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Mössbauer Effect in Molecular Iodine Crystals

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The Mössbauer effect of the 26.8-keV transition in I^{129} has been studied in molecular iodine crystals. From the quadrupole splitting of the transitions the ratio $Q_{26.8}/Q_{\mathrm{gnd}}$, the quadrupole coupling e^2qQ_{gnd}, and the isomer shift are derived. The sign of the quadrupole coupling shows that the sign of the iodine field gradient is positive. From the isomer shift of I_2 and from those of alkali iodides a linear dependence of the isomer shift on the number of p holes is derived. The intensities of the peaks give a strong indication of an angular dependence of the recoilless fraction $f(\theta)$. The Θ_D of the I_2 crystal, as well as that of the KI crystal, are derived from the temperature dependence of the recoilless fraction.

I. INTRODUCTION

THE Mössbauer effect of the 26.8-keV transition in the I^{129} nucleus was first observed by Jha *et al.*[1] and extensive experiments in various iodine compounds were performed by Hafemeister *et al.*[2] The purpose of the present work was to study the properties of the molecular iodine crystal using I^{129} as the Mössbauer nucleus.

The main feature that distinguishes a molecular crystal from other crystals is that its constituents, the molecules, behave like quasi-isolated aggregates. This is because the intramolecular bonds are covalent and they are much stronger than the van der Waals forces which form the intermolecular bonds. The crystal structure of I_2 and experimental data support its molecular crystal character. Iodine crystallizes in an orthorhombic form with the molecules arranged in planar sheets parallel to the *a-c* plane (see Fig. 1). Nuclear quadrupole resonance experiments[3] with I_2 have shown that its quadrupole coupling in the solid state is almost the same as that calculated for the free atom. Also, recent experiments with far infrared spectroscopy[4] on solid iodine reveal two translational (intermolecular) vibrations in the vicinity of 50 cm^{-1} and a peak at 211 cm^{-1} corresponding to the intramolecular vibration.

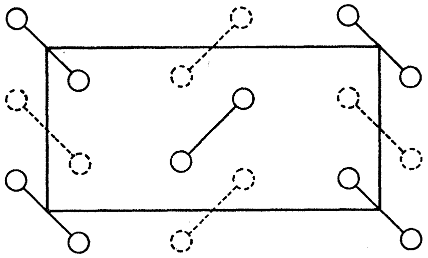

FIG. 1. Arrangement of iodine molecules in their orthorhombic unit cell. The solid lines indicate molecules lying on the plane of the paper (*a-c* plane). The dashed lines indicate molecules in parallel planes. The atomic intramolecular distance is 2.70 Å. The next shortest distance is on the *a-c* plane—3.54 Å. The closest atomic distance between two planes is more than 4.30 Å.

The information obtained by Mössbauer studies on molecular iodine crystals may be divided into two categories: (a) data on the intramolecular orbitals obtained from the quadrupole splitting and isomer shift measurements, and (b) information on the intermolecular vibrations of I_2 obtained from measurements of the fraction of recoilless emission and its temperature dependence. The present work is similarly divided into two parts. The first deals with measurement of the quadrupole coupling and isomer shift, and the second with the temperature dependence of the recoilless fraction f' of the I_2. To compare this dependence with the temperature dependence of an ionic crystal, we made the same measurement with a KI absorber.

II. EXPERIMENTAL

A. Sources and Absorber

The Te^{129} source used was in the form of $Zn^{66}Te^{128}$. This compound was prepared by mixing stoichiometric amounts of enriched Zn and Te at 1100°C in an evacuated quartz ampoule. The product was then powdered and sedimented from benzene containing polystyrene.

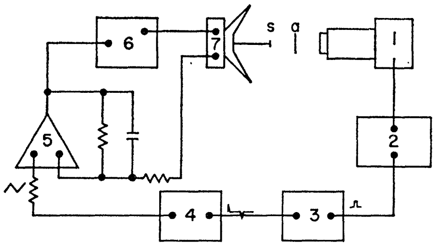

FIG. 2. The electronic circuit of the Mössbauer spectrometer. 1–6810-A RCA photomultipler. 2–Elron SCTD-10X single channel analyzer. 3–TMC 1024 channel analyzer. 4–Hewlett Packard Model 202A function generator. 5–Dymec 2460A operational amplifier. 6–Home-made power amplifier. 7–University C-12HC loudspeaker. *s*-source, *a*-absorber.

