

of distortion axes within the crystal. This originates a broad ESR curve.

T. MITSUMA: What is the origin of reduction of line width below the value of calculated dipole-dipole interaction at the temperature range between 200°K and the transition temperature?

M.U. PALMA: There is little doubt that this is exchange narrowing. The magnitude of this exchange, as estimated from the Curie-Weiss constant, is consistent with the narrowing.

R.D. SPENCE: Is there a color change at the transition?

M.U. PALMA: Yes. We suspected the presence of this effect. Experiments are being made just now by one of our associates at Palermo.

JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN

VOL. 17, SUPPLEMENT B-I, 1962

PROCEEDINGS OF INTERNATIONAL CONFERENCE ON MAGNETISM AND CRYSTALLOGRAPHY, 1961, VOL. I

The Néel Temperature of Mixed Crystals of Zinc and Iron Group Fluorides

J. M. BAKER AND J. A. J. LOURENS

The Clarendon Laboratory, Oxford, England

AND

R. W. H. STEVENSON

*Department of Natural Philosophy, Marischal
College, Aberdeen, Scotland*

An attempt has been made to measure the Néel temperature, T_N , of mixed crystals of Mn/ZnF_2 and Co/ZnF_2 of various composition by finding the temperature T_c at which the nuclear magnetic resonance of the fluorine nuclei disappears on cooling from room temperature. The dependence of T_c upon concentration of paramagnetic ion is compared with theoretical predictions of the concentration dependence of T_N . Measurements of the variation of linewidth with temperature above T_c are also discussed.

The Néel temperature, T_N , of several materials has been measured by observation of the disappearance of the magnetic resonance of nuclei in the material when antiferromagnetism sets in. We have attempted to measure the Néel temperature of mixed crystals of Mn/ZnF_2 by observing the temperature, T_c , at which the fluorine nuclear resonance disappears. Current theories of dilute systems suggest that there is a critical concentration below which antiferromagnetism does not occur, and our measurements were made to test these theories.

The samples were prepared by the Stockbarger technique. The speed of growth used ($\sim 10 \text{ mm hr.}^{-1}$) was considerably higher than normal in order to avoid segregation. Some

of the crystals were of good optical quality, others were polycrystalline and of more doubtful uniformity. In many of the samples pieces from two different places in the sample were analysed to see if the concentration varied.

The fluorine NMR line does not remain unchanged down to T_c and then disappear, but broadens as the temperature is lowered towards T_c . The width of the line, ΔH , is mainly due to interaction with the electronic magnetic moments. At high temperatures the line is narrowed by rapid flipping of these magnetic moments due to exchange interactions between them. As the temperature approaches T_N short range order increases and tends to inhibit the exchange

flipping. This lowers the flipping frequency and further broadens the line until at T_N , when long range order sets in, the line becomes very broad. This contribution to ΔH is small at high temperatures but increases very rapidly close to T_N . In addition in diluted specimens one would expect the random arrangement of paramagnetic neighbours to give rise to a linewidth proportional to the specific magnetisation of the sample χH . Thus in specimens which remain paramagnetic to very low temperatures ΔH should vary as χH , and in specimen which eventually become antiferromagnetic it should vary more rapidly as T_N is approached. Because the line broadens, the signal/noise ratio decreases and the line eventually disappears at T_G . Thus the closeness of T_G to T_N depends upon the sensitivity of the NMR apparatus and may be estimated from the rate of change of ΔH when the line disappears. In our experiments the NMR was usually observed at about 30 Mc/s using a Colpitts plate detector which develops a high r.f. voltage ($\sim 2V$ giving $H_1 \approx 0.1$ G) across the sample coil, and hence gives a strong signal. Using a phase sensitive detector with 1 c/s bandwidth the signal/noise ratio of the derivative of the line at 20°K for a typical case ($c=43\%$) is about 50. For this case T_N may be estimated quite well by extrapolating a graph of $1/\Delta H$ v T to $1/\Delta H=0$, giving $T_G - T_N \approx 0.5^\circ\text{K}$. $T_G - T_N$ will be somewhat larger towards the ends of the range of c , but the value of $T_G = 67.5 \pm 1.0$ for $c=100\%$ is in excellent agree-

ment with the temperature of the specific heat anomaly. The measured values of T_G , here taken as the temperature at which the signal/noise ratio becomes unity, are plotted in the figure.

