SUMMARY

In the preceding, we have presented experimental data which relate, in an unambiguous way, the superconductivity of the Ti-rich Ti-Mn alloys to their metallurgical microstructure. The data establish (1) the existence of localized magnetic states in hcp Ti-Mn, (2) that there is *not* an anomalously large elevation of T_c by dissolved Mn in hcp Ti-Mn, and (3) the superconductivity of the as-cast dilute ($\lesssim 4$ at.%) Ti-Mn is due to a precipitated filamentary structure of enriched β-phase Ti-Mn. The retained β phase is nonmagnetic and sufficiently rich in Mn that the observed T_c can be understood on the basis of Eq. (1) and a reasonable variation of $N(0)$ as a result of alloying. One may conclude, therefore, that the superconductivity of dilute Ti-Mn is not anomalous and ought not be to construed as evidence for a magnetic interaction for the superconducting state.

Note added in proof. Recent measurements by Falge [R. Falge, Phys. Rev. Letters **11**, 248 (1963)], have confirmed the suggestion presented herein that very small additions ($\lesssim 0.8$ at.%) of Mn to Ti *lowers* the superconducting transition temperature of the as-cast alloys. This is in general accord with the solubility limit for Mn in α Ti and may be regarded as substantiating evidence that localized magnetic states in hcp Ti-Mn act to inhibit the superconducting state.

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Far-Infrared Spectra of Two Cerium Double Nitrate Salts*

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Far-infrared transmission experiments have been carried out on cerium magnesium nitrate and cerium zinc nitrate. The energies of the first excited doublets were found to be 36.25 and 30.2*k*, respectively. The frequencies of the longest wavelength lattice absorptions have also been determined.

CERIUM magnesium double nitrate (CMN) is well known to the low-temperature physicist for its useful magnetic properties. All magnetic ions are equivalent, the interactions between the ions are very small and the g tensor in the ground Kramers doublet is highly anisotropic. These properties make the crystal very suitable for use in adiabatic demagnetization and as a magnetic thermometer.

In recent years there have been several estimates of the splitting Δ_1 between the two lowest Kramers doublets. Relaxation measurements[1–3] all give $\Delta_1 = 34k$. Finn *et al.*[1] perform their experiments on pure CMN whereas Ruby *et al.*[2] and Cowan and Kaplan[3] use CMN diluted with LaMN. The analyses of magnetic susceptibility data[4–6] give values of Δ_1 in the range 33 to 43*k*. Estimates of the energy Δ_2 of the second excited doublet vary even more widely and lie roughly in the range 80-290*k*. In view of the lack of agreement prevailing and the interest that many physicists have in CMN, far-infrared transmission experiments have been carried out in an attempt to measure both Δ_1 and Δ_2 directly. The techniques used were standard.[7] Experiments were also carried out on cerium zinc double nitrate (CZN) which is isomorphous with CMN. The observed spectra were very similar as would be expected, and only that for CZN is given in Fig. 1. The data are summarized in Table I.

The absorption at Δ_1 (the following remarks apply to both salts) has the expected temperature behavior: Its

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TABLE I. Results of far-infrared measurements on CMN and CZN. Δ_1 is the energy splitting between the ground state and the first excited doublet; Δ_L marks the onset of the lattice spectrum. ΔE_1 is the full width between points where the absorption coefficient has half its maximum value.

	Δ_1/k(°K)	$\Delta E_1/k$(°K)	Δ_L/k(°K)
CMN	36.25±0.4	2	74.5±6
CZN	30.2±0.4	2	71.0±4

frequency is temperature-independent, whereas its intensity is proportional to the population difference between the electronic states concerned. The intensity agrees within a factor of two with that expected for magnetic dipole transitions using the wave functions computed by Leask *et al.*[4] for CMN. The electric dipole matrix element is not necessarily zero as the environment of the Ce^{3+} ion does not have inversion symmetry. It is possible to admix into the $4f^1$ ground configuration a little of the excited configuration $5d^1$ of opposite parity which has an excitation energy[8] of about 40 000 cm^{-1}. Electric dipole matrix elements within the perturbed $4f^1$ configuration are then allowed. Recent crystallographic studies[9] of CMN indicate that the departure from an even parity arrangement of the twelve nearest neighbor oxygen atoms is small (~0.03 Å for a Ce-O bond length ~2.65 Å). Thus, the odd-parity components of the crystal field would be expected to be at least 50 times smaller than the even parity components. The even-parity crystal field produces splitting ~100 cm^{-1}.[4] Hence the admixture of $5d^1$ might be expected to be $\sim 10^{-4}$, leading to a transition probability for electric dipole transitions at least several orders of magnitude less than that for magnetic dipole transitions.

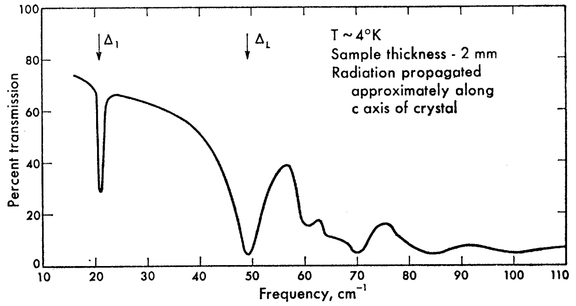

FIG. 1. The far-infrared spectrum of CZN. Δ_1 is due to transitions between the ground state and the first excited doublet; Δ_L marks the onset of the lattice spectrum. The residual transmission at high frequencies probably indicates the presence of false energy.

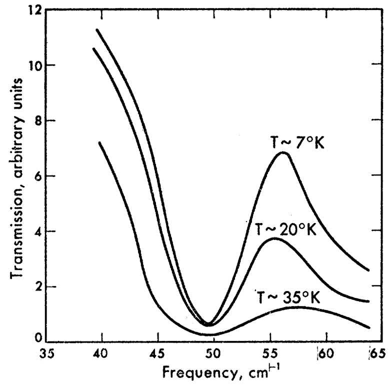

FIG. 2. The temperature dependence of the lattice absorption marked Δ_L in Fig. 1.

At frequencies where transitions to the level at Δ_2 might be expected to occur a number of broad absorptions (Fig. 1) were found. It is presumed that these are due to the lattice because they are much more intense and show a quite different temperature dependence than would be expected for magnetic dipole transitions between electronic energy levels. Experiments were also performed at elevated temperatures (of order Δ_1) where it was hoped to observe transitions of energy $\Delta_2-\Delta_1$ which might occur below the lattice absorptions. The results were negative.

In Fig. 2 is shown the sharp temperature dependence of the lattice absorption Δ_L observed near 50 cm^{-1}. The strong temperature dependence of the lattice spectrum (Fig. 2) makes it almost impossible to recognize magnetic absorptions which occur in the same frequency interval. Unfortunately, it was not possible to construct a reliable plot of the integrated adsorption at Δ_L versus temperature because of the many other strong absorptions at higher frequencies which are not sufficiently well separated from that under consideration.

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