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[1] S. Jha, R. Segnan, and G. Lang, Phys. Rev. **128**, 1160 (1962).

[2] D. W. Hafemeister, G. DePasquali, and H. deWaard, Phys. Rev. **135**, B1089 (1964).

[3] T. P. Das and E. L. Hahn, *Nuclear Quadrupole Resonance Spectroscopy* (Academic Press Inc., New York, 1958), p. 174.

[4] S. H. Walmsley and A. Anderson, Mol. Phys. **7**, 411 (1964).

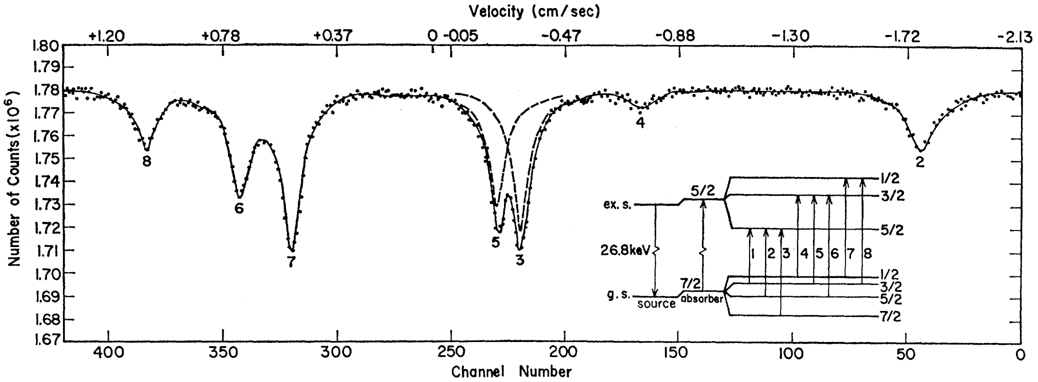

FIG. 3. The quadrupole splitting of I_2^{129} at 100°K. The source is $Zn^{66}Te^{129}$ at 120°K. The numbers under the peaks correspond to the nuclear transition shown in the decay scheme. Zero velocity is in channel 256. Each channel corresponds to 0.0835 mm/sec.

The sources consisting of 15 mg of Te^{128} were irradiated for one hour in a flux of 10^{13} neutrons/cm^2-sec at the Nahal Soreq swimming-pool-type reactor IRR-1.

The I_2^{129} was purchased from Oak Ridge in the elemental form. The absorber was prepared by condensing iodine vapor onto a thin Teflon backing, to form a thin layer (22 mg/cm^2) of very small crystals. The prepared absorber was placed in a hermetically sealed Teflon container. The KI^{129} was purchased from Oak Ridge. A thin absorber of about 6 mg/cm^2 was prepared by mixing the KI powder with polystyrene powder.

Source and absorber were both placed inside a cryostat made of Styrofoam. The temperature of the source was kept constant at 120°K and that of the absorber could be varied between 100–200°K.

B. Radiation Detection

The 26.8-keV gamma rays were detected with a 1 mm NaI(Tl) scintillator attached to a 6810A photomultiplier. Because of the short half-life of Te^{129} (72 min) the counting rate dropped appreciably during the counting period (3 h), and a special voltage divider was therefore designed to minimize the resulting changes in photomultiplier amplification. Pulses from the last dynode of the photomultiplier were directly fed to a fast single-channel analyzer (Elron SCTD-10X). A typical counting rate from a freshly inserted sample was 20 000 counts/sec. The activity of the Xe^{129} K x-rays emitted from the long-lived (10^7 yr) radioactive absorber was reduced by a Sn critical absorber. Because of the high source activity and the Sn absorber, the background from the I^{129} amounted to only a few percent.

C. Driving System and Storing of Data

The source was attached to a C-12HC University loudspeaker driven in a parabolic motion (see Fig. 2). A simple feedback circuit was used for this purpose. The triangular wave function was generated by a Hewlett Packard (Model 202 A) function generator triggered by the output of the last address binary of a TMC 1024 channel analyzer, operating in the multiscaler mode.

