigated.
e) Average of 4 samples investigated.

the explicit one electron Schrödinger equation is given by [5]

$$[-(\hbar^2/2m)\nabla^2 + V(\boldsymbol{r})]\,\psi(\boldsymbol{r}) = E\psi(\boldsymbol{r}), \qquad (3)$$

where E is the energy eigenvalue and m an appropriate electron effective mass.

If we substitute for (2) in (3) and recognize the orthogonality [19] of the plane waves [exp ($i\boldsymbol{k}\cdot\boldsymbol{r}$)] we have [2,20]

$$(\hbar^2/2m)k^2 C(\boldsymbol{k}) - EC(\boldsymbol{k}) + \sum_{k'} \bar{V}_{k-k'} C(\boldsymbol{k}') = 0, \qquad (4)$$

where $\bar{V}_{k-k'}$ is the Fourier transform of the dielectrically screened impurity potential. In general terms, the true impurity potential at a distance $\boldsymbol{r}$ from the parent hole is given by

$$V(\boldsymbol{r}) = -e^2/\kappa r + v(\boldsymbol{r}), \qquad (5)$$

where κ is the static dielectric constant of the material and the "central cell" term $v(\boldsymbol{r})$, represents the deviation of the impurity potential from the true Coulomb form ($-e^2/\kappa r$). For situations in which the EMA is valid,

$$v(\boldsymbol{r}) \approx 0$$

and eq. (4) represents the hydrogenic Schrödinger equation in momentum space, with the impurity level characterized by an effective mass ($m = m^*$) appropriate to an electron in the conduction band [3]. Under these circumstances the donor ground state wavefunction can be written explicitly, as [5,17,18]

$$\psi_{\text{donor}}(\boldsymbol{r}) = \sum_{i=1}^{N} \alpha^{(i)} \psi_k^{(i)}(\boldsymbol{r}) F^{(i)}(\boldsymbol{r}), \qquad (6)$$

representing a linear combination of modulating envelope functions $F^{(i)}(\boldsymbol{r})$ and Bloch waves $\psi_k^{(i)}(\boldsymbol{r})$ at the ith conduction band minima of which there are N. $\alpha^{(i)}$ represents the relative contribution from the ith valley.

Rice and Jortner [2] first pointed out that the arguments leading up to eq. (4) are quite general; the essential requirement being that an excess electron in the host conduction band be described as a plane wave state [eq. (1)]. Specifically if the "resistivity" relaxation time (τ_{res}) for an electron in the Bohr orbit is longer than the time (τ_{Bohr}) required to circumscribe the orbit, a bound state can exist [2]. If, in addition, the lifetime of this phase coherent state is of the order of the electron-spin relaxation time (T_1), a spin resonance absorption may be observed.

Squaring (6) and evaluating the wavefunction at the donor nucleus, we have [5,17]

$$|\psi(0)|^2_{\text{donor}} = N|F^{(1)}(0)|^2\,|\psi_k^{(1)}(0)|^2, \qquad (7)$$

where $F^{(1)}$ and $\psi_k^{(1)}$ are evaluated at $k^{(1)}$ and $|F^{(1)}(0)|^2 \approx 1/\pi(a^*)^3$ where a^* is the Bohr radius of the impurity state.

We expect, therefore, that true Wannier–Mott impurity states have values of $|\psi(0)|^2_{\text{donor}}$ which are independent of the nature of the donor atom.

We interpret our experimental results for the ${}^{X}\text{M}_{\text{A}}$ species as follows:

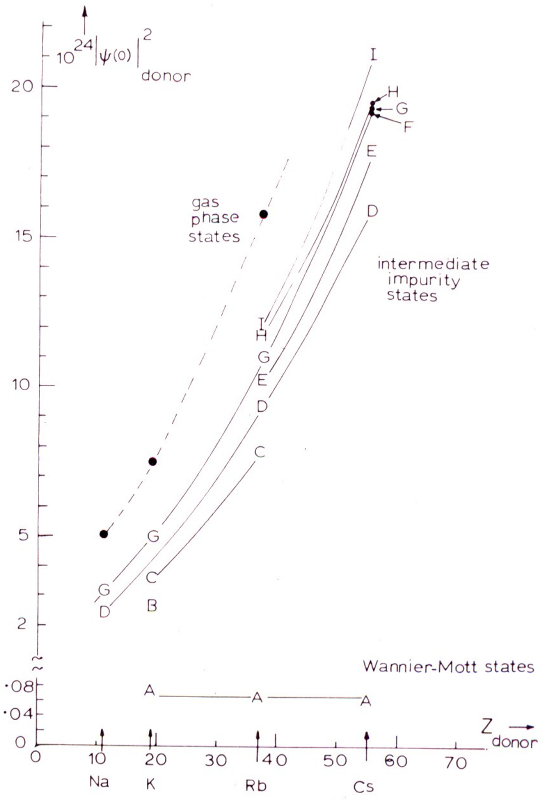

Fig. 2. The variation of $|\psi(0)|^2_{\text{donor}}$, the unpaired electron spin density at the donor nucleus, with Z_{donor}, the isolated (gas-phase) donor atomic number, for Wannier–Mott (A in the figure) and intermediate (B–I in the figure) impurity states in metal–HMPA glasses. The gas-phase values for sodium, potassium and rubidium atoms are also included. The gaseous caesium atom has $|\psi(0)|^2_{\text{Cs}} = 26.4508 \times 10^{24}$ electrons cm^{-3}. Note the change of scale between data for the different types of impurity states.

