Positron Annihilation Study of the Semiconductor to Metal Transition in Ti₂O₃

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An increase of positron mean life is found to accompany the semiconductor-metal transition in Ti₂O₃. This agrees well with the recent finding that the unit cell volume increases during the transition.

Positron annihilation is known to be very sensitive to various second order transitions as well as first order transitions. A change of the positron annihilation parameters during the semiconductor to metal transition in V₂O₃ has been reported in the literature. In this note, we briefly report our findings on positron annihilation in Ti₂O₃ during its semiconductor to metal transition.

The resolution of the apparatus for the positron lifetime measurements was about FWHM = 300 psec. The sample was obtained from Alfa Products as 99.9% pure and in powder form. The sample was sealed with a ²²Na source deposited on thin mica (< 2 mg/cm²) and evacuated to less than 10⁻⁵ torr. The measurements were made in a temperature range from room temperature to 670 K. After each measurement, which took 20 hours, the temperature was raised or lowered, and the next measurement started. Two ascending and descending series of measurements were made. Both two exponential components and single exponential component curves were used for data reduction and analysis.

The two exponential components analysis gave τ₁ ~ 200 psec and τ₂ ~ 400 psec with an intensity of the latter of ~ 5%. Due to the closeness of the values of τ₁ and τ₂ and the small intensity I₂, the statistical uncertainty was very high and no definite trend could be found. The result obtained from the single exponential analysis is shown in Figure 1. At room temperature and up to nearly 370 K, the values of positron meanlife τ are about 210 psec and at temperature higher than ~ 470 K, τ increases to about 224 psec. The transition region covers a wide temperature range and lies within the range of the semiconductor to metal transition region reported.

In general, an increase in the positron meanlife with temperature in solid media can be attributed to either the availability of more free volume within the expanding lattice or more trapping in thermal vacancies, or both. Past studies indicated that there is a 1% decrease in the volume of the unit cell of Ti₂O₃ in the range of 390 to 470 K. A more recent, refined single crystal study, however, shows that there is a slight increase of about 0.4% in the volume of the unit cell in the range 370 - 570 K as shown in Figure 2. The result of the positron annihilation measurements is consistent with the latter finding and seem to support the free volume model.

It may be noted that the lifetime increases abruptly during the first-order phase transition of NH₄Cl which is accompanied by a marked increase in volume. The increase in lifetime in the case of the Ti₂O₃ transition is small and gradual since this transition is of second order. More studies along these lines would throw light on the mechanism of positron annihilation in inorganic solids.

Fig. 1

Fig. 2
1 Reprints should be addressed to the author.
2 See, for example, V. I. Goldanskii, Atomic Energy Rev. 6, 3 [1968]; R. N. West, Adv. Phys. 22, 3 [1973].
5 S. J. Tao, IEEE NS-15, 1, 175 [1968].