The velocity scale was calibrated before and after the experiments with a source of Co^{57} diffused in Cu and an α-Fe_2O_3 absorber. The calibration was made according to the absolute measurement of Kistner and Sunyar.[5]

III. RESULTS AND DISCUSSION

The spectrum of the hyperfine splitting of the I_2 crystal at 100°K is shown in Fig. 3. Transition No. 1 corresponds to a velocity position of about 100 channels to the right of peak No. 2. Because of its relatively low intensity (less than 0.2%) no effort was made to scan it. The average linewidth of the I_2 peaks is 7.8×10^{-8} eV. This corresponds to a lifetime $T_{1/2}=11.6$ sec, and is 25% smaller than the value achieved by electronic measurements.[6]

A. Quadrupole Splitting

The interaction of the nuclear quadrupole moment with the electric field at the iodine nucleus splits the 26.8 keV nuclear transition into eight transitions. In the case of a non-axially symmetric electric field, the positions of the peaks ΔE_i are given by[7]:

$$\Delta E_i=\frac{c}{E_\gamma}\frac{e^2qQ^*}{4I^*(2I^*-1)}(C_0^*+C_2^*\eta^2)$$
$$-\frac{c}{E_\gamma}\frac{e^2qQ}{4I(2I-1)}(C_0+C_2\eta^2)+\delta(\text{cm/sec}), \quad (1)$$

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[5] O. C. Kistner and A. W. Sunyar, Phys. Rev. Letters **4**, 412 (1960).

[6] S. C. Pancholi, Nucl. Phys. **66**, 323 (1965).

[7] R. Bersohn, J. Chem. Phys. **20**, 1505 (1952).

where e^2qQ is the quadrupole coupling,

$$C_0=3m^2-I(I+1)\,,$$

$$C_2=\tfrac{1}{12}[f(I,\,m-1)/(m-1)-f(I,\,m+1)/(m+1)]\,,$$

$$f(I,m)=\tfrac{1}{4}(I^2-m^2)[(I+1)^2-m^2]\,,$$

η is the asymmetry parameter of the field gradient, δ is the isomer shift, and * stands for the excited state. Inserting the value[8] of $\eta=-0.16$ into (1) we found by the least-square method the following results:

$$e^2qQ=-1426\pm15 \text{ Mc/sec}$$

$$Q^*/Q=+1.232\pm0.004$$

$$\delta=+0.082\pm0.001 \text{ cm/sec}.$$

The Q^*/Q ratio is the same as that obtained by Hafemeister *et al.*[2] with the less resolved spectrum of KIO_3. Using the ratio[9] $Q(129)/Q(127)=0.701$ we found $e^2qQ=-2085\pm20$ Mc/sec for I^{127} at 100°K. This is in agreement with the value obtained by the nuclear quadrupole resonance (NQR) technique at 4.2°K (2156 Mc/sec).[3] As a further check, we substituted this last value (2156 Mc/sec) in Eq. (1) and found again by the least-square method:

$$Q^*/Q=+1.237\pm0.002$$

$$\delta=+0.082\pm0.001 \text{ cm/sec}.$$

Since the sign of Q is negative,[10] the sign of eq is positive. This is expected, since the field gradient at the iodine nucleus is due to a p-electron vacancy in the Xe closed shell which behaves like a positive charge.

B. Isomer Shift

There is strong evidence that the interhalogen bonds are essentially pure p bonds.[11] The structure determination[12] of the polyhalide ions I_5^-, I_7^-, I_9^-, $I_8^{=}$ reveals the universal occurrence of bond angles close to 90° and 180°. The same property is noted in the interhalogen molecules. For example, ICl_4^- and BrF_4^- are square, ICl_2^- is linear and ClF_3 and BrF_3 are T shaped. It is reasonable, therefore, to assume that the intramolecular bonds of I_2 are of a pure p character and that there is no spd hybridization. Therefore, the measured isomer shift $\delta=+0.082$ corresponds exactly to the removal of one p electron from the Xe shell.