Table 2
Unpaired electron spin densities at the donor nucleus in shallow impurity states

Host matrix	Donor	$10^{24}\,|\psi(0)|^2_{\mathrm{donor}}$ (electrons cm^{-3})	$|\psi(0)|^2_{\mathrm{donor}}/|\psi(0)|^2_{\mathrm{atomic}}$ (%)
Si	^{6}Li	0.0033 [6]	0.19
	^{7}Li	0.0033 [6]	0.19
	^{31}P	0.43 [6]	≈ 1.0 [a]
	^{75}As	1.73 [6]	≈ 1.6 [a]
	^{121}Sb	1.18 [22]	≈ 1.1 [a]
	^{123}Sb	1.18 [22]	≈ 1.1 [a]
Ge	^{31}P	0.17 [7]	≈ 0.4
	^{75}As	0.69 [7]	≈ 0.6
HMPA	^{39}K	0.073 ± 0.007 [b]	0.97 ± 0.10 [c]
	^{85}Rb	0.065 ± 0.005	0.41 ± 0.03
	^{133}Cs	0.060 ± 0.006	0.23 ± 0.02

[a] Atomic values estimated from the Goudsmit relation, see ref. [21].
[b] This work.
[c] $|\psi(0)|^2_{\mathrm{atomic}}$ for the alkali atoms in question: ^{39}K, 7.4790 × 10^{24}; ^{85}Rb, 15.8225 × 10^{24}; ^{133}Cs, 26.4508 × 10^{24} (electrons cm^{-3}).

(i) The observed $|\psi(0)|^2_{\mathrm{donor}}$ values, when compared with the corresponding gas phase values ($|\psi(0)|^2_{\mathrm{atomic}}$ in table 2) suggest considerable dielectric screening of the electron–hole pair, and a corresponding large Bohr radius for the unpaired electron.

(ii) Experimental values of $|\psi(0)|^2_{\mathrm{donor}}$ are taken to be approximately independent of the donor atom for potassium, rubidium and caesium species. The slight variation between different donors is well within our final error estimates for $|\psi(0)|^2_{\mathrm{donor}}$ (table 2).

We conclude that the states $^{X}\mathrm{M}_{\mathrm{A}}$ (X = 39, 85, 133) in frozen metal–HMPA solutions are best described as true Wannier–Mott impurity *ground* states in a structurally disordered HMPA matrix. As such, these states forfeit any parentage in the electronic states of the gas-phase alkali atoms.

It is interesting to note that when central cell corrections to the impurity potential (5) become appreciable, the Schrödinger equation (3) is no longer truly hydrogenic and impurity states reveal a parentage in the states of the isolated donor atoms. Specifically, unpaired electron spin densities at the donor nucleus show a dependence on Z_{donor}, the isolated (gas phase) donor atomic number. This situation occurs in the intermediate impurity states in the metal–HMPA glasses [12–14] (fig. 1) and also (although to a lesser degree) in shallow impurity states in the doped Group IV semiconductors [5–7] (table 2).

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References

[1] J.A.M. Moreira and N.J. Parada, Solid State Commun. 16 (1975) 561.
[2] S.A. Rice and J. Jortner, J. Chem. Phys. 44 (1966) 4470.
[3] B. Raz and J. Jortner, Proc. Roy. Soc. 317 (1970) 113.
[4] B. Raz and J. Jortner, Chem. Phys. Letters 4 (1970) 511.
[5] W. Kohn, in: Solid state physics, Vol. 5, eds. F. Seitz and D. Turnbull (Academic Press, New York, 1957) p. 257.
[6] G. Feher, Phys. Rev. 114 (1959) 1219.
[7] D.K. Wilson, Phys. Rev. 134 (1964) A265.
[8] G. Baldini, Phys. Rev. 137 (1965) A508.
[9] J. Hermanson and J.C. Phillips, Phys. Rev. 150 (1966) 652.
[10] J. Hermanson, Phys. Rev. 150 (1966) 661.

[11] S. Webber, S.A. Rice and J. Jortner, J. Chem. Phys. 42 (1965) 1907.

[12] R. Catterall and P.P. Edwards, J. Chem. Soc. Chem. Commun. (1975) 96.

[13] R. Catterall and P.P. Edwards, Proceedings of Colloque Weyl IV, Metal–Ammonia Solutions, Michigan State University, June 1975; J. Phys. Chem. 79 (1975) 3010, 3018.

[14] R. Catterall and P.P. Edwards, Chem. Phys. Letters 42 (1976) 540.

[15] R. Catterall and P.P. Edwards, Advan. Mol. Relaxation Processes 7 (1975) 87.

[16] T.G. Castner, Phys. Rev. 115 (1959) 1506.

[17] W. Kohn and J.M. Luttinger, Phys. Rev. 98 (1955) 915.

[18] J.M. Luttinger and W. Kohn, Phys. Rev. 97 (1955) 869.

[19] N.W. Aschcroft and N.D. Mermin, Solid state physics (Holt, Rinehart and Winston, New York, 1976) p. 138.

[20] C. Kittel, Introduction to solid state physics, 3rd Ed. (Wiley, New York) p. 257.

[21] W. Kohn and J.M. Luttinger, Phys. Rev. 97 (1955) 883.

[22] Eisinger and G. Feher, Phys. Rev. 109 (1958) 1172.