It is an interesting, as yet unexplained, empirical fact that for specimens well above the critical concentration, including the undiluted material, we measure a total line width which varies as $(T - T_G)^n$ where n is nearly $-1/3$. For samples well below the critical concentration n is nearly -1 . In all cases there are departures from this simple relation at high temperatures. Unfortunately around the critical concentration the temperature dependence is intermediate between these extremes so that the temperature dependence of ΔH does not form a good way of measuring the critical concentration.

For comparison with our results in the figure the theoretical curve of Sato, Arrott and Kikuchi (1959) has been drawn for eight neighbours, appropriate to the body centred tetragonal structure of ZnF_2 . The result are in qualitative agreement with the theory in giving a critical concentration, and the lack of quantitative agreement is probably due to the fact that each paramagnetic ion interacts with two types of near neighbour. This is also probably the reason for the difference between the curves for Co and Mn, although some of the theoretical discussions do suggest that the shape of the curve of T_G against c should be different for different values of effective spin. In fact Dr. B. Heap (1961) has obtained fair agreement with the experimental points and critical concentration for Mn by including the effects of exchange to two types of neighbour. However to obtain this fit one has to assume values for the exchange interactions which disagree with those measured by Owen (1961), also it seems unlikely that the theory will fit the Co results as well.

Although it is unlikely that T_G and T_N differ by very much, the fact that there is uncertainty stimulated attempts to measure T_N by specific heat measurements (C. A. Bailey, unpublished) and anisotropy measurements, but neither gave clear cut results.

Thus so far the measurements appear to give the sharpest determination of T_N but confirmatory experiments using another tech-

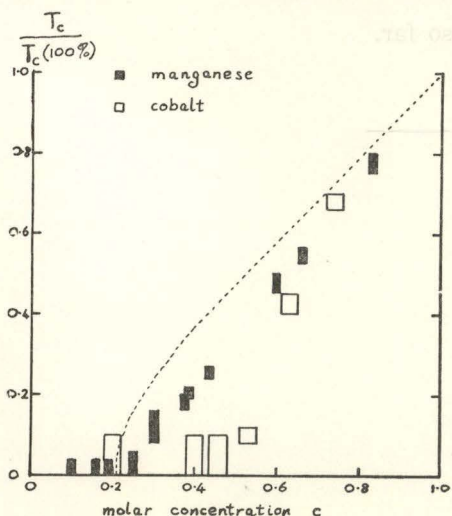


Fig. 1.

nique would be valuable.

References

1 B. Heap: Thesis, Oxford University (1961).

2 J. Owen: J. App. Phys. **32** (1961) 213.

3 H. Sato, A. Arrott, and R. Kikuchi: J. Phys. Chem. Solids **10** (1959) 19.

DISCUSSION

J. W. STOUT: Are there X-ray measurements on the $\text{MnF}_2\text{-ZnF}_2$ and $\text{CoF}_2\text{-ZnF}_2$ mixtures which indicate that solid solutions are formed over the entire composition range?

J. M. BAKER: For Mn-ZnF_2 , yes. X-ray structure measurements show a uniform variation of lattice constants with concentration. Such measurements have not yet been done for Co-ZnF_2 mixture.

C. J. GORTER: I wonder whether the notion of a Néel temperature has much sense for a solid solution. The case is different for the Curie temperature of a ferromagnetic solid solution since the spontaneous magnetization constitutes a well defined long range order parameter. Are there indications of a sharp specific heat anomaly? If it would exist at all I would expect it might in many cases to be below the Schottky maximum of short range order.

W. C. MARSHALL: We should be careful to distinguish a point of principle from one of practical difficulty. It is true that short range order is much more important in the dilute systems and this tends to obscure any observation of the Néel temperature but nevertheless it is possible in principle to define a Néel temperature through the behaviour of the spin correlation function at long times. However it may be very difficult to establish experimentally the difference between short and long range order.

S. FONER: The AFMR results in the $(\text{Cr}_2\text{O}_3)_{1-x}(\text{Al}_2\text{O}_3)_x$ system indicate long range order over a wide range of temperature and composition. This is indicated by the following.

- 1) The AFMR line widths are the same as for the pure Cr_2O_3 .
- 2) The Néel temperature, indicated by the sudden disappearance of the ESR is quite sharp ($\pm 2^\circ\text{C}$).
- 3) Often the crystals show only one AFMR line. Since the AFMR is very sensitive to composition, we would not expect a sharp AFMR line unless large regions were coupled by long range forces.

These results have been observed for $x \leq 0.2$ so far.