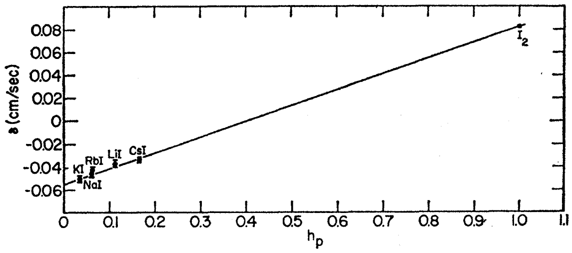

FIG. 4. Dependence of the isomer shift (δ) on the removal of p electrons from the Xe shell (number of p-holes-h_p).

The plot of the isomer shift as a function of the number of p holes gives a straight line (see Fig. 4). This graph is based on our data and those obtained by Hafemeister *et al.*[2] Using the least-square method we got the following expression for the isomer shift with respect to the ZnTe source:

$$\delta=0.136h_p-0.054 \text{ (cm/sec)}\,, \qquad (2)$$

where h_p is the number of p holes with reference to the $5s^25p^6$ configuration. For a closed p shell ($h_p=0$), corresponding to Xe, we obtain $\delta=-0.054$ cm/sec, in agreement with Ref. 2.

C. Intensity of the Absorption Peaks

Table I presents the experimental intensities, together with the expected intensities which are proportional to the square of the Clebsch-Gordan coefficients $[CG]^2$. By normalizing the experimental intensities to the $[CG]^2$ for each transition, one immediately notes that the proportionality holds for transitions with the same Δm ($\Delta m=0$, $\Delta m=\pm1$ and the mixed transition $\pm\frac{1}{2}\rightarrow\pm\frac{1}{2}$). This fact could only be due to an angular correlation between the gamma absorption and the electric field axis, which for the case of I_2 crystals practically coincides with the molecular axis.

In our case there are two main reasons which might lead to such an angular dependence:

1. The molecular electric field axis might be oriented at an angle θ relative to the direction of the incoming gamma rays. Then the ratio of the intensities for transitions $\Delta m=0$ and $\Delta m=\pm1$ will be

$$R(\Delta m=\pm1)/R(\Delta m=0)=\tfrac{3}{2}(1+\cos^2\theta)/3(1-\cos^2\theta)\,. \quad (3)$$

To fit with out experimental result, θ should be 90°. This would imply that the crystals grown on the Teflon backing lie in the a-c plane (see Fig. 1).

2. The crystals might be randomly oriented, but the recoil-free fraction is anisotropic. Then the ratio of the intensities normalized to the $[CG]^2$ will be ("Goldanskii effect"):

$$\frac{R(\Delta m=\pm1)}{R(\Delta m=0)}=\frac{\frac{3}{2}\displaystyle\int_{-1}^{+1}(1+\cos^2\theta)f(\theta)d(\cos\theta)}{3\displaystyle\int_{-1}^{+1}(1-\cos^2\theta)f(\theta)d(\cos\theta)}\,. \quad (4)$$

From this relation it is impossible to determine $f(\theta)$. One can only make a guess at its behavior. If we assume

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[8] K. Tsukada, J. Phys. Soc. Japan **11**, 956 (1956).

[9] R. Livingston and H. Zeldes, Phys. Rev. **90**, 609 (1953).

[10] *Nuclear Data Sheets*, compiled by K. Way *et al.* (Printing and Publishing Office, National Academy of Sciences—National Research Council, Washington 25, D. C.), NRC 61-1-130, Appendix 1.

[11] R. Bersohn, J. Chem. Phys. **36**, 3445 (1962).

[12] E. E. Havinga and E. H. Wiebenga, Rec. Trav. Chim. **78**, 724 (1959).

TABLE I. Comparison of the experimental intensities with the square of the Clebsch-Gordan coefficients $|CG|^2$.

