PHYSICAL CHEMISTRY

E. E. VAINSTEIN, B. I. KOTLYAR, and R. M. OVRUTSKAYA

1961

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

E. E. VAINSTEIN, B. I. KOTLYAR, and R. M. OVRUTSKAYA

STUDY OF THE FINE STRUCTURE OF THE X-RAY *K*-ABSORPTION EDGES OF MANGANESE IN MnTe IN THE TEMPERATURE RANGE OF THE ANTIFERROMAGNETIC TRANSITION

(Presented by Academician A. P. Vinogradov, July 4, 1960)

Recently (1) it was suggested that certain features of the fine structure of the x-ray absorption spectra of atoms of transition elements in ferrites may be connected with the influence on these spectra of the antiferromagnetic ordering in the arrangement of electron spins in the materials under study. This conclusion, made on the basis of analysis of the structure of the iron absorption spectra obtained in (1) in various ferrites, which were not always sufficiently well characterized from the point of view of their structure and magnetic properties, was, however, preliminary in character and required further verification and refinement in a series of more purposefully arranged experiments. From this point of view, a study of the temperature dependence of the fine structure of the x-ray spectra of magnetoactive atoms in an antiferromagnet in the temperature range of its magnetic transition seemed very essential. Among the relatively small number of antiferromagnetic compounds suitable for such a study, we chose MnTe. This compound has been studied rather well by x-ray methods (2,3) and has a Néel point convenient for carrying out experiments ($T_N = 310^\circ$ K).

The sample of manganese telluride subjected to investigation was kindly placed at our disposal by N. P. Grazhdankina, to whom the authors express their gratitude. It was obtained by fusing finely dispersed and thoroughly mixed powders of manganese and tellurium in an evacuated and sealed quartz ampoule at 800°C.* To remove gases, the manganese was remelted in a high vacuum.

After preparation, the manganese telluride was subjected to low-temperature annealing. X-ray structural analysis of the alloy showed the presence of the MnTe phase and only traces of $MnTe_2$. Grazhdankina (3) studied a number of physical characteristics of this alloy in the temperature interval from 250 to 370°K, within which the Néel point lies.

It was shown that at $T_N = 310^\circ$K in MnTe there is a break in the curves of the temperature dependence of the electrical resistivity and magnetic susceptibility

Figure 1-3: X-ray absorption spectra plots

Figure 1: Figure 1-3: X-ray absorption spectra plots

of the alloy, as well as a change in the course of the curve representing the temperature dependence of the value of the parameter c of the compound' s crystal lattice. No deviations from the linear course of the change with temperature of the second parameter a, nor any change in the type of the crystal lattice of the compound upon passage through the Néel point, are observed. On going from room temperature (the antiferromagnetic state of the alloy) to temperatures exceeding T_N, only an anomalous expansion of the crystal along the c axis is observed, which leads to an increase in the axial ratio c/a and to a corresponding change in the volume of the unit cell of the compound.

* The starting manganese contained 0.07% S and CO and 0.03% P; tellurium—Cu 10^{-4}%; Ag $2 \cdot 10^{-4}$%; Bi $< 10^{-4}$% and up to 10^{-4}% Sb and As.

The manganese X-ray K-absorption spectra in telluride were obtained with an X-ray spectrograph focused by the Johann method. The reflecting crystal was quartz, plane $(1\bar{3}40)$, with constant $d = 1.17$ Å. The radius of curvature of the crystal was 500 mm. The spectra were recorded in the first order of reflection by the photographic method. The iron $K\alpha_{1,2}$ lines were used as comparison lines. The dispersion of the instrument in this region was 2.6 X/mm. The presence in the alloy of large amounts of the relatively heavy component (tellurium) required very careful selection of the optimal

Fig. 1. Manganese K-absorption spectra in $KMnO_4$ (1) and in the metal (2), obtained with a focusing spectrograph in the present work and on a two-crystal spectrometer with ionization recording in work (4) (dashed curves)

Fig. 2. Comparison of the fine structure of the manganese absorption spectra in $KMnO_4$ (1), MnTe at 50°C (2) and 8°C (3) (respectively above and below the Néel point), and in the metal (4)

Fig. 3. Fine structure of the manganese absorption spectra in MnTe at different temperatures: 1—50°C; 2—44°C; 3—38°C; 4—21°C and 5—8°C ($T_N = 310$°K)

absorber thickness, which would provide the best conditions for revealing the details of the structure of the spectra. It was established that optimal conditions for obtaining a clearly expressed fine structure of the absorption edge are achieved when working with absorbers in which the specific content of Mn is 4 mg/cm^2. A decrease or increase in the thickness of the absorber leads to a reduction in the contrast of the edge.

