N. R. J. Poolton · K. B. Ozanyan · J. Wallinga
A. S. Murray · L. Botter-Jensen

Electrons in feldspar II: a consideration of the influence of conduction band-tail states on luminescence processes

Received: 11 May 2001 / Accepted: 6 September 2001

Abstract Most natural feldspars contain many charged impurities, and display a range of bond angles, distributed about the ideal. These effects can lead to complications in the structure of the conduction band, giving rise to a tail of energy states (below the high-mobility conduction band) through which electrons can travel, but with reduced mobility: transport through these states is expected to be thermally activated. The purpose of this article is twofold. Firstly, we consider what kind of lattice perturbations could give rise to both localized and extended conduction band-tail states. Secondly, we consider what influence the band tails have on the luminescence properties of feldspar, where electrons travel through the sample prior to recombination. The work highlights the dominant role that 0.04–0.05-eV phonons play in both the luminescence excitation and emission processes of these materials. It also has relevance in the dating of feldspar sediments at elevated temperatures.

Keywords Feldspar · Luminescence · Hopping transport · Mobility edge · Effective mass

Introduction

Together with the preceding article (Electrons in feldspars I: on the wavefunction of electrons trapped at simple lattice defects), we are attempting to make an initial understanding of the properties and behaviour of electrons in feldspars. Whilst Part I considers the simple case of how an electron spreads out when trapped at a classic hydrogenic defect (referred to as the IRSL electron trap), this article seeks to consider how a free electron moves through the lattice. In both cases, the most readily accessible tools for testing the effects are via luminescence measurements, and the work has application to the luminescence dating of sediments.

The luminescence process that is of particular interest is one in which an electron, located at the IRSL trap, is stimulated optically to recombine with a hole located elsewhere in the lattice. We will assume that the hole is sufficiently far away for direct electron-hole recombination (arising through overlap of their wavefunctions) not to take place. As a consequence, the electron must pass through the conduction band in order to recombine; this electron, then, is to be our probe for examining the properties of the conduction band.

In the alkali feldspars, the depth of the IRSL electron trap’s ground state is ~2 eV below the conduction band (see Part I). However, luminescence can be excited in the samples using photons of energy less than 2 eV in two ways:

1. In the infrared (IR) at ~1.5 eV a resonance is usually observed as the first excited state of the trap is accessed. The luminescence is thermally enhanced, with thermal activation energies in the range 0.02–0.15 eV typically being reported Rieser et al. 1997 (Bailiff and Barnett 1994; Bailiff and Poolton 1991; Poo et al. 1995).

2. The 1.5-eV resonant peak is usually superimposed on a rising continuum, as the photo-excitation energy increases from 1 to 2 eV (e.g. Hütt et al. 1988; Poo et al. 1995b; Jaek et al. 1997). The relative
intensity of this component (with respect to the resonance) and where the low-energy limit occurs, are sample-dependent.

Clearly, the thermal activation energies of 0.02–0.15 eV are too small to represent the energy bridge between the excited state and conduction band (~0.5 eV). However, the low-energy luminescence excitation continuum suggests that there may be a range of energy states available. We will be arguing in this article that these are band-tail states that lie below the high-mobility conduction band; the thermal dependence of the luminescence is explained by their presence, since they strongly affect the electron mobility.

**Origin of the band tails in feldspars**

The presence of just a single charged impurity or non-standard bond angle in an otherwise perfectly crystalline insulator or semiconductor will lead to an isolated deformation in the conduction band potential. Where there are many such imperfections, the potential fluctuations can form “band-tail” states where electron motion is still possible, but with reduced mobility: such tails extend above the valence, and below the conduction bands, into the forbidden gap (e.g. Redfield 1963a, b; Mott and Davis 1971).

For the wide band-gap silicates, we can gain an appreciation of the likely size of these effects from band-structure calculations. In the case of the various polymorphs of crystalline SiO₂, Li and Ching (1985) calculated that a variation of 10° in the Si–O–Si bond angle can lead to a change in the band gap of 0.65 eV; similarly, a bond-length variation of 0.1 Å was found to cause the gap to change by 3.5 eV. Later work by Xu and Ching (1991) confirmed the link between bond length and the energy gap.

Megaw (1974), in summarizing the structure of feldspars, discussed strain-induced variations in Si–O bond lengths, and O–Si–O bond angles within a typical feldspar lattice. In the latter case, a typical example of a bond-angle range from 103 to 116° (an average of about 109.5°) was given. As they are natural minerals, we also know that there are many impurity atoms typically present in feldspar (for sample analyses, see Deer et al. 1992) which will also contribute to localized conduction band fluctuations.

Figure 1 shows a schematic representation of the possible IRSL defect and conduction-band density of states in feldspar. The luminescence to be considered in the following sections arises from recombination at hole-trapping sites (not shown) after excitation from the ground state of the electron trap, either directly into the band-tail states or into the excited state (followed by transfer to the band tails).

**Localization vs mobility in the band tails**

In order to calculate the effects that lattice perturbations might have on electron behaviour in feldspar, we need a model to describe the situation. We will simplify this as much as possible, firstly by considering the solutions in 1-D (then transferring to 3-D), and secondly, by assuming that the perturbations are in the form of square potential wells. This basic model is not new. For example, in the seminal work of Anderson (1958), the energy of a crystalline material was modelled in 1-D by a series of square potential wells, with the potential fluctuations being tied in, varying the well depths. In order to extract the information that is useful to us, however, it is possible to greatly simplify Anderson’s model still further. We do this by providing a well-defined zero-point reference energy for the calculations (the conduction band edge E_c of the unperturbed lattice) and consider that the wells arise purely from the potential fluctuations appearing below E_c, as shown in Fig. 2a.

In order to appreciate what effect such a potential might have on an electron, it is necessary to consider two points. Firstly, only certain energies are allowed for electrons within the wells: these energies depend on the well width, depth, effective electron mass and proximity of neighbouring wells. Secondly, the electron wavefunction is not entirely confined within the well, but extends beyond the boundaries – as shown in Fig. 2b. This feature enables the electron to interact with, and transfer to, other wells elsewhere in the lattice.

The course of the following calculations is as follows: in the following section we first consider only isolated wells, and then weakly interacting wells of varying depth. This provides a basis for understanding thermally activated diffusion of electrons through the lattice. Later, we consider the more special case of strongly interacting wells, which lead to the appearance of extended electron states below E_c and possible routes for more rapid electron diffusion through the lattice.