Number of peak	Transition	$\|CG\|^{2\text{a}}$	Experimental intensity[a]	$R=$ Experimental$/\|CG\|^2$ $\Delta m=0$	$\Delta m=\pm1$	$\pm\frac{1}{2}\to\pm\frac{1}{2}$
2	$\frac{5}{2}\to\frac{5}{2}$	7	10.5	1.5		
4	$\frac{1}{2}\to\frac{3}{2}$	3.5	2.7		0.8	
3	$\frac{7}{2}\to\frac{5}{2}$	25	20		0.8	
5	$\frac{3}{2}\to\frac{3}{2}$	12	17	1.4		
7	$\frac{1}{2}\to\frac{1}{2}$	21	24			1.14
6	$\frac{5}{2}\to\frac{3}{2}$	18	16		0.9	
8	$\frac{3}{2}\to\frac{1}{2}$	12	8.6		0.7	
			Relative angular dependence		*Transition*	
$R(\Delta m=\pm1)/R(\Delta m=0)=0.55$			$I(\Delta m=0)=3\sin^2\theta$		$\frac{5}{2}\to\frac{5}{2},\ \frac{3}{2}\to\frac{3}{2}$	
			$I(\Delta m=\pm1)=\frac{3}{2}(1+\cos^2\theta)$		$\frac{1}{2}\to\frac{3}{2},\ \frac{7}{2}\to\frac{5}{2},\ \frac{5}{2}\to\frac{3}{2},\ \frac{3}{2}\to\frac{1}{2},\ \frac{3}{2}\to\frac{5}{2}$	
			$I(\pm\frac{1}{2}\to\pm\frac{1}{2})=(1+\frac{3}{2}\sin^2\theta)$		$\pm\frac{1}{2}\to\pm\frac{1}{2}$	

[a] Normalized to give a sum of 100.

that $f(\theta)$ is a function with one maximum, one can show, by approximating $f(\theta)$ with the delta function $\delta(\theta-\pi/2)$, that this maximum should be in the vicinity of $\theta=90°$.

The crystallographic data and the asymmetry parameter $\eta=(q_{xx}-q_{yy})/q_{zz}=-0.16$ justify the assumption that the strongest molecular bonding is in the *a-c* plane. Therefore $f(\theta)$ will have a maximum in this plane, along the partially covalent bonds. But if this is the picture there should be a maximum also at $\theta=0°$ (see Fig. 1). We could not fit any function with maxima at 0° and 90° to our experimental results. On the other hand, the possibility that the crystals were grown in the *a-c* plane on the Teflon backing is not reasonable. The way the crystalloids were prepared, and the fact that they were probably "crushed" under low temperature conditions, do not favor this possibility.

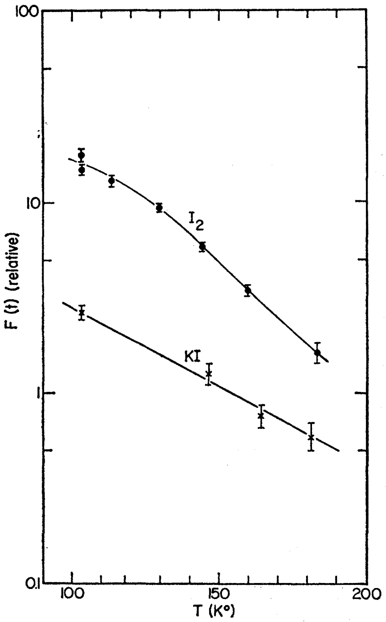

FIG. 5. The temperature dependence of the recoilless fraction plotted on semilog paper. The ordinate values are proportional to the absorption dip (see text).

D. The Temperature Dependence of the Recoilless Fraction

For a thin absorber, the dip of the absorption line is proportional to $f'(=e^{-2W(T)})$.[13] Figure 5 shows the temperature behavior of f', the source temperature having been held constant. It can be seen that the molecular recoilless fraction (I_2) decreases more sharply than the ionic one (KI) as one would expect. Assuming a Debye model for both crystals, it thus turns out that Θ_D of I_2 is smaller than that of KI.

We calculated Θ_D from the slope of the curve assuming the following approximation when $\frac{1}{2}\Theta_D<T$:

$$2W(T)=(R/k\Theta_D)(\tfrac{3}{2}+6kT/k\Theta_D). \qquad (5)$$

For KI, we found that $\Theta_D=103°K$ which is in good agreement with the theoretical value recently obtained from the heat capacity.[14]

In the case of the I_2 crystal, one knows *a priori* that there are both acoustical modes and optical modes. Since the optical modes of the molecular iodine are high in comparison with the temperature range of our experiments, we can assume that for the recoilless process the whole molecule behaves as an aggregate. We thus assumed that R, the recoil energy, is due to the I_2 molecule as a whole. From the slope of Fig. 5 (Eq. 5) we calculated a $\Theta_D=60°K$. Recently, far infrared experiments revealed two absorption lines corresponding to $\sim$60°K and $\sim$80°K. These lines were interpreted as corresponding to two translational oscillation modes between the molecules in the *a-c* plane (see Fig. 6). However, as was pointed out by

FIG. 6. Translational oscillations of the I_2 molecules as interpreted from far infrared absorption. (Walmsley and Anderson).