The optimal tube operating regime was 30 kV and 40 mA. The exposure was 6 h. To obtain absorption spectra at different temperatures of the sample, the absorber was deposited on aluminum foil, which was tightly pressed to a round copper holder through which liquid from an ultrathermostat was passed under pressure. Good contact between the aluminum foil and the polished surface of the holder ensured constancy of temperature in all parts of the absorber throughout the entire exposure time. The temperature was measured with an accuracy of 0.2–0.3°C by a potentiometric method using a copper-constantan thermocouple tightly pressed to the sample.

The Mn absorption spectra in MnTe were studied at five different temperatures in the range from 280 to 325°K ($T_N = 310$°K). At each temperature, 3–4 spectrograms were obtained, which after photometry in several sections were averaged. To check the resolving power of the spectral instrument used by us, absorption spectra in the metal and in $KMnO_4$ were obtained with it and compared with the corresponding

corresponding curves obtained on a double-crystal spectrometer with ionization recording by Hanson and Beeman (⁀4). The results of such a comparison for both substances are presented in Fig. 1. In Figs. 2 and 3 the experimental results obtained by us are compared with one another. Their consideration makes it possible to draw the following conclusions.

1. In the transition from the metal to manganese telluride, a significant decrease in the energy of the 4*p*-state of the transition metal takes place. The magnitude of the long-wavelength shift, observed in this case, of the corresponding maximum on the manganese absorption curve in MnTe reaches 5.4 eV.

2. In the paramagnetic region of the MnTe alloy, a long-wavelength "white" absorption line is clearly manifested at the manganese absorption edge; its position is very close to the position of the "initial-absorption region" in the spectrum of the metal and practically coincides with the position of the maximum of the intense "white" absorption line observed in the spectrum of this element in $KMnO_4$. In the latter case, the connection between the appearance of this line in the spectrum and transitions of photoelectrons into the region of hybridized 3*d*-states of the transition metal in the compound may now be considered sufficiently well proven (5,6).

3. As the Néel point is approached in the paramagnetic region of the MnTe alloy, the manganese absorption spectrum shows a systematic and smooth decrease in the intensity of the white absorption line, indicating, apparently, a gradual change in the probability of the corresponding electronic transitions. It may be supposed that this is connected with the smooth (linear) change, found for the alloy in this temperature region (2,3), in the parameters of the crystal lattice of manganese telluride and the corresponding decrease in the c/a ratio of the hexagonal lattice of the compound.

4. On passing through the Néel point, there is observed the disappearance or a significant decrease in the intensity of the long-wavelength white line in the absorption spectrum of the transition metal. The position and relative intensity of the first absorption maximum, associated with transitions of photoelectrons of the absorbing atom into the region of the 4*p*-states of

the metal in the compound, as in the transition through the ferromagnetic Curie point (7,8), remain practically unchanged.

Thus, the results of the present investigation are in good agreement with our earlier observations (⌒1) and with conclusions concerning the influence of antiferromagnetic ordering in compounds on the fine structure of the X-ray absorption spectra of the transition metals contained in them. As for the question, important for theory, of the degree of participation of tellurium atoms in the interaction between manganese atoms in antiferromagnetic MnTe and the possibility of transferring to this case ideas about the role of oxygen atoms in antiferromagnetic crystals of transition-metal oxides, it cannot yet be resolved solely on the basis of analysis of the experimental data obtained and requires further investigations.

Institute of Inorganic Chemistry
Siberian Branch of the Academy of Sciences of the USSR

Odessa Pedagogical Institute
named after K. D. Ushinskii

Received
29 VI 1960

REFERENCES

1. E. E. Vainshtein, B. I. Kotlyar, G. A. Shapiro, DAN, **125**, 55 (1959).
2. S. Greenwald, *Acta Crystallogr.*, **6**, 396 (1953).
3. N. P. Grazhdankina, D. I. Gurfel, ZhETF, **35**, 907 (1958).
4. H. Hanson, W. W. Beeman, *Phys. Rev.*, **76**, 118 (1949).
5. R. L. Barinskii, E. E. Vainshtein, K. I. Narbut, DAN, **83**, 199 (1952).
6. R. L. Barinskii, E. G. Nadzhakov, *Izv. AN SSSR, ser. fiz.*, **24**, 407 (1960).
7. E. E. Vainshtein, *X-ray spectra of atoms in molecules and chemical compounds and alloys*, Izd. AN SSSR, 1950.
8. A. V. Trapeznikov, Dissertation, Sverdlovsk, 1956.