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[13] S. Margulies and J. R. Ehrman, Nucl. Instr. Methods **12**, 131 (1961).

[14] Y. Disatnik, D. Fainstein, and H. J. Lipkin, Phys. Rev. **139**, A292 (1965).

Ref. 4, these modes correspond to $K=0$ vibrations, i.e., they are optical modes. A more detailed calculation is now in progress to derive a more realistic model for I_2, taking into account these optical modes as Einstein oscillators.

The departure from linearity ($\sim 15\%$) in the I_2 curve at low temperatures is not yet understood. It could be due either to a slight saturation (for this case the dip is not proportional to f') or to a phase transition. Experiments will be performed at lower temperatures to clarify this point.

ACKNOWLEDGMENTS

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Magnetic Structures of Metallic Erbium*

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Single-crystal neutron-diffraction data were obtained for metallic erbium at sample temperatures from 4.2 to 298°K. Three distinct regions of long-range magnetic order were observed. In the high-temperature region (52–80°K) the ordered moments are confined to the c-axis direction and are sinusoidally modulated with a modulation wavelength of $3.5C_0$. The amplitude of this modulation saturates at 52°K with $\mu_z(\max) = 7.6\ \mu_B/\mathrm{Er}^{3+}$. Below 52°K the basal-plane component of the moment begins to order, and a third-order modulation along the c axis is observed. These effects are interpreted on the basis of a squared elliptical spiral with its major axis tilted relative to the crystal c axis. However, the structural details in this region are obscured by a temperature variation of the modulation wavelength and by the incommensurability of the modulation and the lattice. In the low-temperature region (4.2–20°K) a ferromagnetic spiral structure is indicated. At saturation the ferromagnetic c-axis component is $7.9\ \mu_B/\mathrm{Er}^{3+}$ and the spiral basal-plane component is $4.3\mu_B/\mathrm{Er}^{3+}$. The total ordered moment is then the free-ion value of $9.0\mu_B/\mathrm{Er}^{3+}$.

INTRODUCTION

THE neutron-diffraction study which revealed many of the magnetic structural details of metallic erbium has up to now been reported only partially in a brief communication,[1] and we give here a complete report of these results. As with the other rare-earth elements it was necessary to make the measurements on single crystals in order to determine the rather complicated magnetic structure properties. This became apparent in some earlier powder-diffraction measurements[2] in which the existence of both an antiferromagnetic phase below 80°K and the development of ferromagnetism at lower temperatures was observed. These results were then consistent with previous magnetization measurements[3] which had indicated the onset of antiferromagnetic ordering at 80°K and a transition to ferromagnetism at 20°K. Specific-heat measurements[4] had indicated anomalies at these temperatures and also at 53°K. The nature of these transitions were determined in the single-crystal neutron-diffraction studies which we report here. The most significant aspect of this study was undoubtedly the first definite observation of a modulated-moment type of structure as contrasted with the more common spiral type.

EXPERIMENTAL

The magnetic and thermal data indicated that neutron measurements were required in the 4.2- to 80-°K region. Since the previously described[5] low-temperature goniometer was designed for operation in the 1.3- to 4.2-°K region it was necessary to modify the goniometer for this experiment. This was done by enclosing the crystal mount and control-rod mechanism in an exchange gas chamber and by the incorporation of a heater coil and a calibrated copper-constantan thermocouple on the Al shaft above the crystal mount. With the exchange gas chamber evacuated and with no heat input the equilibrium temperature was 20°K, while with heat input the sample temperature could be raised to liquid-nitrogen temperature without the production of a prohibitive helium loss rate. It was possible to obtain temperatures below 20°K by the introduction of helium exchange gas into the chamber.

The metallic erbium single crystal was a pillar of

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